# Understanding Nanoscale Plasticity by Quantitative In Situ Conductive Nanoindentation

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Electronic materials such as semiconductors, piezo- and ferroelectrics, and metal oxides are primary constituents in sensing, actuation, nanoelectronics, memory, and energy systems. Although significant progress is evident in understanding the mechanical and electrical properties independently using conventional techniques, simultaneous and quantitative electromechanical characterization at the nanoscale using in situ techniques is scarce. It is essential because coupling/ linking electrical signal to the nanoscale plasticity provides vital information regarding the real-time electromechanical behavior of materials, which is crucial for developing miniaturized smarter technologies. With the advent of conductive nanoindentation, researchers have been able to get valuable insights into the nanoscale plasticity (otherwise not possible by conventional means) in a wide variety of bulk and small-volume materials, quantify the electromechanical, understand the dielectric breakdown phenomenon and the nature of electrical contacts in thin films, etc., by continuously monitoring the real-time electrical signal changes during any point on the indentation load-hold-unload cycle. This comprehensive Review covers probing the electromechanical behavior of materials using in situ conductive nanoindentation, data analysis methods, the validity of the models and limitations, and electronic conduction mechanisms at the nanocontacts, quantification of resistive components, applications, progress, and existing issues, and provides a futuristic outlook.

# 1. Introduction

The fast-growing semiconductor industry, as well as the rapid development of nano/microelectromechanical systems such as micro-electro-mechancial systems (MEMS) actuators and sensors, memristors, and energy storage have always given a vast demand for the advancement of characterization technologies to measure and understand the simultaneous electrical and mechanical response during the mechanical deformation of materials.<sup>[1–3]</sup> Knowledge of the phenomena occur during mechanical deformation such as phase transformations,<sup>[4–7]</sup> dielectric breakdown,<sup>[8]</sup> and piezoelectric response<sup>[9,10]</sup> help

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researchers to incorporate and revise the existing electrical devices and design smarter technologies.<sup>[11,12]</sup>

The conventional ex situ measurement methods that provide quantitative information on the electrical resistance include a two- and four-probe and the scanning probe techniques. The two-point and four-point probe methods<sup>[13,14]</sup> measure the spreading resistance and resistivity but fail in providing information on the mechanical deformation mechanisms due to the difficulty in controlling the load and lack of contact area  $(A_c)$  details.<sup>[11]</sup> Scanning probe methods then proved to dominate quantitative electrical measurements, but tip shape determination is a complex process in quantifying electromechanical properties.<sup>[15]</sup> Further, they cannot provide real-time information on the mechanical deformation under applied stress and the simultaneous electrical response measurement concerning mechanical stress. For example, the piezoelectric materials are used in the electric field as well as external mechanical stress as actuators and transducers, and

the mechanical properties are field-dependent due to the electromechanical coupling. Therefore, it is crucial to have a better understanding of simultaneous electrical and mechanical property measurements. All these challenges have led to the necessity of developing a novel in situ characterization technique.<sup>[10]</sup>

The development of the nanoindentation technique (i.e., controlled penetration of a rigid indenter (usually diamond) of known geometry into the sample) immensely helped the scientific community in quantifying the mechanical properties such as hardness (H), elastic modulus (E), and fracture toughness ( $K_c$ ) of a wide range of bulk and small-volume materials at the nanoscale.<sup>[16-19]</sup> Also, the continuous monitoring of indenter penetration (useful in observing pop-in and pop-out phenomena in load/force, (P) penetration depth/displacement (h) curves) to the applied force, postindent high-resolution electron microscopic imaging of the residual indent, and development of in situ methods such as environment-controlled indentation, dynamic force indentation, indentation coupled to a micro-Raman spectrometer,<sup>[20]</sup> and electron microscopes<sup>[21,22]</sup> together have provided significant insights into several nanoscale contact phenomena, such as the pressure-induced phase transformations and effect of temperature on the phase transformation

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kinetics and pathways,<sup>[7,23,24]</sup> structure–property correlation in organic crystals,<sup>[25,26]</sup> and the onset of plasticity of metals.<sup>[22]</sup> Even though nanoindentation has been in the spotlight to study the deformation mechanisms at nanoscale efficiently, the postindent imaging of the residual indents failed to observe the presence/formation of metastable high-pressure phases during loading/unloading. Although the basic indentation was very well utilized by the scientific community to probe various materials' mechanical behavior at the nanoscale, the in situ techniques were not well explored.

A decade ago, the in situ electrical characterization technique during indentation, i.e., indenting with a conducting tip (boron-doped diamond, BDD), was developed to monitor the electric current changes during phase transformations (semiconducting to metallic, among others,) and for simultaneous quantification of the electrical and mechanical behavior of semiconductors.<sup>[6,27,28]</sup> DeWolf et al.<sup>[29]</sup> determined the charge carriers' spatial distribution in Si structures using an implanted atomic force microscopy (AFM) diamond tip as a spreading resistance probe.<sup>[29]</sup> With the development of conductive tips, researchers have realized that conductive nanoindentation is more advantageous than the pure electrical probe techniques due to the precise application of force and measurement of indenter penetration depth with high resolution. In addition, there are well-developed models for accurately estimating the  $A_{\rm c}$  of different geometry tips.<sup>[16,30]</sup>

Despite the emergence of this new field with in situ conductive nanoindentation, to date, there is no comprehensive review available in providing an in-depth understanding, its importance, data analysis methods, models for estimating the contact area, electron transport mechanism at different regimes, quantification of resistive components, and the wealth of information obtained so far. At this stage, it is crucial to understand the advantages and disadvantages of this versatile characterization technique and the validity of the developed models, monitor the progress, and discuss the existing issues and future opportunities.

Therefore, this Review focuses on nanoelectrical contact resistance measurement system (nano-ECR) coupled with nanoindentation, which is being used to characterize the simultaneous electrical and mechanical properties of a wide variety of bulk and small-scale materials. As this is the first Review article on the electromechanical characterization of materials using nano-ECR coupled with nanoindentation, we have reviewed almost all the available published articles on this topic and summarized the wealth of information obtained so far. In Section 2, we describe the background of the nanoelectrical contact resistance technique. This includes basic theory and working principles, methodology, details of the conductive tips, basic resistive components of the circuit, electron transport mechanisms at different regimes, the influence of surface roughness on the contact conductance, and quantification. In Section 3, the wealth of information obtained so far using this technique is reviewed. In the last section, a summary is provided and futuristic applications of this technique are discussed.

Thus, we believe that this Review provides an in-depth understanding to readers across various disciplines on the full potential of the in situ nano-electrical contact resistance measurement technique coupled with nanoindentation, useful for unraveling various nanoscale contact phenomena during the mechanical deformation of materials. We have also considered a few articles that measured electrical current measurement through an external circuit while indenting with an undoped diamond tip.

# 2. Background

# 2.1. Plasticity

Before understanding the nanoscale plasticity in materials using in situ electrically conductive nanoindentation, it is imperative to understand the deformation behavior of materials under the indenter at the nanoscale. Therefore, we brief a few known concepts of the mechanical behavior of materials. Plasticity is defined as the ability of a material (solid) that undergoes permanent deformation without fracture and is an important property for metallic materials for engineering applications. The dislocation mobility and the availability of slip systems determine plasticity in crystalline materials. Twinning, grain rotation, grain boundary sliding, etc. are other modes of deformation that largely determine plasticity if the number of slip systems is not enough to meet von Mises's rule.<sup>[31]</sup> In metals, the plastic deformation depends on dislocation generation and movement,<sup>[32]</sup> and the plasticity is typically determined by the inherent crystal structure and availability of slip systems. Even annealed metals contain a statistical density of dislocations enough to allow the material to deform plastically.<sup>[33]</sup> At least five independent slip systems (<slip direction> and {slip planes}) are required for a metal to plastically deform without forming a crack. The number of independent slip systems is 12 in face-centered cubic (FCC) (<110> {111}) and 48 in body-centered cubic (BCC) (<1 1 1> and {1 1 0}, {1 1 2}, {1 2 3}) metals. Although the number of slip systems is more in BCC than in FCC metals, all of them cannot appear simultaneously. Therefore, the metals with FCC and BCC crystal structures have higher plasticity that helps in shaping and forming easily by rolling, forging and extrusion, etc. However, the hexagonal close-packed (HCP) metals have less than five (i.e., three) slip systems (<1, 1, -2, 0>; {0, 0, 0, 1}, {1, 0, -1, 0} {1, 0, 1, 1}); therefore, deformation twinning is the dominant mode (to meet von Mises's requirement) beyond a certain plastic strain. Thus, the plasticity in HCP metals is lower than in FCC and BCC metals. In addition, microstructures and defect densities can affect the plasticity of metals. The pinning of dislocations by interstitial atoms reduces the plasticity and may lead to a ductile-to-brittle transition in steels below a critical temperature  $(T_c)$ .<sup>[34]</sup> The plasticity observed can be different for different deformation modes. The Burgers vector, b, denotes the magnitude and direction of the atomic displacement that occurs when a dislocation moves. Dislocations are either edge-type (deformation  $\perp$  to the line defect) or screw-type (deformation  $\parallel^{el}$  to the line defect) geometries, and mixed dislocations exhibit intermediate character.[33,34]

To generate plastic strain, the dislocations glide on closepacked planes. These are widely separated in a structure, so the stress required for shear deformation for sliding over each other is the lowest.<sup>[34]</sup> Therefore, dislocations move on



close-packed planes in close-packed directions.<sup>[32]</sup> Though the crystals contain several possible slip systems, the active systems will have the highest resolved shear stress. The Schmid factor (i.e., the ratio of the resolved shear stress on the slip system to the applied stress) for an active slip system will likely be high. When the stress on dislocation reaches a critical value  $(\tau_c = \sigma \cos\phi \cos\lambda)$ , the plasticity begins. This is called the critical resolved shear stress (CRSS). Here, tensile stress is represented by  $\sigma$ , the angle between the slip direction and applied force direction by  $\phi$ , the angle between the normal of the slip plane and the applied force direction by  $\lambda$ , and the product of  $\cos\phi$  and  $\cos\lambda$  is the Schmid factor. The knowledge of texture is required to estimate the relationship between macroscopic yield stress ( $\sigma_{\rm v}$ ) to cause plastic strain and the critical stress experienced by the dislocation on its slip plane. The stress required to move a dislocation in a perfect lattice is given by the Peierls–Nabarro equation;  $\tau_{\rm p} = 3Ge^{\frac{-2\pi\omega}{b}}$ , where *G* is the lattice shear modulus, and  $\omega$  is the width of a dislocation ( $\approx 10$  atomic spacings in metals).<sup>[35]</sup> The lattice imperfections increase the stress to move dislocation either through the interaction between elastic strain fields of dislocation and imperfection or through physical obstacles<sup>[35]</sup> (i.e., twin boundaries, high-angle grain boundaries, and incoherent precipitates and dispersed particles).<sup>[32]</sup>

Twinning is an entirely different mechanical deformation mechanism from dislocation movement. In this process, localized shear cooperatively shifts the lattice planes into crystallographically different configurations. Under some conditions, twinning can occur in addition to dislocation glide or preference to dislocation glide.<sup>[32]</sup> However, it commonly occurs when dislocation glide becomes difficult (i.e., low temperatures and high strain rates). In HCP crystals, twinning is the dominant mode of deformation. In BCC metals also it is common at low temperatures. In FCC crystals, it is uncommon (though observed in Cu at 4 K or high strain rates).<sup>[32]</sup>

Although dislocations are carriers of plastic shear in many crystalline materials, there are a few materials, such as austenitic steels, transformation-induced plasticity (TRIP) steels, twinninginduced plasticity (TWIP) steels, shape memory alloys (SMAs), and brass, in which the deformation occurs not only by slip but also by displacive transformations.<sup>[36,37]</sup> Diffusionless collective motion cluster of atoms occurs during the transformation. Two such mechanisms are 1) martensite transformation,<sup>[38]</sup> in which martensite formation occurs by a shear-induced change of crystal structure involving volume change (first-order transformation), and 2) mechanical twinning, in which shear mechanisms reorient the affected volume into a mirror orientation relative to the surrounding matrix.<sup>[39,40]</sup> We limit our focus here on these mechanisms as the nano-ECR technique coupled with nanoindentation has not been utilized yet to study them.

In polycrystals, the plastic deformation of each of the crystal grains is similar to that of a single crystal.<sup>[41,42]</sup> Kocks et al.<sup>[41]</sup> analyzed the relationship between single crystals and polycrystals by comparing the work hardening, flow stress, strain rate effect, temperature, and grain size. In a polycrystal, the interfacial atomic arrangement between the crystals' grain is irregular due to different lattice orientations. The plastic deformation in polycrystalline materials is relatively smaller due to both



intragranular and intergranular deformation than the singlecrystalline materials. The grains will be staged and slipped in batches instead of all grains slipping simultaneously. Due to uneven deformation, internal stresses are generated in the deformed material, and these residual stresses play a significant role in strengthening or weakening the working stress. The grain boundaries that are present in the polycrystals make them stronger than single crystals. The grain boundary area increases with decreasing grain size and act as a barrier to the dislocation motion, which therefore increases the strength of metals and alloys. The relation between  $\sigma_{v}$  and grain size is expressed by the classical Hall–Petch relationship,  $\sigma_{\rm y}=\sigma_0+\frac{k_{\rm y}}{\sqrt{d}},$  where the resistance of the lattice to the dislocation motion is represented by  $\sigma_0$ , the strengthening coefficient by  $k_y$ , and the average diameter of the grain by *d*. As observed experimentally, a grain size of  $\approx 10 \text{ nm}$  exhibits the highest yield strength; below which yield strength either remains the same or decreases with further decreasing grain size, and this phenomenon is named the inverse Hall-Petch effect.<sup>[42-44]</sup> Several different mechanisms were proposed for this relation, which falls in dislocation-based, grainboundary-shearing-based, diffusion-based, and two-phasebased categories, as suggested by Carlton et al.<sup>[45]</sup>

Ceramic materials are usually considered brittle at room temperature (RT) but exhibit permanent deformation before failure at higher temperatures. In polycrystalline ceramics, the lack of significant plasticity is due to their lower fracture strength than vield strength due to the limited number of slip systems; therefore, they are likely to crack. In ceramics, the ionic charges (electrostatic forces larger than metals) enhance the Peierls stress (the stress required to move dislocation) and determine (mostly) the slip systems for easy glide. In addition to that, the Burgers vector of a ceramic dislocation is longer (e.g., 12 Å for 1/2[111] in Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub><sup>[46]</sup>; therefore, the Peirels stress is very high) than that of metals (e.g., 2.56 Å for the {111}<100> dislocation in Cu).<sup>[46]</sup> Furthermore, the dislocation glide is even more difficult in covalent crystals because covalent bonds are directional. Dislocation pile-ups (due to less mobility) occur at grain boundaries accompanied by stress concentrations, which can be relieved by microcracking (or secondary slip based depending on the strength of the grains).<sup>[47]</sup> Therefore, the fracture can usually be observed before any macroscopic yielding. However, plasticity by dislocation motion was observed in some ceramics at RT (e.g., MgO {110}  $<\!\!110\!\!>,\,SrTiO_3).^{[48-52]}$  In (001) SrTiO<sub>3</sub>, at RT, under Vickers indentation, dislocations generated from two slip systems, <110> {110}<sup>[53,54]</sup> and <011> {100}<sup>[54]</sup> were observed. Yang et al. studied the deformation behavior of <001> SrTiO<sub>3</sub> at RT, analyzed the stress-strain relation, and suggested the deformation mechanism in SrTiO<sub>3</sub> is no different from that of metals.<sup>[55]</sup> Proper control of chemical composition is also shown to control the deformation behavior. Excellent plasticity was observed in SrTiO<sub>3</sub> for a Sr/Ti ratio of 1.04.<sup>[56]</sup> Han et al.<sup>[57]</sup> showed elastic, elastic-plastic, and plastic deformations in single-crystal SiC nanowire using in situ transmission electron microscopy (TEM) nanoindentation. At the bent region, deformation-induced amorphization was observed.



#### 2.1.1. Nanoindentation Deformation of Materials

Indentation is a widely utilized technique to probe the mechanical properties of materials such as H and  $E^{[16,58,59]}$  by continuously monitoring the indenter penetration depth to the applied force with a known tip geometry. The high-resolution capacitive gauges and actuators make this instrument extremely sensitive in detecting/applying subnanometer-level displacements and nanonewton-range forces. The main advantage of using such depth-sensing indentation/instrumented nanoindentation is that the testing can be done at tiny length scales (ranging from nanometer to micrometer length scales). This is beneficial in probing deformation behavior (homogeneous/heterogeneous) of tiny anisotropic materials for examining the origin of plasticity in them. In contrast to the specific-shape (dog-bone) samples required for tensile testing, there is no extensive sample preparation required for performing nanoindentation.<sup>[60]</sup> Therefore, it can be applied to even softer and natural materials where mechanical polishing is not possible. Of course, the samples should be flat, and surface roughness should be as low as possible. Further, a variety of deformation modes (e.g., intermittent plastic events including activation of dislocation source<sup>[25,61–65]</sup> and phase transformations,<sup>[7,66–69]</sup> etc.) can be explored, and mechanical properties (other than H and E, such as hardening components,<sup>[70–74]</sup> creep parameters,<sup>[75–79]</sup> and residual stresses<sup>[80-83]</sup>) can be probed by changing the load-hold-unload time scales and loading conditions, choosing different geometry tips, and applying temperature, dynamic force, and electric and magnetic fields.

#### 2.1.2. Modes of Deformation

Any material, whether elastic, plastic or viscoelastic, brittle, etc. first deforms elastically when the indenter starts contacting the surface of the sample. Elasticity means returning to the original shape of the solid objects and materials once the load is removed. The elastic deformation is time- and rate-independent, and instantaneously reversible.<sup>[60]</sup> For a linearly elastic material, E is a proportionality constant between the applied stress and strain. (i.e.,  $\sigma = E\varepsilon$ ). However, it is not single-valued but straindependent in a nonlinearly elastic material.<sup>[60]</sup> Though some researchers use "M'" (anisotropic elastic constants' weighted average relative to the direction of indentation)<sup>[60]</sup> as the indentation modulus in anisotropic materials,<sup>[84]</sup> most of the reports use *E* or  $E_R$  for representing the reduced modulus or indentation modulus even for anisotropic materials. However, for viscoelastic or poroelastic materials, the E values depend on time or frequency scales due to their viscous flow behavior. The high-E materials are harder to deform elastically, and low-E materials are easy to deform. The elastic limit is the stress value beyond which the material does not recover to its original shape but deforms permanently.

In the case of purely elastic deformation, the P-h curve can be fitted with the elastic indentation solution. While the elastic relationship equation for a spherical indenter<sup>[85]</sup> is

$$P = \frac{4\sqrt{R}}{3} \frac{E}{1 - \vartheta^2} h^{\frac{3}{2}} \tag{1}$$

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for conical and pyramidal indenters.<sup>[86]</sup> Here, the radius of the indenter is represented by *R*,  $\vartheta$  is Poisson's ratio, and  $\gamma(=\frac{\pi}{2})$  is the ratio of the total depth ( $h_{max}$ ) of the contact depth ( $h_c$ ), which deviates significantly for complaint materials.<sup>[87,88]</sup>

As mentioned previously, *plastic deformation* is permanent deformation. Once initiated in the material, an additional increase in stress causes yielding. The materials that can sustain a large amount of plastic deformation are ductile, and materials that undergo fracture without entering plastic deformation are brittle. The tough materials will have high values of ultimate tensile strength,  $\sigma_{\rm u}$ , and strain at fracture,  $\varepsilon_{\rm f}$ . The time-dependent plastic deformation is known as creep.<sup>[89,90]</sup>

Both plastic and fracture modes of deformation exhibit discontinuities (such as pop-ins, a sudden displacement burst) in the loading part of the *P*-*h* curves. However, whereas plastic discontinuity occurs at lower loads and indenter penetration depths, fracture discontinuity occurs at much larger loads and penetration depths, indicating the threshold for elastic-plastic transition is much smaller compared to the threshold for indentation fracture. This scenario is usually for spherical indenters with large radii, where the contact strain generated by a spherical indenter constantly increases with the penetration depth due to its non-self-similar tip geometry; therefore, the P-h data can be represented as a stress-strain curve. There are many advantages with spherical indentation over sharp indentation (such as three-sided pyramidal Berkovich (75 nm radius) and cube-corner (≈30 nm radius) tips). First, the spherical indenter delays the onset of plasticity<sup>[58,91]</sup> and allows one to capture the elastic-plastic transition due to less localization of the strain field induced by a large curvature.<sup>[92]</sup> Second, and further, the analysis and testing are less complex due to the nonsingular nature of the stress fields (elastic) produced by the spherical indenters. In addition, the spherical indenters minimize the extent of damage and plasticity as compared to sharp indenters.<sup>[93]</sup> The sharp indenters cause severe degradation at the lower loads and can nucleate median cracks in samples with no pre-existing flaws due to the high strain generated under the tip. Although plastic deformation does not change the elastic modulus value (as the deformation involves atomic-level defects), the fracture does (as it is associated with the creation of new surfaces, and the microscopic defects reduce the stiffness).<sup>[91]</sup> The plastic deformation can be characterized by  $\sigma_v$ , the point of deviation from the linear stress-strain curve. The indentation plasticity can be measured by measuring the H, defined as the peak load divided by the  $A_c$  ( $H = \frac{P_{max}}{A_c}$ ). When the elastic deformation is small compared to plastic, a linear relationship between H and  $\sigma_{\rm y}$  can be observed.<sup>[94]</sup>

A *fracture* separates a material into two or more parts. If the fracture occurs without much plastic deformation, it is a brittle fracture (i.e., elastic fracture, complete energy absorption). In contrast, ductile fracture involves a large amount of plastic deformation before separation. Toughness is a measure of a material's ability to absorb energy before failure. Lawn and colleagues<sup>[18,95]</sup> developed an expression for fracture toughness by relating the *c*, *H*, *E*, and *P*<sub>max</sub>, namely



$$K_{\rm IC} = \xi \left(\frac{E}{H}\right)^{\frac{1}{2}} \left(\frac{P_{\rm max}}{c^{\frac{3}{2}}}\right) \tag{3}$$

where *c* is the crack length and  $K_{\rm IC}$  is the mode-I critical stress intensity factor. An empirical constant that depends on the geometry of the indenter is represented by  $\xi$ , which is 0.032 and 0.016 for the cube-corner indenter and the Berkovich indenter, respectively.<sup>[96]</sup> Lawn and Marshall<sup>[97]</sup> defined the brittleness of a material as the ratio of *H* and  $K_{\rm IC}$ . The brittleness index (BI) is BI =  $\frac{H}{K}$ .

## 2.1.3. Indentation Data Analysis

The indentation technique became popular after 1992 by developing a method to measure elastic modulus and hardness based on the *P*–*h* curve.<sup>[16,58]</sup> We are not showing the representative *P*–*h* curve here to explain  $h_{\text{max}}$ ,  $h_c$ ,  $h_R$ , etc. because it is well documented in many reports.<sup>[16,58]</sup> Tabor advanced the understanding of the indentation hardness testing and proposed an equation relating *H* and  $\sigma_y$  ( $H = C\sigma_y$ ), where *C* is a constant, which depends on the indenter geometry.<sup>[94,98–102]</sup> Later, a procedure for obtaining the stress (*P*/*A*<sub>c</sub>)–strain(*a*/*R*) curve from the *P*–*h* data of spherical indentation was developed by Kucharski and Mroz.<sup>[103]</sup> Here "*a*" is the contact radius and "*R*" is the radius of the indenter. In the nanoindentation method, unlike other indentation methods, the area  $A_c$  will be directly determined from the contact depth using the following expression:

$$A_{\rm c}(h_{\rm c}) = C_0 h_{\rm c}^2 + C_1 h_{\rm c} + C_2 h_{\rm c}^{\frac{1}{2}} + C_3 h_{\rm c}^{\frac{1}{4}} + \dots + C_8 h_{\rm c}^{\frac{1}{128}}$$
(4)

Here  $C_0 = 24.5$  is used if the Berkovich indenter is assumed as a perfect tip and at higher penetration depths. For the cubecorner tip, it is 2.598. For imperfect tips and shallow depths, the constants on higher terms must be considered, which can be calculated by fitting the tip area function curve.<sup>[90]</sup> The  $h_c$  can be estimated from the *P*–*h* curve (power-law fitting to the upper 10%–25% of the unloading curve), with the following equation

$$h_{\rm c} = h_{\rm max} - \varepsilon \frac{P_{\rm max}}{S} \tag{5}$$

where  $h_{\text{max}}$  is the maximum indentation depth and 0.75(*P*/*S*) denotes the extent of the elastic recovery ( $h_e$ ). Here, the contact stiffness or indentation stiffness S = dP/dh and  $\varepsilon$  is a constant that depends on the indenter geometry. The values of  $\varepsilon$  are 0.72, 0.75, and 1.00 for conospherical, Berkovich, and flat punch tips, respectively. The stiffness of the contact can be used to calculate the reduced modulus

$$E_R = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A(h_c)}} \tag{6}$$

where  $A(h_c)$  is the projected contact area at the  $h_c$  and  $\beta$  is the geometrical constant on the order of unity, and  $E_R$  is related to the  $E_s$  (Young's modulus) through the following relationship for isotropic materials (i.e., with only two independent elastic constants,  $E_R$  and  $\vartheta$ )

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$$\frac{1}{E_R} = \frac{1 - \vartheta_i^2}{E_i} + \frac{1 - \vartheta_s^2}{E_s}$$
(7)

where "i" and "s" represent indenter and sample.  $\vartheta$  is the Poisson's ratio (typically 0.3). For elastically anisotropic materials, Vlassak and colleagues<sup>[104]</sup> have provided an equivalent isotropic solution for efficient estimation of stiffness of the contact and elastic compliance. Because this is a well-known method for analyzing the indentation data, we have just briefed here. Readers are suggested to go through the original studies of Dr. Warren C. Oliver and Prof. George M. Pharr.<sup>[16]</sup>

The maximum shear stress,  $\tau_{max}$ , the stress required to nucleate dislocations, can be estimated using Equation (8) when the *P*–*h* curve exhibits a pop-in (usually for the spherical indentation case as discussed earlier)

$$\tau_{\rm max} = 0.31 \left(\frac{6E_R^2}{\pi^3 R^2}\right)^{\frac{1}{3}} P_{\rm max}^{\frac{1}{3}}$$
(8)

The reader should also note that the hardness estimated using this method may deviate from that of the other methods (such as the Vickers and microhardness tester), where the area is estimated from the residual contact impression. The materials with high elastic modulus slightly deviate from the indentation hardness measurement because of significant elastic recovery during unloading.

Though this technique is exceptionally good for quantifying the mechanical properties of materials, several factors affect the mechanical properties (both H and E). They are vibration during testing, indenter shape and calibrations, surface roughness, surface inhomogeneities, indentation size effects, thermal drift, machine compliance, pile-up/sink-in, etc.<sup>[105–109]</sup> It is known that the Oliver–Pharr method<sup>[16]</sup> overestimates the H and E<sub>r</sub> values (up to 60% and 30%, respectively)<sup>[110]</sup> when there is a pile-up around the indent because their evolution depends on the  $A_c$ . The H values are more affected than E<sub>r</sub> because  $H\alpha \frac{1}{A_c^2}$  and  $E_R\alpha \frac{1}{\sqrt{A_c}}$ . Researchers have proposed several models for determining the pile-up effect<sup>[110–113]</sup> and correct the hardness obtained by the Oliver–Pharr method.<sup>[16]</sup>

The Oliver and Pharr analysis<sup>[16]</sup> was developed based on Hertzian contact theory, and the relationships assume that the materials being studied are elastic, homogeneous, linear, isotropic, and experience small deformation. It does not account for the friction and adhesion between the indenter and the sample. Further, the pile-up of the plastically deformed material and sinkin effects cause improper estimation of the  $A_c$  and hence the mechanical properties. Furthermore, this method assumes the  $A_c$  is a function of  $h_c$ . In comparison, this assumption is correct for elastic, elastoplastic materials, but not accurate for viscoelastic materials as their  $A_c$  depends on both h and time (t). Therefore, creep causes alterations to the unloading curve and results in inaccurate time-dependent mechanical properties.

To avoid the need for estimating the  $A_c$  for calculating the mechanical properties of materials through indentation, Cheng and Cheng<sup>[114]</sup> proposed an indentation energy method based on the scaling relationship between *E*, *H*, and indentation work, *W*. The choice of proportionality coefficient between the *H*-to-*E* ratio and the irreversible work-to-total work ratio



determines the accuracy of the method.<sup>[115,116]</sup> By combining the scaling relationships, indentation H and E, an energy method to determine the H and E of electromagnetic materials was proposed. The equations are

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$$H_{\text{Indentation}}(F) = \left[k\frac{W_{\text{p}}}{W_{\text{tot}}}(F) + l\right]^2 \pi S(F)^2 / 4P_{\text{max}}(F)$$
(9)

$$E_{\text{Indentation}}(F) = \left[k\frac{W_{\text{p}}}{W_{\text{tot}}}(F) + l\right]\pi S(F)^2 / 4P_{\text{max}}(F)$$
(10)

Here, *F* is the electric/magnetic field strength, *l* is the intercept of the scaling relationship between  $H_{\text{Indentation}}/E_{\text{Indentation}}$  and  $W_{\text{p}}/W_{\text{Total}}$ . The field-dependent *H* and *E* can be determined by measuring the  $P_{\text{max}}$ , the initial unloading, and *W* and avoids the estimation of  $A_{\text{c.}}^{[113]}$ 

The size effects at micrometer scales were observed during nanoindentation, wire and thin-film bending, and tension experiments by many researchers. The size-dependent plasticity was attributed to the "geometrically necessary dislocations (GNDs)" (accommodate plastic bending in crystalline materials).<sup>[117]</sup> Though different theories<sup>[118–121]</sup> and models<sup>[122]</sup> qualitatively exhibit size effects under varying conditions, they were not thought to be applicable for nanometer scales, where very few dislocations exist because these models and theories rely on interactions between pre-existing, statically generated, and GNDs. The dramatic increase of H with decreasing indenter penetration depth is known as the indentation size effect (ISE). It is usually observed for materials that are indented with conical and pyramidal indenters (i.e., geometrically self-similar indenters). In continuum concepts and in geometrically selfsimilar tips, no length scales are involved; therefore, hardness should be independent of penetration depth if assuming that plasticity can be described by continuum mechanics. But there are many reports that have observed ISE below 1-10 µm depths. Also, there are a few reports available on reverse ISE<sup>[123-125]</sup> but ascribed to testing artifacts.<sup>[123,124,126]</sup> Initially, the ISE was thought to arise from the sample preparation issues, hardening of surface layers during polishing, indenter tip rounding (i.e., from a pyramid to spherical shape at small h). However, careful studies revealed that the ISE was found to arise due to the limited number of dislocations at shallow penetration depths/smaller deformation volumes. Nix and Gao explained the ISE in crystalline materials using the concept of GNDs.<sup>[127]</sup> The model says that GNDs that exist in addition to the statistically stored dislocations (SSDs) (produced during uniform straining) give the extra hardening component that becomes larger as the indent size decreases. However, GND-based predictions resulted in overestimation of the H values in the nanoregime, and also the *P*-*h* curves exhibited discontinuous features ( $<\approx$ 100 nm), which defied continuum models.<sup>[128]</sup> In the case of spherical indenters, ISE was manifested through the radius of the sphere,<sup>[129]</sup> and not the penetration depth. The mechanism of the ISE in ceramics, semiconductors, and amorphous materials could be due to crack formation, phase transformations, and non-dislocation-based mechanisms of plasticity.<sup>[130-132]</sup> Readers are suggested to read the review article written by Prof. Pharr and colleagues<sup>[133]</sup> on the indentation size effect, shortcomings of the Nix and Gao model, and several critical experimental considerations for measuring meaningful hardness values at shallower contact depths. Sharma and co-workers<sup>[134]</sup> showed that the phenomenon of flexoelasticity (coupling of strain gradients to polarization), as opposed to the dislocation activity, is responsible for the electromechanical indentation size effect in ferroelectric materials.

#### 2.1.4. Discontinuities in the P-h Curves

As discussed before, the nanoindentation response displayed as the P-h curves give the materials' primary mechanical characteristics. The onset of plastic deformation (elastic-plastic transition point) in crystalline materials can be characterized by the sudden displacement burst (known as pop-in) at constant load. Before the first pop-in, the loading part of the *P*–*h* curve can be described by the Hertzian contact theory,  $P = \frac{4}{2} E_R \sqrt{Rh^3}$ .<sup>[128]</sup> These pop-ins are often considered to be the result of dislocation activity<sup>[32]</sup> during indenter penetration.<sup>[63,135]</sup> It was proposed that the pop-in event originates from homogeneous dislocation nucleation beneath the indenter tip.<sup>[32,136]</sup> The pop-ins occur when the  $\tau_{max}$  underneath the indenter approaches the theoretical strength,  $\tau_{\rm th}$ .<sup>[137–139]</sup> The range of  $\tau_{\rm th}$  of crystalline metals is  $G/2\pi$  to G/30. Several electron microscopic studies revealed the intimate correlations between pop-in events and dislocation activities in nanoindentation studies.<sup>[135,140,141]</sup> The possibility of yield associated with the dislocation loops was first demonstrated under the indenter by Kelchner in Au using molecular dynamics (MD) simulations.<sup>[142]</sup> However, the simulation results were not exactly matched with the experimental results due to the size differences in the tip radii and the time scales used in the simulations and experiments.

Knap and Ortiz<sup>[143]</sup> demonstrated the critical effect of this disparity. It was realized that the pop-in event is a heterogeneous process of dislocation source activation or multiplication rather than a homogeneous dislocation nucleation event. Minor and colleagues<sup>[144,145]</sup> showed that the first dislocation activity paralleled with a discontinuity in the P-h curve with the help of an in situ TEM nanoindenter. They showed the initiation of dislocation activity and the interaction of the dislocation structure with grain boundaries in a dislocation-free Al sample during indentation. Schuh and colleagues<sup>[146]</sup> have performed hightemperature nanoindentation on Pt samples at different locations and showed that the first pop-in is thermally activated. They used a statistical model to assess the activation volume and activation energy at the first pop-in in Pt. Their study also suggested that the first pop-in event is associated with a heterogeneous event. There can be many pop-ins beyond the yield point, and they are related to further dislocation movement, multiplication, and evolution of the complex defect structure. However, similar displacement bursts were seen in amorphous materials also in which there are no dislocations.

The pop-in behavior has rarely been investigated in nonmetallic materials<sup>[147–150]</sup> (ceramics) compared to metallic systems.<sup>[128,138,151–156]</sup> As discussed above, while homogeneous dislocation nucleation under sharp tip (where there are no pre-existing dislocations), or by heterogeneous dislocation nucleation/multiplication (if the dislocations are pre-existing in metal-lic materials) are the reasons realized for observing pop-in events

in the loading part of the P-h curve, such mechanism cannot be attributed to the ceramic materials. It is because both dislocations and cracks were observed in ceramic materials after nanoindentation, which makes difficult to find out which is the most dominating mechanism causing a pop-in event. Because both the dislocation density and mobility of nonmetals tend to be much lower than those of metals, they are more likely to crack. However, because the dislocation density is relatively lower than that of metals, the possibility of indenting dislocation-free areas under a sharp indenter is very high. This can lead to the pop-in events associated with the need to nucleate dislocations. Fang et al.<sup>[157]</sup> correlated pop-in events in an oxide material (SrTiO<sub>3</sub>) only to dislocations without crack formation but below a critical tip radius. Page et al.<sup>[158]</sup> pointed out that under very low load nanoindentation, dislocation-mediated plasticity is the dominant mode of deformation in ceramics, as in the case of sapphire. At RT, many oxides, such as MgO,<sup>[159–161]</sup> ZrO<sub>2</sub>,<sup>[162]</sup> ZnO,<sup>[163]</sup> and SrTiO<sub>3</sub>,<sup>[148,164–166]</sup> were found to deform plastically via dislocation activity but often accompanied by the formation of crack(s).

Durst and colleagues have beautifully demonstrated the role of the critical radius of the indenter tip in dictating the mode of the deformation mechanism in SrTiO<sub>3</sub>.<sup>[148,164–166]</sup> Although the popin event due to dislocation-mediated plasticity is the dominant mode below critical indenter tip radius, the crack formation was more dominating along with simultaneous dislocation activity when the tip radius reaches to a critical size. For this, the following theory was considered. First, the ratio of  $\tau_{\rm max}$  at the pop-in to the maximum tensile stress ( $\sigma_{\max}^{\text{tensile}} = \frac{(1-2\nu)P_1}{2\pi a^2}$ , where  $P_1$  is the pop-in load) available beneath the indenter at the point of pop-in<sup>[85,167]</sup> was obtained, which was 0.43. In the second step, the ratio of the upper bound of theoretical shear strength  $(\tau_{\rm th} = G/2\pi = E/16)$  to the cohesive stress  $(\sigma_{\rm c-th} = \sqrt{\frac{E\gamma_{\rm s}}{x_{\rm o}}}) = E/10)^{[168,169]}$  was obtained, which was 1.6. These numbers suggest that during indentation with a spherical tip (irrespective of the radius of the tip), the  $\tau_{\rm max}$  reaches the  $\tau_{\rm th}$ first compared to  $\sigma_{\max}^{\text{tensile}}$  to reach the fracture strength. Indentation experiments on the (001) single-crystal SrTiO<sub>3</sub> surface (the measurement was manually stopped after pop-in to avoid further plastic deformation) with different effective radii tips (100 nm (Berkovich), 2, 5, and 25 µm (spherical)) and postindent scanning electron microscopic (SEM) images revealed only dislocation activities without cracks around the impression for Berkovich (100 nm tip) and spherical (2 µm tip); however, both dislocations and cracks were present near the residual indent in case of the 5 and 25 µm spherical tips. This indicates that the critical condition of shear strength was reached first in the case of a 100 nm tip. Therefore, nucleation of dislocations occurred before crack formation. Kondo et al.<sup>[170]</sup> showed inducing of dislocations without crack formation in SrTiO<sub>3</sub> with a 100 nm radius wedge-shaped indenter tip with the help of in-situ TEM indentation experiments. However, for smaller tips (i.e., the radius of the tips is smaller than the critical radius), for example, a Berkovich tip with 100 nm, the pop-in load (0.1 mN) was very low compared to the crack initiation (from the dislocation pileup) load ( $\approx$ 3 mN). Similarly, for a 2 µm spherical tip, while the pop-in load was 6–7 mN, the load to induce cracks was 11 mN.

However, for larger radius tips (than the critical size), concurrent dislocation activities and crack formation were evident during pop-in events. Such concurrent activity can be easily understood by observing the large pop-in width/magnitude. Therefore, it can be concluded that 1) pop-in events correspond to only dislocation activities in case of the radius of the tip being much smaller than the critical radius, and further loading after pop-in involves only dislocation activity, but no cracks, 2) In the case of the radius of the tip being slightly smaller than the critical radius, purely dislocation activity is responsible for the pop-in event, but a crack can be induced after the pop-in. 3) If the indenter tip has a critical radius, simultaneous crack formation and dislocation activities are responsible for the pop-in event. 4) For a larger tip radius than the critical radius, only crack formation (dominantly) is responsible for the pop-in event.<sup>[164]</sup> Of course. finding the critical tip radius is not easy as the boundary conditions need to be involved and depend on the deformation behavior of materials, slip systems, Burgers vector, pre-existing defect distribution, surface chemistry, humidity, rate dependence of the mechanical properties, mechanical properties of the tip, etc. Further, pop-in events can also happen due to pressure-induced phase transformation (crystalline-crystalline or crystalline-amorphous) in some of the brittle materials such as GaAs and Si under high-hydrostatic-pressure conditions.<sup>[5,150,171–175]</sup> We will discuss more on the mechanical deformation in various semiconductors in the coming sections. Readers are suggested to read the articles published by Karsten Durst.<sup>[176]</sup> who did pioneering work in this area, for a detailed analysis and discussion.

In metallic glasses, where the plastic deformation is unstable, bursts were attributed to the shear-banding events. The nanoindentation was shown to resolve individual shear events.<sup>[177]</sup> Moser et al.<sup>[178]</sup> observed the shear band formation during the in situ SEM indentation experiment and correlated the pop-in events with the appearance of individual shear bands at the periphery of the indenter. Chinh and co-workers<sup>[179–183]</sup> observed "jerky flow" of solid solution alloys during indentation, attributed to lattice dislocation interaction with solute atoms that led to instantaneous negative strain rate sensitivity and localization flow.

The  $\tau_{\text{max}}$  that drives the dislocation activity can be determined from the first pop-in load ( $P_1$ ). The maximum contact pressure for Hertzian contact (regardless of the elastic anisotropy) is given by

$$P_0 = \left(\frac{6PE_R^2}{\pi^3 R^2}\right)^{\frac{1}{3}}$$
(11)

For a given *n*th slip system, the maximum resolved shear stress,  $\max\{\tau_{RSS}^{(n)}(x_i)\}$  should be found by searching the entire stress field. The indentation Schmid factor *S* for this slip system is

$$S^{(n)} = \frac{1}{P_0} \max_{x_i} \left\{ \tau_{\text{RSS}}^{(n)}(x_i) \right\}$$
(12)

Equation (12) allows one to search all the slip systems. The largest indentation Schmid factor indicates the first activated slip system among all the slip systems,  $S = \max_n (S^{(n)})$ .

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From Equation (11) and (12), the relationship between the first pop-in load and pop-in stress ( $\tau_{\text{pop-in}}$ ) can be written as

$$P_1 = \left(\frac{\tau_{\rm pop-in}}{S}\right)^3 \frac{\pi^3 R^2}{6E_R^2}$$
(13)

and the corresponding contact radius<sup>[128]</sup>

$$a_{\rm pop-in} = \frac{\pi R \tau_{\rm pop-in}}{2E_R S} \tag{14}$$

While the discontinuities on the loading of the P-h curves are called pop-ins, a similar discontinuity on the indentation unloading curves is known as pop-out. The pop-out is a characteristic event during unloading of the indenter, indicating phase transformations (but not the onset of phase transformation) due to sudden volume expansion from highly dense crystalline phase to lower dense phases that does mechanical work against the indenter tip, producing the pop-out effect.<sup>[184]</sup> For example. under hydrostatic pressure conditions (even under nanoindentation where both the hydrostatic component and shear components of stress are present) the diamond cubic Si phase transforms to a metallic phase ( $\beta$ -Sn) between 10 and 12 GPa. Depending on the unloading rate, the unstable metallic phase further transforms to a mixture of rhombohedral (R8) and body-centered cubic phase (bc8) or an amorphous phase.<sup>[185]</sup> While the formation of the R8 and bc8 phases is usually accompanied by a pop-out event,<sup>[66,68,69,186–188]</sup> the formation of the amorphous phase is accompanied by an elbow.<sup>[186,189,190]</sup> The amorphous bands formed from the metallic silicon during unloading aligned the expected slip systems for the diamond cubic (dc)-Si, as observed by Suprijadi et al.<sup>[191]</sup>

# 2.1.5. Estimation of Dislocation Densities

The difference in dislocation densities in crystalline metals influences the indentation *P*–*h* curves. The *P*–*h* curves in the elastic–plastic regime can be described by  $P = HA_c = C\sigma A_c$ , where *C* is Tabor's factor (transferring complex to uniaxial stress state underneath the indenter) and  $A_c = 24.5h_c^2$  is the contact area of the Berkovich tip. The  $\sigma$  in FCC metals is controlled by the Taylor stress;  $\sigma_{\text{Taylor}}$  (accounting for dislocation interaction) is described by

$$\sigma_{\text{Taylor}} = M \alpha G b \sqrt{\rho} \tag{15}$$

where *M* is the Taylor factor and  $\alpha$ (=0.5) is an empirical factor that depends on dislocation structures.  $\rho$  is a function of indentation depth and is a linear superposition of  $\rho_{SSD}$  and the  $\rho_{GND}$ .  $\rho_{SSD}$  can be estimated using the following equation

$$\rho_{\rm SSD} = \left(\frac{H_0}{MC\alpha Gb}\right)^2 \tag{16}$$

 $H_0$  is the depth-independent hardness of the material. Using Equation (16), Barnoush<sup>[192]</sup> estimated the  $\rho_{SSD}$  for a very low dislocation density Al (designated as (Al-A) sample and a cyclically deformed Al (designated as Al-F) by setting the G = 23 GPa, b = 0.286 nm, and the depth-independent hardness of 0.1 GPa. The  $\rho_{\rm SSD}$  for Al-A and Al-F samples were  $1\times 10^{13}$  and  $2\times 10^{14}\,{\rm m}^{-2}.$ 

The  $\rho_{\text{GND}}$  can be estimated using an equation developed by Nix,<sup>[127]</sup>  $\rho_{\text{GND}} = \frac{3}{2bh} \tan^2 \theta$ . The equation was further modified as  $\rho_{\text{GND}} = \frac{3}{2bh} \tan^2 \theta$ , after Durst et al.<sup>[193]</sup> who defined a factor, *f*, ranging from 1 to 3.5, to account for a more realistic deformation volume (larger hemispherical plastic volume was found than predicted). Therefore, by combining these equations, the following equation can be obtained.

$$P = A_{\rm c} M C \alpha G b \sqrt{\rho_{\rm SSD} + \frac{3}{2} \frac{\tan^2 \theta}{f^3 b h}}$$
(17)

Equation (17) fits exceptionally well with the *P*-*h* curves, which will not only allow estimating the  $\rho_{SSD}$ , but also the correction factor describes the behavior of the samples due to the difference in plastic size in them. Using Equation (17), Remington et al.<sup>[194]</sup> estimated  $ho_{GND} = 1.9 imes 10^{16} \, {
m m}^{-2}$  for tantalum samples for an indentation depth of 100 nm and f=1. However, after Durst et al.<sup>[193]</sup> the  $\rho_{GND} = 2.6 \times 10^{15} \text{ m}^{-2}$  when f = 1.9 is chosen. This value closely matched the dislocation density measured from the transmission electron micrograph  $(1.2 \pm 0.5) \times 10^{15} \text{ m}^{-2}$ ). Since the *f* can vary in the range of 1–3.5, the  $\rho_{GND}$  can be in the range of  $1.9 \times 10^{16}$  -  $3.9 \times 10^{14}$  m<sup>-2</sup>.<sup>[194]</sup> Once the  $\rho$  values are known, the average spacing between dislocations, l, also can be estimated using  $l = \sqrt{\rho^{-1}}$ .<sup>[192]</sup> If the stressed zone underneath the indenter is smaller than the *l*, the probability of pre-existing dislocation under the stressed volume will be low. Therefore, for plasticity to occur, the  $\sigma$  must reach a high value to nucleate a dislocation. This will be observed in the form of a pop-in.<sup>[192]</sup> For annealed metals, the mean dislocation spacing will be larger than the highly stressed zone formed under the indenter (both Berkovich and conical tips).<sup>[192]</sup> Therefore, it is likely that all the indents will have pop-ins in the *P*-*h* curves. In conical indenters with a large radius, the  $\tau_{\rm max}$  will have maximum lateral coverage and increases with increasing contact radius. The probability of hitting the dislocation sources also increases. Therefore, the likelihood of observing pop-ins decreases. The Al-F samples show a 42% reduction in pop-in probability when the Berkovich tip is of the order of the dislocation spacing. However, when using a conical tip of a large radius, it was reduced to 21%.<sup>[192]</sup> Therefore, the indenter tip geometry and contact radius play a significant role in determining the nature of plasticity during nanoindentation.

The surface roughness of the sample can suppress the occurrence of pop-ins in the P-h curves due to the activation of preexisting dislocations and heterogeneous dislocation nucleation at surface steps. Further, the interstitial atoms influence the pop-in behavior by blocking pre-existing dislocations. The grain boundaries, dislocation density, and grain orientation relationships also affect the pop-in behavior. However, the pop-in behavior was found to be independent of the crystallographic orientation.<sup>[195]</sup>

By now, we have revised the basics of plasticity, indentation, and different modes of deformation, indentation data analysis, the indentation size effect, pop-in analysis, pop-out phenomena, etc. We will see how these concepts were understood/confirmed www.advancedsciencenews.com

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with the help of an in situ nanoscale electrical contact resistance technique during the indentation of various materials.

# 2.2. Nano-ECR

The novel nano-ECR measures electrical and mechanical properties simultaneously with precise control over the applied P and h. Compared to the conventional electrical probe techniques, the correlation between many parameters such as P (nanonewton to micronewton range), h (from angstrom to micrometer range), deformation, current, I (picoampere to microampere range), voltage, V (microvolt to volt range), and probe positioning have made the nano-ECR an efficient in situ electromechanical characterization technique at the nano-scale level and in designing next-generation materials and devices. Nano-ECR is also a useful tool to understand the charge transport mechanism and other functional properties of various systems under high strain, which can be applied to a localized area at the nanoscale. It allows one to probe any nanosize contact area and study the localized electromechanical properties.<sup>[196]</sup>

The nanoECR instrument (through-tip electrical measurement with conductive diamond tip) was codeveloped by Hysitron Inc. (now acquired by Bruker USA) and S. Ruffell, J. E. Bradby, and J. W. Williams<sup>[28]</sup> from the Australian National University. It showed contact resistance measurement at different penetration depths according to the voltage–current curves.<sup>[28,171]</sup> A schematic of the experimental setup is shown in **Figure 1**.<sup>[197]</sup>

The system consists of a conductive sample stage (typically Cu), a three-plate capacitive transducer, and a conductive indenter probe. The conductive tip is mechanically connected to the center plate of the three-plate capacitive transducer with electrical isolation.<sup>[198]</sup> In nanoindentation, the indenter tip penetrates the sample, and from the *P*–*h* curve, *H* and *E* can be measured. For the electrical measurement, a current (*I*) is passed from the SourceMeter instrument to the conductive stage, to which the sample is electrically coupled. The electrical measurements can be made in two modes: 1) continuous monitoring of the current flowing through the conductive tip during a complete indentation cycle (i.e., load–hold–unload segments) with a fixed voltage (*V*) across the sample–tip system. This method provides *I*–*h* curves, which help in understanding the real-time deformation mechanism of the sample. 2) Sweep mode, where





the voltage is varied (e.g., -10 to +10 V), and the current is measured at each step of voltage (*I*–*V* curves) and any point in the loading/hold/unloading cycle.<sup>[28]</sup> Thus, by penetrating the conductive probe into the sample using both methods concurrently, the force, displacement, current, and voltage can be measured simultaneously. In a typical measurement, the source meter's two channels act as a source and current–voltage amplifier to transmit current to the computer, respectively. All the parameters can be controlled through the software.<sup>[197]</sup>

# 2.3. Indenter Tips for In Situ Electrical Measurement

The development has begun of the usage of stainless steel (SS), tungsten (W), tungsten carbide (WC), and cobalt alloys (WC–Co), and conductive diamond as conductive tips.<sup>[10]</sup> BDD tips were widely used for in situ electrical characterization coupled with P-h data. However, the clustering of dopants resulted in the non-uniformity of conductivity in BDD. This led to the development of alternative hard yet conducting ceramic tips.<sup>[10]</sup> The details will be discussed in the coming sections.

# 2.3.1. BDD Tips

Understanding structural, electrical, and dopant properties and the surface of BDD tips is essential as the quality of electrical characterization depends on the properties of the tips. A nonuniform doping profile and lack of consistency in doping will lead to electrically inactive centers. This will result in poor reproducibility, efficiency, and accuracy of in situ conductive nanoindentation.<sup>[199]</sup> Sprouster et al.<sup>[199]</sup> conducted a detailed study on the electrical properties of BDD tips. They classified BDD tips based on the I-V curves (See Figure 2). Rectifying I-V curves (nonlinear) were shown by the family "S" and Ohmic I-V curves (linear) by the family "O." Nonlinearity was also observed at low loads in "O" family tips. Ruffell et al.<sup>[28]</sup> observed non-Ohmic I-V curves at low indenter penetration depths due to the smaller  $A_c$  between the sample and tip. Fang et al.<sup>[200]</sup> observed the same result while indenting bulk Cu. Further, surface oxidation or nonuniform doping also results in nonlinear I-V curves.

The electrical properties of BDD tips depend on the dopant concentration. If the dopant concentration is below  $\approx 10^{19}$  cm<sup>-3</sup>, then the contact between the tip and metal substrates will be dominated by a Schottky contact. At RT, the boron acceptors' bonding energy will be high at this concentration, which will result in a lower number of ionized boron donors. Between  $10^{19}$  and  $10^{20}$  cm<sup>-3</sup>, the nearest-neighbor hopping is the conduction mechanism mode, whereas, at  $B \approx 2 \times 10^{20}$  cm<sup>-3</sup>, the diamond behaves like a metal. Thus, the rectifying *I*–*V* curves in the family "S" were due to low active B concentration, and the Ohmic *I*–*V* curves in the family "O" were due to high active dopant concentration.<sup>[199]</sup>

Ruffell et al.<sup>[27]</sup> used BDD tips to study the electrical properties and pressure-induced phase transformations in Si, and Stauffer et al.<sup>[198]</sup> used BDD tips to study plasticity in thin metal films. Fang et al.<sup>[200]</sup> used conductive diamond tips to measure the  $A_c$  from nonlinear *I*–*V* curves. Nowak et al.<sup>[171]</sup> used heavily doped ( $\approx 1 \times 10^{21}$  cm<sup>-3</sup>) BDD tips to study the current spike





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**Figure 2.** *I*–*V* curves obtained on a,b) gold and c,d) glassy carbon standards using nanoindentation equipped with in situ nano-ECR at different loads. The *I*–*V* curves shown in (a,c) are for S-family tips and those in (b,d) are for O-family tips. The insets show the *P*–*h* curves. Reproduced with permission.<sup>[199]</sup> Copyright 2011, Cambridge University Press.

effect during the electrical–mechanical response of GaAs crystals. Bhaskaran et al.<sup>[9]</sup> used BDD tips with a resistivity of  $3.3 \,\Omega$  cm to study the electromechanical response in piezoelectric thin films and nanoislands.

Even though BDD tips were widely used for in situ conductive nanoindentation, the phase segregation and surface inhomogeneity in B-doped diamond<sup>[198]</sup> with high dopant concentration limited its use. Hence, the usage of BDD tips to extract quantitative information of electrical properties during nanoindentation was reduced as it demanded a priori knowledge of B doping and the electrical and structural properties of a tip.

## 2.3.2. Refractory Carbide Tips

Refractory carbide (e.g., vanadium carbide, VC) materials are known for their high hardness ( $\approx$ 26–35 GPa) and elastic moduli ( $\approx$ 470–500 GPa) and extremely low electrical resistivities ( $\approx$ 5–7 × 10<sup>-4</sup>  $\Omega$  cm). VC is also known for its high scratch and wear resistance and is therefore widely used in harsh environmental conditions such as high-temperature and wear applications and precision mechanical instruments. Dopant segregation and inhomogeneous surface issues due to dopant concentration, limiting BDD usage, were not found in carbide tips. Therefore, vanadium carbide tips are an effective alternative to BDD tips.<sup>[11]</sup>

Sprouster et al.<sup>[11]</sup> studied the electromechanical properties of gold (Au), glassy carbon (GC), and two silicon samples using in situ conductive nanoindentation fitted with a VC tip and compared them with the BDD tip results. The real-time electric

measurement during indenter penetration into GC and Au samples as a function of time is shown in Figure 3a,c. The pile-up formation in the Au sample during loading and the corresponding conductance changes are apparent in Figure 3c. The I-V curves obtained for GC (Figure 3b) and Au (Figure 3d) using the VC tip showed a pronounced difference compared to the BDD tip. The I-V curves obtained using BDD tips were asymmetric and nonlinear,<sup>[199]</sup> whereas for VC tips linear curves were seen. This was attributed to the lower work function difference between the VC tip and the metal sample, eliminating the Schottky contact. Also, there were no traces of intrinsic material issues (doping issues) associated with the tip. Further, Sprouster et al.<sup>[11]</sup> observed that the spreading resistance and contact resistance were the dominant ones among all the resistive components, and the resistance decreased with increasing load (due to the higher  $A_c$ ). Hence, the VC tips were highly efficient in quantifying the electromechanical responses during indentation if the tip-sample and back electrical contacts are Ohmic.<sup>[11]</sup>

## 2.4. Resistive Components in a Circuit

When two conductors are electrically connected, there will be few resistance components associated with them.<sup>[201]</sup> Here, the electrical contact area, which will be represented as the "*a* spot," will be reduced from the real mechanical  $A_c$ . The "*a* spot" is nothing but the constriction to current lines' flow at the contact point<sup>[202]</sup> (see **Figure 4**). This will, in turn, increase the contact resistance due to contamination from oxide formation or surface roughness. The density and shape of the "*a* spot" determine the contact







**Figure 3.** The a,c) *h* and  $\sigma$  versus time (*T*) curves and b,d) *I*–*V* curves obtained during loading for the GC (a,b) (at different loads varying from 0.5 to 6 mN) and Au (c,d) (at different loads varying from 0.5 to 2 mN) samples. An increase in  $\sigma$  with increasing *P* (or increasing tip–sample  $A_c$ ) is evident. Reproduced with permission.<sup>[11]</sup> Copyright, 2014, Elsevier.



**Figure 4.** The flow of electric current from surface A to B and current flow lines' behavior at the contacts/interface.

resistance. Mainly, in the case of in situ conductive nanoindentation, when the conductive tip forms an electrical contact with the sample, a series of resistances comes into consideration (see **Figure 5a**). These resistances were quantified considering the conditions that the contact is Ohmic and the surface roughness and oxidation of the surface are negligible.

A typical plot of *h* and  $\sigma$  versus time is shown in Figure 5b, obtained using a VC Berkovich tip on low-resistivity Si at an applied voltage of +20 V. It is evident that the electric current does not rise at the lower penetration depths; however, a rapid increase is apparent once the *h* corresponds to the onset of semiconducting dc-Si to metallic ( $\beta$ -Sn) transformation. A rapid decrease in conductivity until the pop-out event and again rise

immediately after the pop-out during unloading were attributed to the phase transformation from  $\beta$ -Sn to fully nucleated R8/bc8.<sup>[11]</sup>

# 2.4.1. Spreading Resistance (R<sub>SPR</sub>)

The spreading resistance originates when the current is constricted at the contact point.<sup>[202]</sup> Consider a metallic probe indenting a semiconductor sample; then the current, which is concentrated at the tip, spreads radially out of the tip to the sample. Therefore, it is named spreading resistance.

Considering that the "*a* spot" is circular, the solids are semiinfinite, and the contact interfaces are  $||^{\text{el}}$ , then the resistivity of the solids is given by  $\rho = \frac{\rho_1 + \rho_2}{2}$  and the "*a* spot" radius is given by *a*, and

$$R_{\rm SPR} = \frac{\rho}{2a} \,\Omega \tag{18}$$

This is referred to as the Holm equation. Depending on the shape of the "*a* spot," the spreading resistance (Equation (18)) also changes.<sup>[202]</sup> If the contact interfaces are not  $||^{el}$ , then the angle factor is also included in Equation (19). Ideally, when two conductors come into contact, the current flow can happen from the probe to the sample and vice versa. Then the  $R_{SPR}$  includes two components<sup>[13,201,203]</sup>

$$R_{\rm SPR} = \frac{\rho_{\rm s}}{2\pi r} \arctan\left(\frac{2t_{\rm s}}{r}\right) + \frac{\rho_t}{2\pi r} \arctan\left(\frac{2t_{\rm t}}{r}\right) \tag{19}$$

 $\rho_{\rm s}$  and  $\rho_{\rm t}$  and  $t_{\rm s}$  and  $t_{\rm t}$  correspond to the sample's and tip's resistivity and thickness and *r* is the radius of the contact. For





**Figure 5.** a) Resistive components involved in the conductive indentation (through-tip) measurement of Si. b) The variation of  $\sigma$  with increasing *h* of low resistivity ( $\rho$ ) Si (9.10 × 10<sup>-3</sup>  $\Omega$  cm) as a function of time during conductive nanoindentation. Reproduced with permission.<sup>[11]</sup> Copyright 2014, Elsevier.

a thicker sample and large contact, Equation (19) will be similar to the Holm equation (Equation (18)).<sup>[11]</sup> The  $R_{SPR}$  can also be utilized to calculate the sample's bulk resistance, provided the contact area is known.

## 2.4.2. Contact Resistance $(R_C)$

The  $R_{\rm C}$  dominates when there is an increase in the load, and the  $R_{\rm SPR}$  is negligible. It occurs when the electrical contact area is less than the mechanical  $A_{\rm c}$ . It is calculated under Ohmic conditions and is essential while probing nonmetallic samples.<sup>[13]</sup> The  $R_{\rm C}$  depends on the contact area and doping conditions of the semiconductor.<sup>[11]</sup> The difference between the actual resistance and the ideal resistance occurs when there is a difference between the actual contact and the ideal contact.

 $R_{\rm C} = R_{\rm a} - R_{\rm i} \tag{20}$ 

 $R_{\rm a}$  and  $R_{\rm i}$  are the actual and ideal resistances measured between a common reference potential and the actual contact and ideal contact, respectively.

The actual contact is said to be away from the ideal contact under the following conditions<sup>[204]</sup>: 1) At the interface, when the charge carrier density differs from the bulk of the sample due to the work function difference of the metal contact and semiconductor. 2) The presence of foreign matter at the interface of the metal contact and semiconductor. This may be due to the formation of insulating oxide layers or other contamination.

In an ideal contact, there is no interfacial layer.<sup>[204]</sup> Since  $R_{SPR}$  is calculated without considering the contamination layers, the  $R_c$  is the sum of  $R_{SPR}$  and the resistance due to contamination layers. Therefore, knowledge of the volume of material in contact with the probe is vital to calculate  $R_C$ .<sup>[205]</sup> The  $R_C$  for an idealized Ohmic contact is given by

$$R_{\rm c} = \frac{R_{\rm C}'}{\pi r^2} \tag{21}$$

 $R'_{\rm C}$  is the specific contact resistance (ohm cm<sup>2</sup>).

Both  $R_{\text{SPR}}$  and  $R_{\text{C}}$  can be calculated considering that the radius of the "*a* spot" is larger than the mean free path (MFP) of the electron flow. This is known as the diffusive regime. In terms of conductance, *G*, the Maxwell conductance model<sup>[206,207]</sup> (derived for elastic contacts in a circular constriction for a "ball and flat" model,  $G = d/\rho_{\text{e}}$ ), relates  $A_{\text{c}}$  to changes in conductance caused by a constriction in electronic transport. Here, the contact diameter is represented by *d*, which is much larger than the MFP of an electron, and  $\rho_{\text{e}}$  is the average resistivity of the indenter and the substrate. A very small contact (of the order of a few square nanometers) is said to be in the Sharvin, or ballistic limit ( $d \leq$  MFP of an electron).<sup>[208,209]</sup> In this region, where the conductance is directly proportional to the square of *d* 

$$G = \frac{3\pi d^2}{16\rho_{\rm e}\lambda} \tag{22}$$

Wexler correction describes the transition between ballistic and diffusive contacts and connects the Sharvin limit to the Maxwell limit.  $^{\left[210,211\right]}$ 

The same concept in contact resistance terms can be written like this. If the radius of "*a* spot" is much smaller than the MFP of the electron, then it is ballistic regime and the resistance can be calculated using the Sharvin resistance or Knudsen resistance equation<sup>[208,209,211,212]</sup> where  $R\alpha r^2$ , where *r* is the contact diameter. In the ballistic regime, tip shape anomalies and poor electrical contact result in imperfect quantitative resistance measurement.<sup>[11]</sup> Surface roughness plays a significant role in the actual contact area.<sup>[207,213,214]</sup> More details on these regimes are provided in Section 2.4.3.

# 2.4.3. Other Resistive Components and Calculation of Total Resistance $(R_T)$

Further resistance components other than  $R_{\text{SPR}}$  and  $R_{\text{c}}$  that come into consideration during in situ conductive electrical characterization include back contact resistance  $R_{\text{BC}}$ , sample resistance  $R_{\text{s}}$ , and bulk resistance  $R_0$ . As the name indicates,  $R_{\text{BC}}$  is the



resistance offered by the back contact with the sample, which is usually very less and negligible. The  $R_s$  can be calculated from the known resistivity " $\rho_s$ " of the sample.<sup>[11,215]</sup> When the sample thickness is very much higher than the contact radius, the sample resistance will be minimal compared to other resistive components. In such cases,  $R_{SPR}$  and  $R_C$  play the dominant role.<sup>[11]</sup> The bulk resistance,  $R_0$ , is the sum of resistances offered by the conductive tip and the circuit's external components.<sup>[11,215]</sup> Hence, the  $R_T$ , in an entire nano-ECR experimental setup, can be written as

$$R_{\rm T} = R_{\rm SPR} + R_{\rm C} + R_{\rm s} + R_{\rm BC} + R_0 \tag{23}$$

In the case of thick samples, with thickness >>r

$$R_{\rm T} = R_{\rm SPR} + R_{\rm C} + R_{\rm BC} + R_0 \tag{24}$$

Substituting for  $R_{\text{SPR}}$  and  $R_{\text{C}}$  from Equation (18) and (21), we obtain

$$R_{\rm T} = \frac{\rho}{2r} + \frac{R_{\rm C}'}{\pi r^2} + (R_{\rm BC} + R_0)$$
(25)

Therefore, in practical cases, the  $R_{\rm T}$  measured depends upon three main resistance quantities. They are 1) the  $R_{\rm SPR}$ , which is inversely proportional to r, 2) the contact resistance, which is inversely proportional to  $r^2$ ; and 3) the bulk resistance, which is the sum of the tip resistance and the external circuit resistance, which is constant throughout the experiment.<sup>[11]</sup> Tip resistance can be calculated if we know the tip resistivity,  $\rho_{\rm tip}$ , and the constant  $\alpha$ , which is related to the geometry of the tip.

$$R_{\rm tip} = \alpha \cdot \frac{\rho_{\rm tip}}{h_c} \tag{26}$$

where  $h_c$  is the contact depth. If the tip defect is included, which is given by the rounded apex of height  $h_0$ 

$$R_{\rm tip} = \alpha \cdot \frac{\rho_{\rm tip}}{h_c + h_0} \tag{27}$$

The expression is based on two assumptions: that the current flow is homogeneous through the tip and that the tip inside the sample will affect the tip resistance linearly. The resistivity of the most commonly used Berkovich BDD tip is in the range [0.2–2]  $\Omega$  cm,<sup>[216]</sup> whereas for the VC tip, it is in the range of  $5 - 7 \times 10^{-4} \Omega$  cm.<sup>[11]</sup>

Sprouster et al.<sup>[11]</sup> showed that it is possible to fit  $R_{\rm T}$  as a function of the other three terms' contact radius and quantify the resistance components. **Figure 6** shows the *R* versus *h* curve for low-resistance silicon. This method of calculation is applicable only in Ohmic conditions. Also, while converting *h* to  $A_c$ , proper calibration of the tip area is required, which will be discussed in the next section.

Equation (25) uses  $\rho$ ,  $R'_{\rm C}$ , and  $(R_{\rm BC} + R_0)$  as floating parameters. It is clear from the Figure 6 that the  $R_{\rm T}$  fits very well for all radii above 125 nm. It also shows the onset of dc-Si to  $\beta$ -Sn (shown with an arrow in Figure 6) and hence Ohmic-like contact between the sample and the tip. Below the contact radius  $\approx$ 125 nm, the contact between dc-Si and the tip is not Ohmic, and therefore, the proposed Equation (25) could not fit well.





**Figure 6.** Variation of the measured total resistance as a function of contact radius for the low- $\rho$  Si along with fitted circuit resistances. Reproduced with permission.<sup>[11]</sup> Copyright 2014, Elsevier.

Using quantitative analysis, Sprouster et al.<sup>[11]</sup> obtained the values of  $\rho_s$ ,  $R'_C$ , and  $(R_{\rm BC} + R_0)$  as  $9 \times 10^{-3} \Omega \,{\rm cm}$ ,  $10 \,\Omega \,{\rm cm}^2$ , and  $10 \,\Omega$ , respectively, which were in good agreement with the independently measured values. Therefore, Sprouster et al.<sup>[11]</sup> concluded that it is possible to quantify the resistive components involved in in situ through-tip electrical contact resistance measurement during nanoindentation on Si and the extent of metallic phase formation under the indenter with increasing load.

# 2.4.4. Electron Transport in Different Regimes

Very recently, Volpi and colleagues<sup>[217]</sup> reported the results of experimental, analytical, and numerical studies of contact resistance on (100) Au bulk and polycrystalline films using custommade resistive nanoindentation using a BDD tip (0.2–2  $\Omega$  cm) to understand the evolution of contact resistance at different regimes, the effect of surface oxidation (on Cu and Al), surface rheology effects, etc. As we have already discussed in the previous section, the total resistance includes the sum of the resistance of the setup, sample, tip, and interface.

$$R_{\text{contact}} = R_{\text{setup}} + R_{\text{tip}} \left( \alpha \frac{\rho_{\text{tip}}}{r} \right) + R_{\text{interface}} \left( \alpha \frac{\rho_{\text{interface}}}{r^2} \right) + R_{\text{sample}}$$
(28)

Here *r* is the contact radius, defined as  $\sqrt{\frac{A_v}{\pi}}$ . However, Equation (28) is valid only in the pure diffusive regime, which we will discuss in the coming sections. The  $R_{tip}$  equation is valid only on two conditions. One, the distribution of current within the tip before contact with the sample is homogeneous. Second, after the contact, the tip penetration into the sample affects the tip resistance linearly. However, as BDD tips are highly resistive (approximately five orders) compared to the sample (metallic), the current will be localized at the periphery rather than be homogeneously distributed upon contact. Nakamura et al.<sup>[218]</sup> confirmed that the electrical resistance of ring contacts is equal to the total resistance at the contact surface divided by the shape factor (SF). The SF is the amount of current that flows through

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the peripheral ring of width ( $t_r$ ) normalized to the total current. Volpi et al.<sup>[217]</sup> showed that the SF would be constant throughout the indentation experiment by studying the current constriction lines and plotting SFs with different penetration depths. The  $\rho_{\text{interface}}$  term plays an important role when there is an oxide layer on the surface. The  $R_{\text{sample}}$  includes the spreading resistance, and it can be neglected, as it is proportional to the sample resistivity and the resistivity of metals is very low compared to that of BDD tips. Hence, the  $R_c$  can be simply written as a linear quadratic with the reciprocal of r, the contact radius.

$$R_{\rm c} = A + \frac{B}{r} + \frac{C}{r^2} \tag{29}$$

Where the *A* and *B* constants depend only on the experimental setup and *C* describes the interfacial behavior.

At the very early stages of penetration during indentation (i.e.,  $\approx 1 \text{ nm}$  depth), the resistance values are highly dispersed, with extremely high resistance values ( $\approx 10^{12} \Omega$ , usually recorded up to the sensitivity of the source meter), and rapidly fall to  $\approx 10^5 \Omega$ . Volpi et al.<sup>[217]</sup> beautifully demonstrated such a plot by fitting the *R*-*h* curve with equations representing different electron transport regimes.

*Tunneling Regime*: Before the surface is detected by the indenter tip (i.e., before the tip–sample contact, 2-3 nm above the surface), the flow of electrons can take place from the tip to the sample (because a *V* is given to the sample) through tunneling phenomena. The corresponding tunneling resistance can be obtained by

$$R_{\rm tunneling} = A_{\rm T} e^{-2\alpha h_{\rm QS}}, \ h_{\rm QS} \le 0 \tag{30}$$

where  $h_{\rm QS}(h - \sqrt{2}\delta h)$  is the quasi-static penetration depth,  $A_{\rm T}$  is constant (1 × 10<sup>14</sup> in Volpi et al.<sup>[217]</sup> experiment),  $\alpha = \frac{\sqrt{2mE_{\rm tunnel}}}{\hbar}$ , where  $E_{\rm tunnel}$  is the barrier height for the electrons to cross and  $\delta h$ is the RMS tip oscillation (0.65 nm). The tunneling barrier height can be estimated by subtracting the applied bias and negative electron affinity of diamond (0.5 eV)<sup>[219]</sup> to the bandgap of diamond (5.5 eV). The contact depth is the actual penetration depth in this range.

*Ballistic Regime:* Once the indenter starts contacting the sample, the tip meets surface roughness (assume 2–5 nm), squeezes the local points, and tries to flatten the surface for ballistic conduction. There are a few such localized spots that are in contact with the indenter. On those points, the local contact radius r is smaller than the electron MFP; therefore, electrons collide elastically while crossing the interface. The ballistic resistance can be written as

$$R_{\text{ballistic}} \propto \frac{\lambda_{\text{mfp}}}{r^2}$$
 (31)

As the penetration depths are shallow, the tip radius can be considered a sphere with a large radius. Therefore,  $r = \sqrt{2Rh_c - h_c^2}$ , but, because  $R >> h_c$ , Equation (31) can be written as  $R_{\text{ballistic}} = \frac{A_{\text{B}}}{h_c}$ , where  $A_{\text{B}}$  is constant (8 × 10<sup>4</sup> in Volpi et al.'s<sup>[217]</sup> experiments). When  $R = \lambda_{\text{mfp}}$ , a transition from ballistic to diffusive will occur. For the BDD tip where holes dominate conduction, the MFP is 1–10 nm, and for Au, it is 38 nm. Volpi

et al.<sup>[217]</sup> observed that the ballistic regime extends up to 5.0 nm, which is more than the surface roughness of the sample ( $\approx$ 3 nm).

*Diffusive Regime*: As discussed in the ballistic regime, when the local contact radius is larger than the electron MFP, electrons flow continuously. Here, the constriction resistance is linearly proportional to the reciprocal of contact resistance  $\left(\frac{\rho_{\rm tip}}{r}\right)$  and the tip shape changes continuously (with increasing penetration depth) from the spherical apex to self-similarity; two domains (diffusive/spherical apex and diffusive/tip body) can be observed. From simple geometrical consideration, the constriction resistance of the spherical apex can be obtained as

$$R_{\rm apex} = \frac{\rho_{\rm tip}}{\pi R} \times \left[ a \tanh\left(\frac{R-h_{\rm c}}{R}\right) - a \tanh\left(\frac{R-h^*}{R}\right) \right]$$
(32)

This is valid if  $h_c$  is less than the defect extent  $h^*$ . Beyond this point, self-similarity dominates, where *r* will be proportional to  $h_c$ . For higher penetration depths,  $R = h_c + h_0$ ; thus,  $R_{\text{tipbody}} \propto \frac{\rho_{\text{tip}}}{h_c + h_0}$ . Most of the studies we describe in Section 3 can be explained using Equation (32).

Volpi et al.<sup>[217]</sup> fitted the *R*-*h* curve (log–log plot) to Equation (30)–(32) of different regimes and explained the depth-dependent evolution of contact resistance between the tip and the sample, as shown in **Figure 7**. Readers are suggested to read the original research study of Volpi et al.<sup>[217]</sup> for a detailed discussion.

Volpi et al.<sup>[217]</sup> conducted numerical modeling of these experiments to validate the analytical calculations and identified the capabilities, such as bounds, sensitivity to tip defect, sensitivity to rheology, and the effect of an oxide layer, for conductive nanoindentation.

# 2.5. Contact Area and Its Calibration Methods

Sprouster et al.<sup>[11]</sup> adopted the methodology based on the nanoindentation of fused quartz with varying loads to convert the penetration depth into the contact area from the unloading curves.<sup>[16]</sup> The conversion of *h* measured as a function of the load to the contact area is an essential step in calculating the  $R_{\rm T}$ . The projected contact area,  $A_{\rm proj}$  of a Berkovich tip indenter is given by

$$A_{\rm proj} = 3\sqrt{3}h_{\rm c}^2 \tan^2(\theta) \tag{33}$$

where  $\theta$  is the Berkovich tip's face angle (65.3°) and  $h_c$  is the contact depth. The surface area  $A_{surf}$  of the tip in contact with the sample is given by

$$A_{\rm surf} = \frac{3a^2}{4\sqrt{3}{\rm sin}\theta} \tag{34}$$

where  $a = 2\sqrt{3}h_c \tan(\theta)$ 

Combining equation,<sup>[33,34]</sup> we get

$$A_{\rm surf} = 1.1 A_{\rm proj} \tag{35}$$

The contact radius for the given penetration depth can then be calculated as





**Figure 7.** The *R* versus *h* curves (in the log–log scale) obtained from in situ conducting nanoindentation using a BDD tip on bulk (100) Au at an applied bias of 2 V. a) The full-scale graph covering resistances up to  $10^{12} \Omega$ ; b) a zoom-in view of (a) highlighting other mechanisms such as ballistic, diffusive spherical, and diffusive apex. The penetration depth along the *x*-axis was artificially shifted by the authors for better visualization. Reproduced with permission.<sup>[217]</sup> Copyright 2019, AIP Publishing LLC.

$$A_{\rm surf} = \pi r^2 \tag{36}$$

The method is applicable only for cases where h > 100 nm. For h < 100 nm, tip rounding, inaccuracy in tip-area calibration, and poor electrical contact play a major role.

In general, the  $A_c$  can be calculated from the penetration depth using Equation (4) in Section 2.1.3.

Recently, Dassonneville et al.<sup>[216]</sup> proposed a method to calibrate  $A_c$ . They reduced the total measured resistance to

$$R_{\text{measured}} = A + \frac{B}{h_{\text{c}} + h_0} \tag{37}$$

*A* and *B* are constants independent of the specimen but dependent on experimental setups such as tip geometry, circuit resistance, and resistivity. A standard electrical calibration was done on a bulk gold sample.  $R_{\text{measured}}$  versus  $\frac{1}{h_c+h_0}$  was plotted, and from the linear curve, the *A* and *B* constants could be determined, as shown in **Figure 8**. The process to compute  $A_c$  is as



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**Figure 8.** The R versus reciprocal of the corrected contact height graph of the Au sample. The constants A and B were determined from the linear fit. Reproduced with permission.<sup>[216]</sup> Copyright 2019, Cambridge University Press.

follows. The tip geometry is determined with the projected area to contact depth equation given by  $Oliver-Pharr^{[16]}$ 

$$A_{\rm c} = \pi (\alpha_{\rm tip} (h_{\rm c} + h_0))^2$$
(38)

 $\alpha_{\rm tip} = 2.67 \alpha_{\rm tip}$  for the BDD tip, and  $h_0$  is the rounded apex height of the tip. In a recent article by Volpi et al., the *A* and *B* constant were determined (245,  $2.52 \times 10^5$ , respectively)<sup>[217]</sup> using  $R_{\rm contact}$  versus  $\frac{1}{h_c+h_0}$ . Because of the  $h_c$  term involved in the equation, it is possible to monitor  $A_c$  by increasing *h* continuously (because the calibration step relates  $R_{\rm contact}$  and  $h_c$ ). In general, in the case of soft thin films on stiff substrates, the contact area is determined using the Fredholm integral<sup>[220–222]</sup> (or finite element model (FEM) studies) coupled with a postmortem AFM scan of the residual indent at a given *h*. Doerner, Nix, and Saha have developed several empirical approaches for estimating  $A_c$ .<sup>[223,224]</sup> However, the  $A_c$  estimated using Oliver– Pharr,<sup>[16]</sup> and Saha–Nix methods<sup>[224]</sup> underestimated the  $A_c$  by 50%, but the Saha–Nix model<sup>[224]</sup> worked well up to 40% of the film thickness (i.e., for low penetration depths) and deviates at higher penetration depths, as explained by Han et al.<sup>[220]</sup>

Fang et al.<sup>[200]</sup> carried out conductive nanoindentation using a BDD tip on annealed copper to understand the instantaneous  $A_c$  and H. The voltage was swept between -10 and +10 V in 20 equal steps; thus, both P-h and I-V curves were obtained. The experimental setup and I-V curves obtained are shown in **Figure 9**. This method was effective in overcoming the drawbacks of the Oliver–Pharr method.<sup>[16]</sup> The I-V curves obtained were nonlinear, thus making the Holm equation ineffective in calculating the area. The area under the contact I-V curve, denoted as  $\Gamma$ , was measured at each  $P_{\text{max}}$  after the hold time. A power-law function fitted the data from the  $\Gamma$  and the in situ  $A_c$  (Figure 9c).





**Figure 9.** a) In situ conductive nanoindentation setup. b) The *I*–*V* curves obtained during loading at different loads (the inset shows the *P*–*h* curve at 5.2 N). c) The variation of  $A_c$  with the absolute area under the *I*–*V* curve (I). The blue line represents the power-law fitting to the data point using Equation (17). d) The variation of *H* with  $P_{max}$  ranging from 2.2 to 5.2 N. Reproduced with permission.<sup>[200]</sup> Copyright 2011, Cambridge University Press.

$$A_{\rm c} = (5.279 \pm 0.354) \times 10^{-7} \times \Gamma^{1.754 \pm 0.028} \tag{39}$$

Equation (39) is valid only for  $\Gamma$  values between 0.0483 and 0.134, i.e., in the applied load range 1.2–5.2 N. Using Equation (39), the  $H \left(=\frac{p}{A_c}\right)$  was calculated (see Figure 9d). The higher hardness at lower loads was attributed to the indentation size effects. Therefore, this technique proved helpful in calculating the in situ  $A_c$  for non-Ohmic conditions and for successful study of pile-up, thin films, and other dynamic mechanical properties.

#### 2.6. Influence of Surface Roughness on Contact Conductance

In many numerical models and simulations, generally, researchers neglect surface roughness because it dictates the thermal/electrical contact conductance at the initial contact of the indenter and the surface (i.e., at the very low loads). However, once the indenter starts penetrating more depths, the surface roughness contribution on the contact resistance is significantly minimal compared to the influence of the contact area. But one must understand the role of surface roughness while investigating the evolution of contact resistance between the tip and the sample at various initial depths and quantifying the resistance terms. The contact conductance problem is very well studied in thermal science, and such relationships can be used for electrical contact resistance because both the contact resistances are primarily a function of P on the contact and state of the surfaces. At low

loads, a tiny area of the total gross area of the contact is between the sample and conducting tip. Increasing the load flattens the asperities (such as hills) and reduces both thermal and electrical contact resistances. This phenomenon is called "spreading resistance" because the flow of electric current or heat must spread out after passing through restricted areas in contact with the tip and the sample. A thin film of foreign material (typically oxide) on the surface of contacting hills causes another resistance known as interfacial resistance.<sup>[225]</sup>

The following equation developed based on the assumption that the distribution of surface heights is Gaussian relates the thermal contact conductance and the roughness (standard deviation of the profile heights)<sup>[226]</sup>

$$\frac{h_c}{k}\frac{\psi}{\tan\theta} = 1.45 \left\{\frac{P_a}{H}\right\}^{0.985}$$
(40)

where  $h_c$  is the contact conductance,  $\psi$  is the standard deviation of profile heights, k is the thermal conductivity or electrical conductivity, H is the hardness,  $\tan\theta$  is the mean of the absolute slope of a profile, and  $P_a$  is the contact pressure. Though Equation (40) was developed for the problem of thermal contact conductance between two surfaces in a vacuum, it can be directly used for understanding electrical contact conductance because the effect of surface asperities on thermal conductivity at the interface of tip and sample is analogous to the concept of electrical contact resistance, involving roughness-restricted transport

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of phonons rather than electrons. One of the popular relationships between electrical contact conductance and thermal contact conductance is the Wiedemann–Franz law:  $L = \frac{k}{\sigma T}$ , where *k* is the thermal conductivity,  $\sigma$  is the electrical conductivity, and *L* is the Lorentz number.<sup>[227]</sup>

# 2.7. Influence of Dislocations on the Electrical Conductivity

The lattice strain associated with the dislocations causes electron scattering (due to the alteration of local potential energy by dislocations), which reduces the MFP of electrons, thus increasing the electrical resistance. If the dislocations are fewer in number, there is less strain and less electron scattering and therefore higher conductivity. It is because  $G \propto \zeta$  ( $\zeta$  is the mean time between two scattering events). Anything (even grain boundaries, solute atoms, vacancies, dislocations, etc.) that creates a strain field within atomic lattice increases the electron scattering. We will discuss this more in Section 3.3.

Brown et al.<sup>[228]</sup> obtained a universal expression for dislocation-limited resistivity in metals of arbitrary band structure,  $\mu\beta = \frac{3e}{8\hbar}$  (=5.70 × 10<sup>14</sup> V<sup>-1</sup> s<sup>-1</sup>); here  $\mu$  is the dislocation-limited mobility of electrons,  $\beta$  is the dislocation density, and  $\hbar$  is the reduced Planck's constant. This was developed by assuming the resonance scattering of electrons (in Fermi level) by the core of the dislocation and neglecting interband scattering.

Buch et al.<sup>[229]</sup> studied the combined electric and mechanical behavior of CdTe and reported that the plasticity causes a change in the  $\sigma$  in both p- and n-type CdTe. When CdTe is deformed permanently, the  $\{111\}$  (110) slip occurs by the motion of  $60^{\circ}$ dislocations. While the dislocations with a core of Cd act as electron traps, dislocations with a core of Te act as donors. Though both the dislocations were generated in equal numbers, the dislocations with a core of Cd were believed to have higher mobility than the Te (i.e., donor dislocations). The annihilation at the free surface happens for the Cd dislocations due to their movement to the sides of the crystal when slip occurs along {111} (110). This creates a situation in which the number of donor dislocation sites (i.e., Te) is higher than that of the electron trap sites (i.e., Cd). The conductivity changes begin exactly at the yield point (known due to rapid multiplication of dislocations) when samples are compressed at 0.05 mm min<sup>-1</sup>, indicating that the dislocations are responsible for such changes in electrical conductivity. Such changes in conductivity can be used to determine the microvield point of ionic and covalent crystals where the microyield is hard to identify in the  $\sigma$ - $\varepsilon$  curve. The change in the conductivity in both p- and n-type CdTe was attributed to the shift in the Fermi energy to the conduction band. The authors estimated the electronic states associated with the dislocations and native point defects. This study was done by compression test on millimeter-sized samples.

Similar results were seen in n- and p-type Si containing parallel arrays of edge dislocations.<sup>[230]</sup> At 750 °C, using plastic deformation, dislocation densities of  $\approx 10^6 - 10^7$  per cm<sup>2</sup> were introduced in the samples. The electrical conductivity was observed to be highly anisotropic for both parallel and perpendicular measurements, indicating space charge cylinders surround dislocation in p- and n-type Si. This denotes that in n-Si, the

dislocation has an acceptor state, and in p-Si, the dislocation has a donor state.

Furushima et al.<sup>[231]</sup> explored the relationship between the characteristic dislocation structures and their electrical conduction properties in LiNbO<sub>3</sub> bicrystals with low-angle-tilt grain boundaries. They observed high electrical conductivity  $(10^{-4}-10^{-3} \Omega^{-1} \text{ cm}^{-1} \text{ in contrast to } 10^{-14}-10^{-7} \Omega^{-1} \text{ cm}^{-1})$  (after reduction treatment) for (0001)/[1120] 2° tilt grain boundary, and lower activation energy for electronic conduction than the bulk region. They realized that only the grain boundary of 2° with a higher tilt angle exhibits such a distinct electrical conductivity, although the parent LiNbO<sub>3</sub> is insulating in nature with a bandgap of 3.89 eV, due to the characteristic dislocation structure with a large Burgers vector of 1/3[1102]. The enhancement in the electronic conductivity could be because of the dislocations that would have shifted the Fermi energy near to the conduction band.

In fact, a high number of dislocations exhibited electrical properties in the same way as the accepted doping.<sup>[232]</sup> Therefore, in electroceramics, the introduction of dislocations is termed 1D doping.<sup>[233]</sup> Porz et al.<sup>[234]</sup> put effort into deconvoluting the mesoscopic structure (core charge and space charge), which enabled the effect of dislocations on the electrical properties of SrTiO<sub>3</sub> films. It is important because the electric properties observed from the plastically deformed zone are the combination of a range of complex mesoscopic dislocation structures and arrangements (core charge and space charge). At RT, the active slip system for [001] SrTiO<sub>3</sub> is (110){110} and at elevated temperatures, (100){100} for the [110] orientation. The results revealed that dislocation-mediated functional property changes in electroceramics depend on mesoscopic structures, core structure and change, and the surrounding space charge. The temperature and oxygen partial pressure were observed to not to alter the conductivity measurements. Interestingly, the disordered surface dislocations altered the electrical properties than controlled bulk deformation in SrTiO<sub>3</sub>. Very recently, Höfling et al.<sup>[235]</sup> introduced a network of dislocations using uniaxial compression into BaTiO<sub>3</sub>, which enhanced the dielectric and piezoelectric properties ( $\varepsilon_{33} \approx 5800$  and  $d_{33} \approx 1890$  pm V<sup>-1</sup>). These studies provide evidence that dislocation-based anisotropy could be utilized as a tool for altering the functional properties of oxides.

# 3. Applications of Nano-ECR

This section describes how nanoindentation coupled with in situ electrical contact resistance measurement was utilized on various materials by various researchers to understand the indentationinduced deformation mechanisms, probe the electromechanical properties, and link the nanoscale mechanical response to the evolution of the electrical contact resistance. We have reviewed all the published articles that have utilized this technique to date to the best of our knowledge. In addition, a few articles that used AFM conducting nanoindentation were also considered to understand the contact conductance mechanisms at the nanoscale. We summarize the results and opinions of the original studies and authors and offer possible alternate interpretations, suggestions, and comments wherever possible. However, we strongly suggest the readers go through the original versions of the reviewed articles for more information because we focus only on the portions relevant to this Review's topic. Further, we had to reproduce a good number of figures from some of the published articles that were necessary to understand the discussion.

# 3.1. Semiconductors

# 3.1.1. Phase Transformations in Si

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The phase transformation from dc-Si to metallic  $\beta$ -Sn at a pressure of  $\approx \! 11\,\text{GPa}$  was identified as the dominant mode of deformation mechanism in Si by indentation at RT.<sup>[236–240]</sup> During pressure release/on unloading, the  $\beta$ -Sn further transforms to the R8 (rhombohedral phase with eight atoms per unit cell) and bc8 (body-centered cubic with eight atoms per unit cell) phases rather than transforming back to the parent phase (dc-Si).<sup>[67,185–187]</sup> The R8 phase was predicted to be a narrow-bandgap semiconductor.<sup>[241,242]</sup> The bc8 was found to be a semimetal,<sup>[243]</sup> but Zhang et al.<sup>[244]</sup> showed bc8-Si as a direct-bandgap semiconductor with an ultranarrow energy gap of  $\approx \! 30 \, \text{meV}.$ 

However, in dc-Ge, both the plastic deformation by slip and phase transformations were dominant modes of deformation at RT, depending on the indentation conditions.<sup>[141,185,245,246]</sup> Interestingly, phase transformations were observed in amorphous Si (a-Si) and Ge films, but under some conditions<sup>[247]</sup> only plastic deformation of the amorphous phase was evident.<sup>[246,248-250]</sup>

The Pressure-induced phase transformation (PIPT) studies in semiconductors have always been a challenge with ex situ methods as most of the high-pressure phases (HPPs) are reversible, and the dimensions of the indents are too small for further postmortem characterization. However, in situ conductive nanoindentation has proved successful in overcoming the drawbacks of the ex situ methods such as Raman microspectroscopy and cross-sectional transmission electron microscopy (XTEM) to understand the phase transformation pathways.<sup>[11]</sup>

The first in situ electrical resistance measurement during nanoindentation was performed on dc-Si, lying in the gap between two gold electrodes by Gridneva et al.<sup>[239]</sup> They observed a significant decrease in resistance with increasing loading (i.e., the indenter bridged the gap between electrodes), and it regained its original value on unloading. The decrease in resistance was attributed to the phase transformation (PT) of dc-Si to the β-Sn phase (0.05 µm thick), which created an Ohmic contact between the gold contacts and thus increased the current flow. Later, Clarke et al.<sup>[236]</sup> conducted similar experiments on Si and Ge and reported several vital observations. They mentioned that the gap-birding indentations between gold electrodes are not necessary for observing resistance drop during *dc*-Si to the metallic phase transformation, and the indentation directly on the electrodes also results in the same. Further, they observed rectifying to Ohmic contact change during loading and a reverse transformation during unloading. However, their experiments could not differentiate whether the change of *R* was either due to changes in the contact characteristics or due to a decrease in the intrinsic  $\rho$ 



**Figure 10.** a) The schematic of the specimen geometry used for the study. b-e) The SEM images of metallic wire and pad arrangement on silicon sample, b) indentation made on Au pad, c) indentation made in the gap (i.e., between electrodes), d) indent bridging the gap between electrodes, and e) indent covering Si and only one Au pad. f) The *R* changes as a function of *h* for an indent for which *R* recovers fully on unloading and g) the *R* changes as a function of *h* for an indent in which there is no *R* recovery on unloading. Reproduced with permission.<sup>[4]</sup> Copyright 2011, Cambridge University Press.





of Si. Then, Pharr et al.<sup>[4]</sup> conducted several experiments (**Figure 10**) similar to Clarke et al.<sup>[236]</sup> using nanoindentation and reported that contact resistances would dominate the changes in resistance of the Si phase transformed into a metallic phase. Smith et al.<sup>[251]</sup> confirmed Pharr et al.'s<sup>[4]</sup> experimental results with their simulations on the nanoindentation loading in crystalline Si.

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Mann et al.<sup>[5,6]</sup> performed in situ electrical measurements with a conductive VC indenter tip and confirmed that the resistance changes due to the transformation from Schottky to Ohmic contact due to phase transformation (see **Figure 11**). They believed that the reverse transformation during unloading from the metallic phase was quite sluggish. However, even with the above in situ conducting-tip experiments, a clear correlation was not seen between the features of *P*–*h* curves and associated electrical measurements. In 2003, Bradby et al.<sup>[23]</sup> used an in-situ electrical measurement method, which relies upon an Al–Si Schottky contact that converts to Ohmic during phase transformation from dc-Si to  $\beta$ -Sn. They chose a structure that had a high-resistivity epitaxial layer (5  $\Omega$  cm and 7  $\mu$ m thick) on a high-boron-doped, low-resistivity (6 × 10<sup>-3</sup>  $\Omega$  cm) substrate and a large-area Al–Si Schottky contact fabricated on the epitaxial layer (**Figure 12**a). The technique effectively studied the dc-Si to metallic phase transformation under high pressure and aided well in correlating P-h data features during loading to the electrical property changes during phase transformation (to bc8/R8 or a-Si) under pressure (Figure 12b,c).

As shown in Figure 12, on loading, in the beginning, the dc-Si to  $\beta$ -Sn transformation was observed at 11 GPa (Figure 12d). The pop-in was due to the ductile  $\beta$ -Sn phase's extrusion beyond the region under the indenter (Figure 12e). The extruded material beyond the region under the indenter was converted to a-Si (Figure 12f). On the indenter's rapid withdrawal, the  $\beta$ -Sn phase transformed to a-Si (Figure 12g). This was accompanied by a sharp decrease in the current as the amorphous phase is highly resistive. The metallic phase transformed into bc8/R8 phases for slow unloading, as evident from the pop-out during unloading. (Figure 12h). However, the technique was not sensitive to detect the electrical changes during the higher-pressure phases formed during the unloading because it relies on  $\frac{R_{\text{bds}}}{R_{\text{dc-Si}}} \cong \frac{\text{Indented area}}{\text{Al contact area}}$ . Though Mann et al.<sup>[6]</sup> performed experiments with a conductive indenter for measuring the contact resistance, this sensitivity problem could not be addressed in detail.



**Figure 11.** The *P*-*h* and corresponding *R*-*h* curves were obtained by the in situ conductive nanoindentation using a VC tip at the critical load ( $\approx$ 40 mN). Below the critical load, *P*<sub>critical</sub> (specific to each tip), no discontinuities were observed in the *R*-*h* curves, where above *P*<sub>critical</sub> discontinuities were always present. However, at *P*<sub>critical</sub>, a) some exhibit no discontinuities and b) some show the discontinuities in the unloading part of the *R*-*h* curves. Most importantly, there were no measurable acoustic emissions during the discontinuity. In addition to the constant voltage mode measurements (for *I* or *R*-*h* curves) throughout the load–hold–unload cycle, voltage swept at different parts of the unloading curves (marked *A*-*H* in (c) and (d)). c) A gradual change from Ohmic to Schottky behavior is evident (A–D) with unloading tip from 40 mN for small contacts. d) For larger contacts, there is a gradual increase in rectification (E–G) before the pop-out in the *P*-*h* curve, but after the pop-out, rectification falls sharply. Rescaling of the curves in (c) and (d) was to compare different contact sizes. Reproduced with permission.<sup>[5]</sup> Copyright 2011, Cambridge University Press.

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**Figure 12.** a) Schematic of the experimental setup used for the in situ electromechanical study. A highly resistive (5  $\Omega$  cm) epilayer of thickness 7  $\mu$ m was grown on a low-resistive Si wafer (6 × 10<sup>-3</sup>  $\Omega$  cm). An Al film of 20 nm was deposited on the top and bottom for the purpose of contacts. b) *I* versus *P* curve with a spherical tip (*R* = 4.2  $\mu$ m). A *P*<sub>max</sub> of 100 mN was reached in 20 steps during loading and unloaded in 20 steps. The pop-in event was observed with an arrow. c) The applied *P* and corresponding *I* variation as a function of time in dc-Si. d–h) Schematics of the plastic deformation sequence under the spherical indenter. d) Initiation of semiconducting metallic (β-Sn) transformation during loading. e) Extrusion of the β-Sn phase with increasing *P*. f) The formation of a-Si (at the regions shown) from the β-Sn phase due to the metastable nature below 11 CPa. g,h) With further unloading (i.e., at lower mean contact pressure), the metallic phase transforms to a bc8/R8 mixture or a-Si depending on the pressure release rate. Reproduced with permission.<sup>[23]</sup> Copyright 2003, American Physical Society.

Ruffell et al.<sup>[23,27,28]</sup> described a through-tip electric current measurement method across the tip/sample contact to address the aforementioned issue. With this experimental setup (**Figure 13**a), the *I*–*V* characteristics can be recorded and allow one to investigate the electrical barrier potential for different Si phases at any point on the *P*–*h* curve. Here, the electrical signals were recorded during indentation in two modes: 1) The current that was flowing through the tip and the sample was measured continuously, keeping the voltage constant, and 2) the voltage was swept between -8 and +8 V for 0.1 s at different positions on the entire cycle, and the *I*–*V* curves were drawn. Parameters such as  $R_{\rm C}$ ,  $R_{\rm SPR}$ , and  $A_{\rm c}$  were taken into consideration in this technique.

**Figure 14** shows the *I*–*V* curves recorded at various points during loading and unloading. As expected, when the conducting tip contacts the semiconducting p-Si surface, a Schottky contact is observed. Such a rectifying contact turns Ohmic (Figure 14a) with increasing load due to the  $\beta$ -Sn phase formation. On rapid unloading from the  $P_{\text{max}}$ , the Ohmic contact turns into a rectifying contact again due to the formation of a-Si, and the interfaces are  $\beta$ -Sn–a-Si–dc-Si, similar to the metal–thin-film-oxide silicon structure (Figure 14b). Figure 14c,d shows the PT mechanism under the indenter during loading and unloading. The formation of high-pressure phases such as bc8 and R8 was neglected from initial unloading until pop-out. This formation includes nucleation and is mostly observed on the slow release of pressure.

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**Figure 13.** a) Schematic of the in situ through-tip electrical measurement method during indentation. The voltage is applied to the stage, and the current flow is measured through the sample and tip. b) The equivalent circuit diagram of various resistance components and rectifying junctions involved in through-tip electrical measurement on Si. Reproduced with permission.<sup>[28]</sup> Copyright 2011, Cambridge University Press.

As shown in **Figure 15**, the forward bias current increased with the residual indent depth. The density of the phases formed on unloading determined the residual depth,  $h_r$  of the indent.

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The a-Si and bc8 are less dense by 24% and 14%, respectively than the metallic  $\beta$ -Sn phase.<sup>[23]</sup> Therefore, the  $h_r$  of a-Si was observed to be smaller than the bc8 phase. However, the small volume of HPPs surrounded by a-Si will also vary the  $h_r$  and therefore the current. The occurrence of pop-out is the sudden formation of a large volume of HPPs during loading. Hence, the  $h_{\rm r}$  was higher, which led to a hike in the forwarded bias current. With in situ electrical measurement, Ruffell et al.<sup>[27]</sup> probed pressure-induced phase transformations in Si at any point during loading and unloading and unravelled a method to track the information related to the formation of the end phase depending on the unloading rate without the need for performing postmortem TEM or Raman characterization. Further, they could observe that the forward bias current increased with the  $h_r$  of the indent. The I-V characteristics and biased current (forward) were susceptible to the volume of HPPs. Also, the variation in the I-V characteristics was apparent in the presence of a pop-out and a no pop-out regime because of HPPs still present in the high volume of a-Si without exhibiting a pop-out in the unloading curve. In the pop-out regime, although the I-V characteristics correlate well with the  $h_r$ , they are HPPs, microstructure, and depth distribution dependent compared to no pop-out with a significant quantity of HPPs within the a-Si. Thus, in situ electrical measurements with a conducting tip were proposed to be useful in identifying phase transformations in Si. Fujisawa et al.<sup>[252]</sup> used the same method and studied the pressure-induced phase transformation behavior of Si under cyclic loading conditions.

As the bc8 phase was the dominating end phase during pressure release<sup>[243]</sup> in diamond anvil cell (DAC) experiments, it was found to be semimetallic (a p-type semimetal with an RT carrier concentration of  $\approx 5 \times 10^{20}$  cm<sup>-3</sup>) and agreed with density functional theory (DFT) calculations.<sup>[241,253,254]</sup> However, as the end phase followed by depressurization was not R8 in DAC experiments, the electrical properties of the R8 phase were unknown, though it was predicted to be either a semimetal or a narrow-bandgap semiconductor using DFT calculations.<sup>[242,253,254]</sup> Malone et al.<sup>[241,242]</sup> predicted that the R8 phase of Si is a narrow-bandgap semiconductor (with an energy gap  $E_{gap}$  of 0.24 eV).

Ruffell et al.<sup>[255]</sup> conducted several ex situ electrical measurements using different methods on residual indents containing R8-Si to provide the first experimental evidence to the theoretical predictions<sup>[241,253,254]</sup> on the semiconducting/semimetal behavior of R8- Si. The schematics of the device structure and its corresponding I-V curves are shown in Figure 16. The mixed phases (dominantly R8) were formed in relaxed a-Si using spherical indentation. The Raman measurements confirmed that the mixed phases contain the R8-Si dominantly. Even recent studies by Wong et al.<sup>[256]</sup> confirmed the formation of a large volume ( $\approx$ 70%) of the stabilized R8 phase within the spherical indent. Both through-wafer probing with a conducting BDD tip and postindentation Hall-effect (HE) measurement on the test structures were carried out to measure the electrical conductivity and carrier mobility of mixed phases (dominantly R8-Si). They demonstrated that the R8-Si is a semiconductor with a distinct electrical behavior compared to the conventional dc-Si. However, experimental verification of the bandgap of the R8 phase has not been done yet.

Further, Ruffell et al.<sup>[255,257]</sup> fabricated a device structure that consists of ion-implanted but relaxed a-Si (50 nm) on p-type (100)

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**Figure 14.** a,b) *I–V* curves show contact transformation from Schottky to Ohmic with increasing load due to metallic phase formation in Si and reverse transformation from Ohmic to Schottky with decreasing load. The 0.1 mN curve is the preindentation contact. c–e) Schematics showing the formation of the metallic and a-Si/R8/bc8 phases during loading and unloading, respectively, their volumes, and the interfaces determining the measured current. In the case of loading (c), two interfaces are evident: A between the BDD tip and  $\beta$ -Sn phase and B between  $\beta$ -Sn and dc-Si. In unloading (d,e), C is a new interface between  $\beta$ -Sn and the phase-transformed material. D is the interface between the phase-transformed volume (a-Si for high-speed unloading and dominantly bc8/R8 for slow unloading) and the dc-Si. With further unloading, interface A will be between the phase-transformed volume and tip. Reproduced with permission.<sup>[27]</sup> Copyright 2007, AIP Publishing.

dc-Si (B  $\approx 10^{15}$  cm<sup>-3</sup>). To achieve different B concentrations (i.e.,  $10^{19}$  or  $10^{20}$  cm<sup>-3</sup>), some parts of the a-Si layer were implanted with B, and R8, and bc8 phases were induced using a Berkovich tip with a  $P_{\text{max}}$  of 10 mN (as shown in Figure 16a). Since the indenter  $h_{\rm max}$  reached  $\approx$ 230 nm at 10 mN load, both the a-Si layer and underlying dc-Si wafer contained the residual R8/bc8 zone on complete unloading. Then, the residual R8/bc8 zone in each indent was probed with a BDD tip at lower forces (<1 mN) and the I-V characteristics were recorded, as shown in Figure 16b. Under forward bias, the effect of the B concentration is apparent, indicating the semiconducting nature of R8/bc8. The Schottky behavior of the I-V curves was attributed to the contact between the B-doped R8/bc8 Si and the underlying p-Si wafer. In Figure 16c, the device structure, such as metalinsulator-metal (M-I-M), consists of highly conducting dc-Si pads with an insulating a-Si layer (relaxed) on SiO<sub>2</sub>/dc-Si wafer. With the help of a spherical indenter with R of 10  $\mu$ m, a  $P_{\text{max}}$  of 200 mN was used to make a few overlapping indents to create a line of 4 µm width and 200 nm depth (up to the bottom SiO<sub>2</sub> layer). The *I*–V characteristics in Figure 16e were recorded using the structure for different B doping levels in the R8/bc8-Si phase.

Furthermore, the carrier mobility (p-type carrier conduction with mobility of  $17 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the  $10^{19} \text{ cm}^{-3}$  B-doping concentration) was measured using a microsized van der Paux structure (not shown here) by a series of overlapping R8/bc8 phases

on a Si-on-insulator (SOI) wafer.<sup>[258]</sup> Also, they demonstrated the phosphorus doping of R8/bc8-Si. In addition, "writing" conducting zones in insulating a-Si wafer/layer by overlapped residual indents containing R8/bc8-Si and writing insulating a-Si patterns in conducting dc-Si were also shown to be possible under fast unloading conditions.

Though the indentation-induced PT behavior of Si at RT was well understood, there were several inconsistencies in understanding the temperature dependence of the mechanical deformation of Si. Singh et al.<sup>[258]</sup> observed an unidentifiable phase along with the possibility of a tetragonal Si on unloading during in situ high-temperature indentation experiments (20–135 °C). However, Ruffell et al.<sup>[259]</sup> found that the R8/bc8 formation probability increased with increasing temperature but was absent when unloaded at 0.2 mN s<sup>-1</sup> at 125 °C. Bhuyan et al.<sup>[260]</sup> suggested  $\beta$ -Sn to dc-Si reverse transformation at elevated temperatures. Therefore, the mechanical deformation at elevated temperatures remained unclear for a long time.

To clear inconsistencies in the literature and provide insight into the temperature-dependent deformation mechanism in (100) dc-Si, Kiran et al.<sup>[7]</sup> conducted experiments coupling hightemperature nanoindentation and in situ electrical measurements at different temperatures starting from RT to 200 °C. The experimental setup used for such a study is shown in **Figure 17a**. Before performing experiments, the Schottky contact was ensured<sup>[23]</sup> (by measuring *I*–*V* curves) between 20 nm Ti and ADVANCED SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com



**Figure 15.** a) *P*–*h* curves (with pop-outs) and b) corresponding *I*–V characteristics (postindentation) for three residual indents. The forward-bias current increases with  $h_r$ . The *I*–V curves for B (the smallest  $h_r$ ) are similar to that of the case with no pop-out. Reproduced with permission.<sup>[27]</sup> Copyright 2007, AIP Publishing.

 $\approx$ 7 μm dc-Si with a  $\rho$  of 5 Ω cm. Schottky contact was formed under reverse bias due to significant depletion layer thickness in the epilayer under contact. As the indenter  $A_c$  ( $\approx$ 1 μm<sup>2</sup> at  $P_{\rm max}$  of 10 mN) is several orders smaller than the Schottky contact ( $\approx$ 1 cm<sup>2</sup>), this Schottky to Ohmic contact transformation during dc-Si to metallic transformation can be detected with high sensitivity.

Figure 17b shows both P-h (insets) and I-h curves obtained at different temperatures. First, the pop-out event, which appears clearly up to 100 °C, disappears from 125 °C, indicating that the volume of the high-pressure phases formed during unloading is not sufficient to cause a pop-out. At this point, the authors carried out in situ electrical characterization during nanoindentation to understand the temperature-dependent mechanical deformation mechanism in dc-Si and the annealing kinetics of the PIPTs. The whole device was fixed on a high-temperature stage and I-h and P-h curves were measured at different temperatures during indentation. The idea was to observe whether the Schottky to Ohmic contact transformation occurs at all temperatures. ADVANCED ENGINEERING MATERIALS www.aem-journal.com

As shown in Figure 17b, as expected, the leakage current increased with increasing temperature. The gradual current rise that was observed during loading after a  $h_{\rm max}$  of 40  $\pm$  5 nm (at all temperatures) was attributed to the dc-Si to metallic β-Sn phase transformation. Up to 125 °C, the same trend was observed. The current rise during loading was  $\approx 14 \,\mu A$  for 25 and 50 °C,  $\approx$ 8.3 µA for 100°*C*, and  $\approx$ 2.2 µA for 125 °C, which was attributed to the volume of phase-transformed material under the indenter. The decrease of the phase-transformed volume with increasing temperature indicates other modes of deformation than phase transformation. This fact is more clearly explained in Figure 17c. As the temperature increased, the likelihood of dc-Si to  $\beta$ -Sn transformation decreased, and the defect-induced deformations started to rise. The temperature between 50 and 150 °C witnessed both phase transformation and defect propagation, whereas at 200 °C, the dominant mode of deformation was defect propagation. With the help of in situ electrical measurements, it was demonstrated that both phase transformations and defect propagation are responsible for the plastic deformation of Si up to 150 °C being phase transformation as the dominant mode. However, deformation by twinning along {111} planes was dominant beyond 150 °C. This study further clarifies that the contribution from the contact area on the increase in current during loading is negligible. Otherwise, a similar increase in current would have appeared at elevated temperatures where there is no metallic phase formation.

Furthermore, a decrease in  $h_{\rm max}$  was observed with increasing temperature. This indicates that the hardness of Si ( $\approx$ 10–12 GPa) is mainly dictated by the metallic phase formation. Otherwise, if there was no metallic phase formation, the plastic deformation (by either a slip or twinning) would require higher stresses, probably due to the presence of covalent bonding and low dislocation density due to well-established and highly controlled growth conditions. Since there is no metallic phase formation at elevated temperatures, the material had to deform by either slip or twinning. In the current case, deformation along with slip along {111}. It is indeed interesting to observe twinning in the diamond cubic crystal structure at 150–200 °C. It is reported that beyond 300–400 °C, deformation by slip can cause significant plasticity in Si.<sup>[261]</sup>

With the knowledge obtained from the in situ electrical and high-temperature measurements, such as electrical and annealing behavior of the R8 phase of Si,<sup>[262]</sup> recently, Sowjanya et al.<sup>[263]</sup> fabricated the large-area R8 phase in a dc-Si wafer using spherical nanoindentation and studied the optical properties, and utilized it for solar applications. The UV-vis optical spectrum showed a 50% lower reflectance for the R8 phase compared to the dc-Si. The refractive index for R8 phases was estimated as  $\approx$ 6.7 at 630 nm, which is 35% higher than dc-Si. The R8 phase was utilized as a solar absorber layer. It provided evidence of a significant improvement in the photocurrent density of a p-n junction Si solar cell after modification of a few hundred microns of the area of the top layer (n-type dc-Si) into a dominantly R8-Si using nanoindentation. They observed that such a small area of R8-Si enhanced the light absorption of the solar cell by ~50% over the visible spectrum and the current density by  $\approx 10$  times.





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**Figure 16.** a) Electrical measurements on the residual indent containing dominantly the R8-Si using the through-tip technique and b) the corresponding *I–V* characteristics. Here, the BDD tip forms a contact with the indented zone containing R8-Si, and the *I* flow through the sample is measured as a function of *V* across the whole setup. c) A second structure for measuring the *I–V* curves of TR8-Si (formed from relaxed a-Si), which is bridging, formed by making several indents next to each other with heavily B-doped contact pads; d) optical image showing the indented bar (i.e., dominantly R8-Si). e) The corresponding *I–V* measurements; the right side of (e) shows the low resistance of the R8/bc8 phases. a,b) Reproduced with permission.<sup>[255]</sup> Copyright 2011, American Physical Society. c–e) Reproduced with permission.<sup>[257]</sup> Copyright 2011, AIP Publishing. a–e) Reproduced with permission.<sup>[215]</sup> Copyright 2015, Elsevier.

## 3.1.2. Linking Electrical Spike to Nanoscale Plasticity in GaAs

Nowak et al.<sup>[171]</sup> used nano-ECR coupled with nanoindentation to study the electric response of 1 µm thick epitaxially grown (100) zinc-blende GaAs (with Si donor concentrations of  $1 \times 10^{16}$  and  $1 \times 10^{18}$  cm<sup>-3</sup>) during mechanical deformation. They observed a sudden current spike during loading in GaAs compared to other semiconductors under the spherical indenter. The experiment was done on the GaAs sample with a BDD tip indenter. The  $P_{\rm max}$  used was 8 mN for highly doped ( $N_{\rm d} = 1 \times 10^{18}$  cm<sup>-3</sup>) GaAs samples and up to 220 µN for low-doped ( $N_{\rm d} = 1 \times 10^{16}$  cm<sup>-3</sup>) GaAs samples.

As seen in the previous section, in situ nanoindentation coupled with electrical measurements on Si shows a gradual rise in current with loading, which is related to pressure-induced phase transformations (metallization). However, in contrast, in GaAs samples, in situ conductive nanoindentation resulted in a current spike and then suddenly reduced to zero, which was attributed to the beginning of the elastic-plastic transition (see Figure 18a), Initially, the contact remained Schottky on nanoindentation, preventing the current under reverse bias from flowing through the junction. In the case of low-doped GaAs, as the indentation depth reached  $\approx 18 \text{ nm}$  and the mean pressure ( $P_{\rm m}$ ) reached  $\approx$ 17.5 GPa, the current started leaking through the junction and increased rapidly to  $\approx 95 \text{ nA}$  and current density (1)  $\approx$ 885 A cm<sup>-2</sup>. Immediately after the spike, when the indentation depth reached  $\approx$ 19 nm, the current reduced to zero. The current spike and pop-in were observed to co-occur, as shown in Figure 18a.

Figure 18b shows the  $I_{\text{Leakage}}$  of the Schottky barrier before and after pop-in. The sudden rise in the current and immediate transformation to the Schottky barrier was attributed to crystal structural change (phase transformation) after the popin. Thus, the electrical response of pressure-induced metallization of GaAs and the current spike observed were compared. The current spike was observed only during the loading cycle and ended up with a Schottky barrier. Bourret and co-workers<sup>[264]</sup> confirmed that dislocation nucleation decreases with increasing doping concentration and is accompanied by a shift up in the pop-in.

In contrast, Nowak et al.<sup>[171]</sup> observed an earlier current spike in highly doped GaAs samples compared to the low-doped one, and the pop-in was shifted down rather than up. Thus, they confirmed that the current spike accompanied by pop-in was not of dislocation origin. Nanoindentation was also done on a region with pre-existing dislocations, and a smooth curve was observed without a pop-in and current spike (red line), which ruled out the possibility of a piezoelectric effect (Figure 18c).

Ab initio calculations confirmed that the spike in current and the pop-in were due to zinc-blende to rock-salt GaAs phase transformation. The schematic of the phenomenon is shown in Figures 18d–f. Initially, the contact between the zinc-blende GaAs and the BDD tip was Schottky (Figure 18d). Later, as the phase transformation to metallic zinc-blende structure began (i.e., before pop-in), the current started spiking up due to leakage of current (Figure 18e). At the pop-in instant, the transformation to metallic rock-salt structure beyond threshold pressure reduced the Fermi energy ( $E_F$ ) of the tip and phase transformed region

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**Figure 17.** a) Schematic of the experimental setup used for high-temperature indentation coupled with electrical measurements. b) *I*–*h* curves and *P*–*h* curves (insets) were obtained at 10 mN at different temperatures up to 150 °C. c) Schematic showing the temperature dependence of phase transformability and defect-induced deformation in dc-Si under a Berkovich nanoindenter. Reproduced with permission.<sup>[7]</sup> Copyright 2015, AIP Publishing.

(junction) (even below the surrounding zinc-blende region); as a result, Schottky contact was restored. (Figure 18f).

Thus, the in situ conductive nanoindentation has provided insight into the fundamental cause of nanoscale plasticity in GaAs, which is originally due to the pressure-induced phase transformation to the metallic phase rather than dislocationmediated plasticity.

# 3.1.3. Origin of Onset of Plasticity in GaAs and InP Crystals

Recently, Chrobak et al.<sup>[172]</sup> used spherical nanoindentation coupled with in situ electrical measurements to study the elastic– plastic transition and its origin in doped (100) GaAs and InP crystals. While the GaAs was doped with Si, InP was doped with zinc (Zn) and sulfur (S), and the effect of the doping concentration was studied. The results of the nanoindentation experiments are shown in **Figure 19**.

The study on GaAs was very much like the studies shown by Nowak et al.,<sup>[171]</sup> which we discussed in the previous section. With the increase in Si concentration, a decrease in the pop-in load was observed along with mean contact pressure ( $P_{\rm m}$ )

(Figure 19a). However, the  $E_r$  (87.2 GPa) was not much affected by doping. From the previous studies, it was confirmed that if the doping of Si on GaAs decreases the transformation pressure, it will lead to phase transformation. In contrast, if it increases the shear stress, dislocation nucleation will trigger and lead to plasticity. Therefore, the results concluded that the nanoindentationinduced elastic-plastic transition (pop-in) in GaAs was due to phase transformation from GaAs-I to metallic GaAs-II. The results shown by doped InP were just opposite to those of GaAs. It was observed that the pop-in load increased with doping; thus, the  $P_{\rm m}$  also increased (Figure 19b). An increase in  $E_{\rm r}$  was also observed with Zn and S doping on InP. From the *P*-*h* curves of both GaAs and InP after the first pop-in (Figure 19a,b), it can be noted that the curves are smoother in the case of GaAs compared to InP and the pop-in width is more extensive in the case of InP. This has led to the prediction that nanoindentation stress has resulted in the nucleation of dislocations in InP. Hence, the elastic-plastic transformation in InP was attributed to the nucleation of dislocations.

However, to prove this experimentally, in situ conductive nanoindentation was performed on Si-doped GaAs and Si-doped InP crystals with Berkovich and spherical indenter tips (due to ADVANCED SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com





**Figure 18.** a) *I–h* curves of GaAs using nano-ECR measurement. Differently Si-doped GaAs crystals exhibited current spikes during indentation loading. For comparison purposes, the *I–h* curve of Si was also included. The dislocation-pinning scenario was dismissed for highly doped GaAs due to the current detected after the spike. b) *I–V* characteristics of GaAs demonstrate a leaking junction (before pop-in) and a perfect Schottky barrier (after pop-in) c) Two depth-time curves, one with pop-in (black curve) and the other without pop-in (red), from different places and their corresponding current response. An electric spike (green colored) was observed in the case of pop-in, and no spike was observed for the no pop-in case, indicating a lack of piezoelectric effect during the deformation of GaAs at the nanoscale. d–f) Schematics showing phase transformation mechanisms in GaAs under the spherical indenter. Reproduced with permission.<sup>[171]</sup> Copyright 2009, Springer Nature.

low carrier mobility of InP) with a reverse bias voltage of 3 and 5 V, respectively. The results are shown in Figure 19c,d. In the case of GaAs, a current spike was observed at the popin and a sudden decay to zero at the pop-in due to the phase transformation, as explained by Nowak et al.<sup>[171]</sup> But in the case of InP, an increase in current was observed at the pop-in rather than at the beginning. It was considered that at the beginning of the transition, the dislocation nucleation was low. This would concentrate on the current carriers, leading to an increase in electric current at subsequent stages due to the new donor states formed at the forbidden energy gap. However, the decrease and the fluctuations in current after the pop-in were attributed to the fluctuated  $A_c$  at the dislocation sites. Therefore, the in situ conductive nanoindentation provided insights into the indentation-induced plasticity in doped GaAs and InP crystals.

As evident from these results, in situ conductive nanoindentation is extremely useful for detecting metallic phase transformations and to understand the transformation pathways in silicon and GaAs and quantify the contact resistance terms. J. S. Williams, J. E. Bradby, and colleagues have provided detailed explanations on the entire circuit resistance terms involved in "through-tip" measurements. They suggested that the currenttime curves should be normalized to know whether the conductivity changes are due to the contact changes or due to subsurface conductivity change because the extruded metallic phase will always be in contact with the tip. Further, it is

important to consider the pressure dependence of the electrical conductivity in Si (i.e., during and after indentation), different phases of Si that introduce new potential barriers at the interfaces. It is compulsory to remove the native oxide layer (common to Si) before performing in situ conductive nanoindentation studies. The native oxide layer can change the mode of mechanical deformation and contributes significant nonlinearity in the contact conductance measurements. In addition, tip wear (usually high for indented hard materials such as Si) can significantly influence the electrical measurements from indent to indent. Therefore, the tip-area calibration must be performed regularly and avoid scanning surfaces using sharp indenters. It is observed that the authors used BDD tips for measuring *I*-*h* and *I*-*V* curves of Si and Ge for quantifying the contact resistance terms. This may be due to the commercial nonavailability/nondevelopment of the highly conducting and hard refractory carbide tips at that period. As shown by Williams and colleagues, the inhomogeneity in B doping causes electrically nonconducting regions that measure nonlinear I-V curves. Although most of the issues were well taken care of by the authors in understanding the phase transformation behavior of electronic materials, the contact conductance issues at the interface between the metallic form and the conducting tip, the adiabatic temperature rise during indentation on electrical measurements, the effect of surface asperities on the contact conductance, and the role of contact area changes due to the formation/extrusion of the metallic phase (though it is amorphous after complete extrusion) on the measured current ADVANCED SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com



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**Figure 19.** The *P*-*h* curves obtained a) for differently Si-doped GaAs crystals—the pop-in load decreases with increasing Si concentration ( $n_1 < n_2 < n_3$ ) and b) for undoped and doped (with S and Zn) InP crystals show an increase of the pop-in load with doping. The *I*-*h*-*t* curve for c) GaAs shows a current spike, and d) InP shows an abrupt current rise at the pop-in event. Reproduced under the terms of the CC BY 4.0 license.<sup>[172]</sup> Copyright 2019, D. Chrobak et al., MDPI Publishing.

can be explored in detail. Further, it is observed that the current starts increasing after a certain penetration depth of the indenter  $(\approx 40 \text{ nm})^{[28,265]}$  (in both ex situ and in situ methods), and it was attributed to the insufficient (or too tiny) volume of the metallic phase to be detected by the indenter tip. However, it is important to explore the mode of deformation and a detailed electron transport mechanism below such threshold depth and at different depth regimes up to  $\approx 50 \text{ nm}$  to understand the evolution of contact resistance at the nanoscale before the metallic phase transformation. Further, during indentation loading on Si, there can be other modes of deformation under the phase transformed zone, for example, slip, and twinning (in case the dislocation density is quite low in that region), including microcracking of Si (though it cannot be imaged). In addition, the interfaces between the phase-transformed zone and the elastic-plastic and elastically deformed regions under the indenter are usually very rough. It is important to understand the role of defects and rough interface on the electron transport mechanism and contact conductance and separate their contributions either by experiments, by simulations, or by modeling. It is further observed that the authors used mostly the Berkovich tip, in which the stress state is highly complex. Therefore, the phase-transformed volume may contain tiny regions of nontransformed regions, amorphous regions, which may significantly influence the electrical transport in "though-tip" measurements. Therefore, non-selfsimilar conducting tips can also be used to study the effect of

tip geometry and compare the results of the nanodeformed zone and the accompanying electrical effects.

In a GaAs study, Nowak and colleagues attributed the increase in the electric current before the pop-in to the pressure-induced metallization of GaAs and a sudden pop-in to the indentationinduced phase transformation to a rock-salt structure at very high mean pressures (>17 GPa) compared to the dislocation origin<sup>[66,136,266-268]</sup> because they used a tip of radius 180 nm, which is very small compared to others.<sup>[66,136,267,268]</sup> Even in the Al<sub>2</sub>O<sub>3</sub>, Nowak et al. hypothesized that the twinning-type transformation is responsible for plastic deformation, and not dislocation nucleation.<sup>[269,270]</sup> However, in situ electrical studies were not used, probably due to the insulating nature of the sample. As discussed in the previous section, when the dislocation density is low, when the distance between dislocations is much larger than the size of the indenter tip radius, and if the indentation mean pressures can reach high to trigger phase transformations, nanoscale plasticity starts with phase transformations in a large class of materials, and dislocation nucleation occurs at the interface between the phases (in GaAs case). Valentini et al.<sup>[271]</sup> showed that plastic deformation by phase transformation is the dominant mode in silicon nanospheres, not dislocation-based plasticity. There are several theories and models based on dislocation-mediated plasticity at the nanoscale in various materials. But the aforementioned studies show a different origin of plasticity in GaAs at much lower length scales and



show that under some conditions and length scales both combined mechanical-electrical coupling leads to the same effects.

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However, in the case of InP, the pop-in width was significantly high than the case of GaAs, but, it is not due to the phase transformation from zinc blende to metallic rock salt structure, which was actually reported to occur at a pressure  $\approx$ 8.56 GPa accompanied by an 18% volume collapse.<sup>[272]</sup> It is known that plastic deformation in InP is due to the nucleation, multiplication, and propagation of dislocations. It is interesting to note that the minimum load to generate the first dislocations is two times lower in the scratch experiment than in indentation. The nucleation starts first at the surface and propagates inside the wafer.<sup>[273]</sup> Upon indenting the (100) surface, the slip bands are oriented at  $\approx$ 54.7°, indicating that the dislocations glide along <110>{111} slip systems. The indentation-generated dislocation loops are of the order of  $\approx 10^4$  with a critical radius of 2.15 nm for the first pop-in event to trigger the plastic deformation in InP.<sup>[274]</sup> In Chrobak et al.'s<sup>[172]</sup> experiment, the current rise in InP at the pop-in is two orders smaller than in GaAs (see Figure 19c,d), indicating that the dislocation contribution on the electrical conductivity in InP is minimal. Further, such a slight rise in the electrical current may be due to the sudden increase in the contact area. However, when the indenter forms elastic contact again after the pop-in, the current starts with a higher value (compared to the before pop-in), which may be due to the presence of dangling bonds at the dislocation sites. There are different opinions that exist on the influence of dislocations on the current density of semiconductors. The acceptor sites at dangling bonds located along dislocations increase the resistivity, resulting in the formation of charged regions that scatter electrons.<sup>[275]</sup> Furthermore, the local band structure will be modified by the high strains in a core of a dissociated dislocation, results in highly conductive channels along the dislocation core.<sup>[276]</sup>

# 3.2. Metal Oxides/Composites

#### 3.2.1. Self-Healing of Mechanically Damaged ZnO Nanobelts

Nanodevices play a significant role in many fields in transforming the world; however, their mechanical damage has substantially limited their usage over the long run. In this scenario, it is essential to understand the relation between mechanical damage of nanostructures in electric fields. Though many in situ techniques (heating, electron beam radiation, etc.) were utilized for repairing mechanically damaged devices, none were efficient in practical use. Hence, Zang et al.<sup>[277]</sup> utilized in situ conductive nanoindentation (note that the measurements are not through the conducting tip) coupled with AFM to study the electrical self-healing process in mechanically damaged ZnO nanobelts. Nanoindentation was performed at a  $\textit{P}_{\rm max}$  of 30.7  $\mu N$  on ZnO nanobelts on a Si<sub>3</sub>N<sub>4</sub> membrane to study the deformation behavior. Even with such a small loading, indentation induced a dislocation density of  $\approx 10^{14} \,\mathrm{m}^{-2}$ , estimated from the brightfield TEM image of the deformed zone (recorded under a two-beam condition with  $g = (\overline{2}110)$ ), while the TEM imaging was along [0110]), and a crack. Edge dislocations with a displacement of  $\frac{1}{4}[0001]$  and edge dislocation loops were observed in the (0002) plane under the indented region. Further, although misorientations of the ZnO crystal were found, no evidence of the amorphous phase was found. The high-resolution transmission electron microscopic (HRTEM) images confirmed the retaining of plastic strain on the ZnO nanobelts even after removing the load due to misorientations and dislocations.

Conductive nanoindentation coupled with AFM measurements was done on a ZnO nanobelt (width = 270 nm, thickness = 50 nm) on a SiO<sub>2</sub> substrate with Ti/Au as top electrodes (Figure 20a). Initially, the indenter was loaded to a  $P_{\text{max}}$  of 14.4  $\mu$ N, followed by 22.7  $\mu$ N, and then the *I*–V measurements were recorded (Figure 20b,c). The AFM images revealed no residual indentation marks for both  $P_{\text{max}}$ , due to elastic deformation. The I-V measurements recorded before and after the nanoindentation showed decrease in conductivity,  $\sigma$ , by 39.9% for 14.4  $\mu$ N (Figure 20b) and 46.4% for 22.7 µN (Figure 20c). The decrease in  $\sigma$  was due to the elastic strain induced by nanoindentation, which altered the electron transportation and widened the local energy gap. Later, the conductivity was recovered to its original value at the end of 11 and 13 min for 14.4 and 22.7 µN, respectively, due to the self-healing process of the mechanically damaged ZnO nanobelt. Finally, after complete recovery, loading was done up to 28.6 µN (Figure 20d), which resulted in a residual indent with no cracks. Here, the current was decreased up to four to five orders of magnitude with a recovery of 20%. Even the nanoindented ZnO nanobelt with crack was recovered to 15% after 21 days (Figure 20e-g).

It is known that homogeneous dislocations nucleation occurs beneath the indenter tip when the maximum shear stress underneath the indenter approaches/is of the order of the theoretical shear strength.<sup>[136,278,279]</sup> Though some of the dislocations anneal out after indentation, many dislocations, together with the plastic strain and misorientations, result in the abrupt decrease of the current. The stored energy (plastic strain) releases when the dislocations annihilate or orient themselves to a lowerenergy configuration. Typically, this process requires thermal activation to overcome the energy barrier of dislocations, resulting in long-range and short-range diffusion. However, in nanocrystals, as their dimensions are low, the atomic diffusion coefficient increases, and the dislocations must travel shorter distances to reach the surface, but this usually takes a longer time at RT. That is why the longtime recovery ( $\approx$ 21 days) was also observed in the ZnO nanobelts. Local heat generated by the flow of current in the deformed nanobelt was also predicted to be the reason for the diffusion of the defects, which could be improved by improving the contact between the metal electrodes and the ZnO nanobelt.

Figure 20i show the generation of dislocations during indentation and healing after the removal of load. In the Fermi level pinning model, the line at a deeper level, which depletes free charge in ZnO, distributes radially from the dislocations to the depletion region, as shown in Figure 20j. As the dislocations increase, these depletion regions overlap and result in decreased conductivity and non-Ohmic I-V curves. However, as the selfhealing process began, the dislocations annealed out, and the plastic strain reduced (Figure 20i), which resulted in an electronic structure with a smaller potential barrier effect, as the depletion layers were no longer overlapped (Figure 20k). Therefore, the conductive nanoindentation coupled with AFM provided insights into the self-healing behavior of ZnO nanobelts. www.advancedsciencenews.com

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**Figure 20.** a) Schematic of the nanoindentation coupled with AFM on ZnO nanobelts. The time-dependent *I–V* curves of elastically deformed nanobelts at  $P_{max}$  of b) 14.4  $\mu$ N and c) 22.7  $\mu$ N. d) The 3D image of residual indent (i.e., plastically deformed) made with a  $P_{max}$  of 28.6  $\mu$ N. e) *I–V* characteristics of as-grown, deformed (plastically), and self-healed ZnO nanobelts. f,g) The *I–V* curves of a plastically deformed nanobelt and their time dependence. h–k) Schematic illustration of the self-healing mechanism of plastically deformed belts. The generation of dislocations during nanoindentation and healing after the retraction of the load. (j,k) The electronic structure of the ZnO nanobelt before and after self-healing. Reproduced with permission.<sup>[277]</sup> Copyright 2011, American Chemical Society.

In this study, the authors attributed variations in electrical conductivity to dislocations (either formed, disappeared, or rearranged into lower-energy configurations via diffusional processes) probably because indentation induced a substantial dislocation density  $(10^{14} \text{ m}^{-2})$  in the ZnO nanobelt, which is similar in metals at higher plastic strain ( $\approx 10^{12} \text{ cm}^{-2}$ ).<sup>[280]</sup> However, the formation of fine-scale cracks (tiny and difficult to detect) during the indentation process could affect the conductivity and heal subsequently via diffusional processes. Even the cracked ZnO nanobelt was also shown to heal via the diffusion process. In addition, the dangling bonds and surface polarity could also significantly affect the electrical conduction.<sup>[281]</sup> Further, ZnO is a stress-sensitive piezoelectric material with a higher  $d_{33}$  $(14-27 \text{ pm V}^{-1})$  for the nanobelt than bulk<sup>[282]</sup> ( $\approx 10 \text{ pm V}^{-1}$ ) and which is orientation-dependent. If the indented face is (0001), the slip systems are (0001) $<\overline{1}2\overline{1}0>$  and  $\{10\overline{1}\overline{1}\}<\overline{1}2\overline{1}0>$ .<sup>[282]</sup> The contribution from stress-induced piezoelectric voltage and the associated generation of electric fields must be considered while analyzing the contact resistance. However, when a nonpolar surfaces such as  $\{2\overline{1}\,\overline{1}0\}$  and  $\{10\overline{1}0\}$  are indented (no net dipole moment), the piezoelectricity effect can be ignored. The possibility of indentation-induced phase transformation in ZnO can also be ignored because deformation by dislocationmediated plasticity was reported under a spherical indenter.<sup>[163]</sup>

# 3.2.2. Creep Behavior of ZnO Nanorods

Time-dependent permanent deformation (creep) in nanodevices plays a critical role in their electrical performance and reliability. However, the time-dependent electromechanical behavior of materials at the nanoscale was not explored due to technological limitations. Conventional mechanical testing with in situ electrical measurements involves the creep deformation of all other components along with the specimen. Kim et al.<sup>[283]</sup> utilized the nano-ECR technique to understand the in situ properties, such as the time-dependent electromechanical behavior of ZnO nanorods at RT. The experiment was done on vertically grown single-crystal ZnO nanorods (**Figure 21**a), and the evolution of resistance with creep was also studied.

As the as-grown ZnO nanorods show rectifying electrical contact (because ZnO is a wide-bandgap semiconductor ( $\approx$ 3.37 eV)) behavior with the conducting tip, Ti and Au metals were deposited on nanorods to make the contacts Ohmic; therefore, the current increased with a significant reduction in  $R_c$ . Asymmetry in the *I*–*V* curve is due to surface asperities, defects, and impurities (Figure 21b).

The *I*–*V* measurements proved that the creep developed at RT on ZnO nanorods was not due to dislocations as the mechanism is known to scatter conduction electrons and reduce electron



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**Figure 21.** a) Schematic diagram showing the complete experimental setup. b) The *I*–*V* curves of as-grown and Ti/Au-coated ZnO nanorods obtained using flat-ended BDD and VC tips. The inset shows the zoomed-in version of the *I*–*V* curve from as-grown nanorods. c) The in situ nano-ECR measurement shows the *I*–*V* behavior of ZnO nanorods. The inset shows the variation in *I* as a function of *V*. d) Both *I*–*t* and  $\sigma_{Engg}$ –*t* curves during creep test under constant *V*. Reproduced under the terms of the CC BY 4.0 license.<sup>[283]</sup> Copyright 2015, Y. J. Kim, Published by Springer Nature Limited.

mobility. A diffusion-controlled mechanism resulting in shortened and wider nanorods was observed for the increase of current during the creep. The  $\frac{\Delta I}{I}$  of the rods initially decreases with increasing voltage and becomes constant. The current measured from -10 to +10 V after the creep test (iii, iv in inset) was higher than for the preloaded rods (ii, v in the inset) due to the Joule heating effect (Figure 21c). A model based on thermionic field emission (TFE) and thermionic emission diffusion (TED) was developed to calculate the current from the nanorod during creep deformation as the resistance depends on the geometry. The rise in current was explained to be due to the increase in the crosssectional area due to the diffusion mechanism accompanied by surface diffusion at RT, especially when the sample dimensions were reduced to the nanoscale. The variance in the electrical resistance can vary with the loading rate, high stresses, and different degrees of creep. As the study was performed within the elastic regime, the measurements were done at  $\approx$ 1 GPa to avoid the elastic strain effect on the electrical resistance (also known as the piezoresistance effect).

The current magnitude was quite low, even for an applied voltage of 10 V, and the *I*–*V* characteristics showed non-Ohmic behavior when using a BDD tip on the Au-coated ZnO rod. However, when using a metal carbide tip, *I*–*V* curves were Ohmic (further reduction in contact resistance after annealing), and the current value increased 5 mA. This is a clear example demonstrating the advantage of VC tips over BDD tips. The current increase at higher voltages (–10 V applied here) at a longer time creep test (close to 4 min in this study) could also be due to an increase in the local temperature (or Joule heating effect) and/or a pressure-induced modification of the bandgap.<sup>[284]</sup> Such high voltages were shown even to weld the ZnO nanowire onto electrodes.<sup>[285]</sup> According to an earlier report, the presence of Joule heating increased the current largely in Pt/ZnO Schottky contacts.<sup>[286]</sup> However, in this study, *I*–*V* characteristics were





recorded for less than 5 s for analysis; therefore, Joule heating issues may not introduce any serious effects for such short-time measurements. The thermal drift may significantly affect the mechanical and electrical measurements; therefore, experiments should be performed at a very low thermal drift rate. Further, the compression behavior cannot be accurately determined if the machine compliance is not accounted for properly prior to measurements.<sup>[287]</sup>

A general suggestion to the readers is that the maximum voltages that can be applied using the Keithley source meter for the in situ conducting tip measurements can be between -10 and +10 V. And, there must be a current cut-off at 1 mA to avoid tip damage due to large current densities (as the contact area will be in nanometers). If VC tips are used for measurements, the voltages can be quite low for metals (assuming no surface oxidation) (e.g.,  $\approx$ 50–100 mV). In the case of semiconductors, 500 mV to 2 V give good *I*–*h* or *I*–*V* curves.

# 3.2.3. Layered Transition Metal Dichalcogenides and Oxides (TMD&Os)

Manipulation of the electronic structure of TMD&Os has always been an active area of research. Though there are many methods to manipulate the electronic band structure, the localized strain was found to be the most effective method.<sup>[196]</sup> The engineered electronic band structure of 2D MoS<sub>2</sub> and MoO<sub>3</sub> by applying strain was proved theoretically but not experimentally. The conductive indentation coupled with AFM experiments were utilized for the same; however, realizing conductance through the layers was impossible due to factors such as  $R_c$ . Hence, Walia et al.<sup>[196]</sup> utilized the nano-ECR technique to study the effect of strain on the electronic properties of quasi-2D thin films synthesized by restacking 2D nanoflakes of MoS<sub>2</sub> and MoO<sub>3</sub> (200-300 nm thick) on substrates with FTO (fluorine-doped tin oxide) coating. Understanding the nanomechanical properties was essential to avoid the inelastic strain as it results in plasticity and fracture. The in situ electrical characterization was done using a VC Berkovich tip, and the I-V responses were studied to realize the effect of the strain.  $P_{\text{max}}$  between 50 µN and 6 mN was applied, which results in elastic strain rather than plastic deformation. A constant bias of -0.1 V was applied, and the load was increased, held at 1, 3, and 6 mN to study the variation of A<sub>c</sub> with the load. From Figure 22, it can be observed that the current increases with load in both cases. The larger current observed in the MoS<sub>2</sub> nanoflake was due to the lower intrinsic bandgap. Also, the decrease in current completely back to zero on unloading confirmed the negligible plastic deformation of 2D layers (Figure 22b,d).

After several partial load–unload tests, the results were repeatable and confirmed highly elastic and reversible deformations under the application of strain. Further, irrespective of the magnitude of *P* (where  $\rho$  at the interface of nanocontact is low), the changes in current had a significant effect on the load, and the observed changes were attributed to the electronic properties of nanoflakes rather than nanocontact interfacial properties. It was reasoned that an increase in applied strain would decrease the atomic bond length. This resulted in the overlapping of atomic orbitals, followed by a shift in energy bands. The alteration in the electronic band structures leads to a change in the conductivity of the nanoflakes. For a particular load, the  $h_c$ of the MoS<sub>2</sub> nanoflake was lower than that of the MoO<sub>3</sub> nanoflake, confirming the harder nature of MoS<sub>2</sub>.



Figure 22. The variation of current with load, depth of indenter, and time for a,b) films made of  $MoS_2$  at constant bias voltage and c,d) for 2D  $MoO_3$  nanoflakes. Reproduced under the terms of the CC BY 4.0 license.<sup>[196]</sup> Copyright 2014, S. Walia, Arxiv.org, Cornell University.



Though the plastic deformation that was mentioned in the study is negligible, the pop-ins in both MoS<sub>2</sub> and MoO<sub>3</sub> indicate their dislocation-mediated plasticity, or phase transformation, or fracture. Probably this is the reason for observing hysteresis in *P*–*h* and *I*–*h* curves after complete unloading. Further, instead of Berkovich indentation, a spherical conducting indenter would help in generating more hydrostatic stress fields, delaying the onset of plasticity (allowing conducting of experiments within the elastic region), and varying the strain with penetration depth. In addition, an adhesion force (composed of capillary force, van der Waals' force, etc.) exists between the conducting tip and the sample surface. The influence of such forces on contact conductance may be considered. Analyzing electronic transport in different regimes (such as tunneling, ballistics, and diffusive) could help us understand the exact contact conductance mechanism in 2D materials. Investigating the electrical contact conductance in layered materials using an in situ conducting tip is interesting because pressure reduces the effective thickness of the monoor multilayers during indentation and separates the bottom electrode and indenter tip, causing conduction through quantum tunneling. Such enhancement in quantum tunneling lowers the whole system's resistance. However, the resistance increases once the system starts relaxing back when the load is gradually removed.<sup>[288]</sup> These effects may be considered when modeling/ simulating/measuring/understanding electrical conductivity using conducting tips. However, pressure-induced phase transformations can be easily observed in layered chalcogenides if the contact pressures can reach a threshold to trigger phase transformations. Although this technique helps measure out-of-plane conductivity in layered materials, in-plane conductivity measurements may not be possible using "through-tip" measurement or may be possible only with special sample preparation.

## 3.2.4. Quantum Tunneling Barrier Height

Percolation theory and quantum tunneling theory have always been critical to study the electrical properties such as piezoresistivity (relation between microstructure and conductivity) of conductive nanocomposites. However, experimental determination of the barrier height of the polymer matrix, the distance between conductive filler particles, and junctions between the conductive networks were challenging. A scanning tunneling microscope (STM) was utilized for the same; however, it requires an aqueous medium to determine the barrier height, making the sample preparation and calculations challenging. As an extension of nanoindentation tunneling microscopy (NTM), Koecher et al.<sup>[289]</sup> suggested a simpler method to find the barrier height of common polymer materials to develop nickel nanocomposites.

Polymer thin films were deposited on Ni substrates, and a conductive BDD tip was used to probe the simultaneous electrical and mechanical properties. The basic equations in the calculation of barrier height were as follows.

The tunneling conductance equation

$$G = G_0 \exp\left(-1.025\sqrt{\lambda}s\right) \tag{41}$$

where  $G_0$  is the conductivity at the tip and plate contact, *s* is the distance between the tip and plate, and  $\lambda$  is the barrier height. Linearizing Equation (41)

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$$\ln(G) = -1.025\sqrt{\lambda}s + \ln(G_0) \tag{42}$$

Understanding  $\sigma$  as a function of gap distance,  $\lambda$  can be calculated as

$$\lambda = \left(\frac{m}{1.025}\right)^2 \tag{43}$$

where m is the slope of the ln(G) versus s plot.

Calibrations of measurements were done by indentations on the Au sample. The *I*-*h* curve (**Figure 23**a) shows the rapid increase of current at the beginning, indicating the tunneling of electrons through the tip to the polymer. Later, an increase in current was observed only after the complete penetration of the tip through the sample and reached the nickel substrate. The conductance *G* was calculated and from the  $\ln(G)$  versus *s* plot. The barrier height was calculated to be in the range of 0.1–1.9 eV.



**Figure 23.** a) *I–S* (distance) curve from the polymer-coated Ni sample. The initial rapid increase of current in the first 5 nm (see the inset) was attributed to the tunneling that occurred before the tip formed contact with the sample. b) The multiple *I–h* curves from the Sylgard 184 sample show the variation of *I* with increasing indenter tip displacement. The initial current jumps were fitted with a linear equation. For clarity, the tests were offset along the *x*-axis. a) Reproduced with permission.<sup>[289]</sup> Copyright 2013, John Wiley and Sons. b) Reproduced with permission.<sup>[290]</sup> Copyright 2015, Elsevier.



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Following the methodology of Koecher et al.,<sup>[289]</sup> Bilodeau et al.<sup>[290]</sup> utilized conductive nanoindentation to determine the quantum tunneling barrier height of Sylgard 184, which was deposited on Ni substrates. Nano-ECR experiments were done and current-depth curves were obtained (Figure 23b). The sudden jump in current at the initial stages was attributed to the tunneling of electrons from the tip to the sample. The zero conductivity at the initial stages was realized from the oscillations around positive and negative values at zero current. The beginning of conductivity was identified by the increase in positive current without negative current. The average barrier height determined was 1.08 eV, with a standard deviation of 0.51 eV.

Though in situ conductive nanoindentation allows determining the tunneling barrier of the conductive polymer nanocomposite even before the indenter forms contact with the sample, the measurement may not be reliable for very thin and compliant films. It is due to the difficulty in finding the exact position of the polymer surface and due to the well-known creep effect in polymers during the hold segment. These two factors, along with surface asperities, make the analysis very complex. The tunneling current is a function of the applied bias voltage, the tip position, the gap between the tip and surface, and the tip geometry. Therefore, VC tips with sharp geometry (e.g.,  $\approx$ 30 nm radius Berkovich tip) may provide reliable tunneling current measurement.

## 3.3. Metals/Interfaces

Dislocation-mediated plasticity is the dominant mode of deformation mechanism in crystalline materials and, most importantly, in metals as their densities and mobilities are relatively large compared to other classes of materials.<sup>[291]</sup> While the mechanical aspect of dislocation behavior is well documented, their role in the electrical properties is not well understood. In bulk systems, Matthiessen's rule<sup>[292]</sup> explains the decrease of electrical conductivity by the scattering effect (driven by lattice vibrations and the existence of impurities and dislocations).<sup>[293]</sup> However, at the nanoscale, quantum effects determine the electrical conductance. For example, when the size is smaller than the MFP of electrons, ballistic conduction occurs.<sup>[294]</sup> Ishida et al.<sup>[291]</sup> observed a gold nanocontact using in situ methods and noted that the dislocation density in gold nanocontact does not affect the electrical conductance, but their movement affects. The electrical conductance was the same for gold nanocontacts with extremely high dislocation density and those with no dislocations at all. In another study, it was observed that the number of free electrons responsible for the electrical transport at the nanocontact was  $2.3 \times 10^{12}$  (free electron density in Au is  $5.9 \times 10^{28} \text{ m}^{-3}$ ).<sup>[295]</sup> Therefore, the dislocation numbers are significantly smaller than the number of electrons in the Au contact, causing no effect on electrical conductance. This section shows how nano-ECR was utilized in understanding the nanoscale plasticity/electromechanical characterization of metals.

# 3.3.1. Investigation of Electrical Contacts

*NiCr/TiW Interface*: Electrodes made of multilayer alloy films play an essential role in the MEMS/(nano-electro-mechanical systems, NEMS) industry. The electrical contact property at the

interfaces will be significantly influenced by the surface properties and work function ( $W_f$ ) of electrodes and external factors such as humidity, temperature, and contamination. Therefore, it is crucial to study the electrical contact properties as they influence the reliability and performance of the devices/systems. In this scenario, Cheng et al.<sup>[296]</sup> studied the mechanical and electrical contact properties of the metal–film interface using the nano-ECR technique. A NiCr/TiW film of thickness 40/30 nm was deposited on a Si substrate and the electromechanical properties were measured by applying loads from 1.5 to 3.5 mN and a voltage of 5 V.

The *I*-*h* measurements obtained using the BDD tip revealed (not shown here) that as the h increased, the  $R_r$  decreased due to increased tip-surface contact area. However, the current decrease with the increasing loading rate was attributed to the distortion of metal films. The distortion resulted in the restricted movement of free electrons, and thus the piezoresistive effect was seen. Below 25 nm depth, the current values were random at different loads due to the size effect and the nonuniform deposition of the NiCr layer. The electric resistance of TiW was negligible compared to NiCr and the Si substrate. The I-h measurement at 3500 µN showed the interface between NiCr/ TiW and Si (step point observed at 70 nm, probably due to the dc-Si to  $\beta$ -Sn transformation) (figures not shown here). Further, the decrease of  $R_c$  at the metal–semiconductor interface was attributed to a 2 nm thick Ti-silicide compound formation during fabrication.

Sn/SnO<sub>2</sub>/W Structure: Electrical connectors play a massive role in all fields and are improving in their size and low loads. However, to maintain their reliability at higher levels, it is essential to understand the mechanism of electrical contacts at the nanoscale. In this scenario, Shimizu et al.<sup>[297]</sup> succeeded in developing a nanoindentation manipulator in an SEM. The device can indent a probe and study the P-h and the electrical resistance by the four-terminal method. The Sn substrate was coated with a SnO<sub>2</sub> oxide layer of 350 nm and tungsten as the indenter probe formed the electrical connection sample. The indentation was done in steps of 20 nm/10 s. At an indentation depth of 1.6  $\mu$ m at 3.2 mN, the electrical resistance decreased from 10<sup>7</sup> to  $10^5 \Omega$ . However, the relaxation of force from 1.1 to 0.5 mN at the 40th second was attributed to the breakage of the SnO<sub>2</sub> layer. From the SEM observations, three types of cracks were confirmed: 1) cracks without any material in it, 2) cracks with Sn penetrated in the middle, and 3) cracks with Sn penetrated on the SnO<sub>2</sub> surface. Hence, it was concluded that, at 60-80 nm, the elastic limit was reached for SnO<sub>2</sub>, and breakage occurred. The penetration of Sn to the cracks and on the  $SnO_2$  surface resulted in the decrease of the  $R_c$ .

*Plastic Response of Native Oxide Layer*: The presence of native oxide layers on metallic thin films influences the mechanical properties. These native oxide layers affect the yield and fracture during indentation in small-scale systems. Stauffer et al.<sup>[198]</sup> employed in situ conductive nanoindentation to gain insights into such processes on Al and Cr films with a native oxide overlayer. As seen in Section 2.3.2, the Maxwell model works well for a metallic contact. The relationship between  $A_c$  and conductance may be similar, as assumed by others,<sup>[298]</sup> for insulating oxide layers.



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As metals undergo plastic deformation, the changes in dislocation mobility cause a local decrease in the electrical contact conductance. According to Matthiessen's rule, the total resistivity term is composed of resistivity of individual contributions such as impurities, lattice vibration (phonons), dislocations, defects, etc. At very large strains, the deviation from Matthiessen's rule should be added. This method is very useful in measuring the dislocation density and point defect concentrations in superconductors and metals.<sup>[299,300]</sup> However, when considering nanoscale insulating oxide layers, one must consider the transport properties of electrons, elastic and inelastic tunneling, hopping transport via defect states, metallic transport through pinholes, etc.

The *G* value was quite low ( $\leq 10^{-11} \Omega^{-1}$  due to the perfect insulating tunneling barrier of oxide Al<sub>2</sub>O<sub>3</sub>) at the initial contact till 10.7 nm. A rapid increase in *G* (almost two orders,  $2.3 \times 10^{-8} \Omega^{-1}$ ) was observed at this point. A similar result (an increase of *G* with oxide fracture) was observed in the Ni sample by Pethica and Tabor.<sup>[301]</sup> However, in this study, the Hertzian deviated from the loading curve well before the oxide fracture. It is believed that the onset of *G* is due to the fracture of the oxide layer occurring along with the load drop. The relationship between *G* and  $\rho_e$  can be written as

$$G = \frac{2\sqrt{2Rh - h^2}}{\rho_{\rm e}} \tag{44}$$

However, the theoretical estimation of  $G = 1.7 \times 10^{-5} \Omega^{-1}$  is  $\approx$ three orders low in this study. The difference could be due to the assumptions (projected area and contact area equivalence at smaller depths; the tip–sample interface is metallic). However, the contact area for fractured oxide film would be smaller, and the contact is not Ohmic, even up to 30 nm depth. The *G* value estimated from Equation (44) was  $2 \times 10^{-5} \Omega^{-1}$ ; the experimentally measured value is  $3.6 \times 10^{-6} \Omega^{-1}$ . This difference is due to the surface roughness effect.<sup>[214,298]</sup> The measured *G* value was  $>10^{-8} \Omega^{-1}$  for a Cr/Cr<sub>2</sub>O<sub>3</sub> system, even before the onset of plasticity, indicating an alternate conduction mechanism (pinholes and the presence of metallic CrO<sub>2</sub>). However, the decrease of *G* at the large displacement extrusion is due to the high local dislocation density near the contact. Nevertheless, this behavior contrasts with the Al/Al<sub>2</sub>O<sub>3</sub> system.

Although pinholes and the presence of metallic CrO2 are attributed to observing high contact conductance in Cr2O3 at smaller depths, the pressure-induced effects within oxide layers also need to be considered because the hydrostatic pressure component under the indenter can decrease the lattice constant and induces changes to the electronic structure, thus modifying the bandgap. The effect of dislocations on the conductivity is usually quite small, particularly at the density levels likely to be present in nonmetals. Alternatively, indentation might have caused fine-scale cracks, which have a substantial effect on conductivity (typically reducing conductivity). This could also be one reason for deviating from Hertzian contact much before the extrusion in Al<sub>2</sub>O<sub>3</sub>. Furthermore, surface asperities (and therefore the number of conducting channels), tip contamination, defect states, dangling bonds on the surface of the oxide layers, and the interfacial issues between Cr<sub>2</sub>O<sub>3</sub> and Cr contribute to the observed conductance.

## 3.3.2. Monitoring Nanoindentation-Induced Delamination

Nanoindentation/AFM coupled with in situ electrical measurements plays a massive role in realizing electromechanical properties of bulk as well as thin-film samples, evaluating the wear of ionic thin films,<sup>[302]</sup> and investigating organic contamination layer presence.<sup>[303]</sup> Some authors<sup>[304,305]</sup> showed that the delamination in thin films could be identified from the pop-in and dP/dh at the end of the unloading process of the *P*-*h* curve. However, the relation between pop-in and delamination was unexplored for a long time. Nguyen et al.<sup>[306]</sup> used the nano-ECR technique coupled with nanoindentation to understand the relation between pop-in and the delamination in a Ti<sub>x</sub>N<sub>v</sub> film of thickness 500 nm deposited on an SKD61 tool steel substrate. The pop-in was seen at  $1200 \,\mu$ N, where the *h* value jumped from 0.19 to 0.68 µm with a significant drop in the current (Figure 24a). Typically, an increase in contact depth results in an increased  $A_c$ , which leads to an increase in electric current. In contrast, in this study, a drop in electric current was observed during the pop-in event. The simultaneous phenomena of pop-in and the drop in current were attributed to the Ti<sub>x</sub>N<sub>y</sub> film delamination from the substrate.

Initially, between 500 and  $1200\,\mu$ N, the penetration depth increased with load and remained constant (pop-in) due to the structural changes in the film/substrate interface. As the load increased (after pop-in), the slow rise of the penetration depth was evident. Thus, the pop-in was attributed to the delamination of the film. The unloading after the delamination showed two stages (Figure 24b) differed by an elbow. It was concluded that when the applied load was large, the delaminated film maintained contact with the substrate due to elastic recovery, which resulted in increased contact stiffness. When the load decreased to sufficiently small values, the debonded film was suspended from the substrate. The elbow indicated that the delaminated film and substrate were just in contact.

Pop-in and the underlying phenomena are shown in Figure 24c,d. The figure shows three deformed zones. The primary zone is the darkest in color and represents the permanently deformed zone. The secondary zone is lighter and represents the delaminated region, whereas the tertiary zone is the remaining area. The impedance due to indenter/film, film/substrate junctions and the impedance due to the conducting film are represented by resistors ( $R_{I/F}$ ,  $R_{F/Sb}$ , and  $R_{Fn}$ ), where *n* represents the deformation zones. It was considered that the delamination zone was larger than the primary zone and buckling occurred due to compressive residual stress in the film. After the pop-in, due to delamination, the film was not in contact with the substrate. As a result, the  $R_{\rm F/S2}$  was turned into a breaker, a key reason for the increase in R<sub>Total</sub> (Figure 24c). On unloading (Figure 24d), when the load reached below the elbow, the elastic recovery was completed, and the delaminated film stayed in a suspended manner from the substrate, which turned  $R_{F/S1}$  into a breaker. Here, the resistance is a function of *P* as it depends on the strain in the film and the changing contact conditions in the film on unloading. Therefore, the electrical measurements during nanoindentation provided insights into the interfacial deformation mechanisms and aided in correlating the pop-in and elbow phenomena to thin-film delamination from the substrate.

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**Figure 24.** a) The variation of *I* and *h* with increasing load. The concurrent occurrence of pop-in and current drop is evident. b) Unloading results after a pop-in suggest two behaviors. i) For smaller loads, the delaminated film gets suspended and ii) the elbow in the unloading curve indicates contact between the substrate and delaminated film. c) Schematic showing the occurrence of pop-in due to loss of interfacial contact between film and substrate, thus a drop in the current. d) Schematic showing the reason for the rapid decrease in depth and hence current after the elbow. Reproduced under the terms of the CC BY 3.0 license.<sup>[306]</sup> Copyright 2011, H. H. Nguyen et al., IOP Publishing.

This study provides experimental evidence, justification, and a model of the current drop mechanism during pop-in due to debonding of the film from the substrate. However, the decrease in current can also be due to a fracture (fine-scale cracking) of the  $Ti_xN_y$  film (known as hard material) and the intercolumnar sliding (often sputter-deposited TiN films grow in columnar grain structure) during Berkovich indentation, which causes a complete loss of the contact between the deformed film and its surroundings. That could also be a reason for the slight increase of current after pop-in (compared to before) due to the weak contact between the sides of the indenter tip and the film surface because a larger current can be expected even after pop-in if the indenter

tip continues to contact the film because the electric conduction always chooses the shortest path (as shown in the model).

Also, another possibility (may be unlikely in this case) is that TiN is known to phase transform from NaCl rock-salt structure to CsCl crystal structure (first-order transformation associated with a volume change) when the stresses are deviatoric.<sup>[307]</sup> As discussed earlier, the elbow in the unloading curve indicates phase transformation in Si from the metallic  $\beta$ -Sn phase to a highdensity amorphous phase. However, such indentation-induced transformations may not be correlated to the pop-in and elbow in the *P*–*h* curve in the present case because the TiN in the CsCl structure is five times higher conducting than the TiN in the

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NaCl structure. In that case, a significant rise in the electric current would be observed, but that is not the case here.

# 3.3.3. MIM Device Characterization

MIM devices are promising candidates in rectenna (such as optical rectenna) and IR detector applications. However, the relationship between the material property and the MIM device performance is not vet explored. It was predicted that a point-contact diode configuration is the most suitable, as a small  $A_c$  can result in high-frequency operation. Therefore, a bent-wire point contact diode MIM configuration was explored, but the lack of control of the diode area and penetration depth has posed a challenge. Thus, Periasamy et al.<sup>[308]</sup> explored the nano-ECR technique equipped with a BDD tip on a MIM device structure to study the electromechanical properties. The MIM structure consists of Nb (90 nm)/Nb<sub>2</sub>O<sub>5</sub> (15 nm) bilayer thin films on a Si substrate sandwiched between metal 1 (Nb) and metal 2 (BDD tip), completing the MIM diode structure. The *P* versus *t* and *P*–*h* curves were measured simultaneously. The MIM device was characterized by two factors-asymmetry and nonlinearity. Asymmetry is the ratio of the I<sub>forward</sub> to I<sub>reverse</sub>, whereas nonlinearity is (dI/dV)\*(V/I).

The in situ electrical characterization revealed the actual properties of the device. Asymmetric and nonlinear curves show that the asymmetry increases with displacement/penetration depth. However, the nonlinearity is independent of the displacement, indicating the reliability of this method (i.e., no effect of geometry on the measurement). From the *I*-V curves (not shown here), it is evident that the current increases with indenter penetration depth due to reduced tunneling distance and increased device (contact) area. The results obtained by the nano-ECR technique were compared with the bent-wire point contact approach and it was found that the MIM diodes fabricated with a conducting nanoindenter (as a top electrode) showed excellent asymmetry (60-300) and nonlinearity (6-9) values above 3 V. Therefore, nano-ECR equipped with nanoindentation is an ideal nondestructive technique and shows great potential for testing MIM combinations for performance without the uncertainty that hinders from a typical bent-wire point contact.

## 3.3.4. Resistive Switching in Memristors

Memristors play a major role in memory technologies, particularly neuromorphic computing, due to their high-density nonvolatile memory, long-lasting cyclic switching, as well as easy ON/OFF switch. Nili et al.<sup>[309]</sup> fabricated an amorphous SrTiO<sub>3</sub> (a-STO)-based perovskite oxide thin film on a MIM configuration. From the analysis of the as-grown and electroformed samples, the nanoionics-driven electrical conduction mechanism in a-STO thin films was predicted.

Microscale asymmetric MIM switching cells  $(20-100 \mu m)$  with Pt/Ti/a-STO/Pt (100 nm oxide layer) configuration were chosen for the experiments. From the preliminary investigation, it was predicted that the resistance switching property of a-STO thin films could be due to conducting channels developed from the nonlinear, field-dependent ionic migration through a

network of point defects. Hence, the nano-ECR technique with a VC Berkovich tip was utilized to reveal the conduction mechanism. The results are shown in Figure 25. Experiments were performed with a  $P_{\text{max}}$  of 100 µN and voltage sweep of ±250 mV at the  $P_{\text{max}}$  on the electroformed samples. The studies showed the Schottky behavior of a-STO/Pt samples till 1 mN. Above 1 mN, the current increased abruptly and nonlinearly due to the increase in the A<sub>c</sub> and nonuniform resistivity of the indentertip contact (Figure 25a). The deformation with increasing *P* is shown in Figure 25b-d. The indentation at low load showed a uniform increase in current due to the development of the conduction path(s) within the sample (Figure 25e). The development of the conduction channel was attributed to the reduction of depletion layer width at the a-STO/Pt interface with increasing P. Thus, the increased migration of oxygen vacancies and high defect density resulted in increasing carrier concentration. However, due to the nonuniform tip shape, the electrical contact area is also distributed along the periphery rather than concentrating at the center. Therefore, the oxygen vacancies diffused through the peripheral electrical contact via the initial point defects, and the expansion of the defect structures resulted in forming a conducting network (Figure 25f).

Further, the ultrathin a-STO films possess insulating characteristics and elastic properties at low loads. The Schottky behavior changes abruptly at higher loads due to the displacement of nanocontacts and deformation in the contact area. Above the threshold voltage, the transport mechanism followed spacecharge-limited conduction (SCLC) at the interface, causing enhanced carrier transport into the oxide layer's conduction band due to low barrier heights. A decrease in width of the barrier and growth of improvement of conducting channels were observed with mechanical compression. Further, the combination of mechanical compression with electric field induced the redox process that transformed the a-STO around the contact into a conducting n-type layer. The authors conclude that whereas the nondeformed regions possess insulation behavior, the deformed regions show high-performance switching due to the partially developed conducting channels with different resistivities. The Ohmic conduction was attributed to the complete breakdown of the electric barrier at higher voltages.

The nano-ECR measurement in this study helped researchers to explain the current conduction mechanism in MIM devices. The origin of contact resistance, alteration of the potential profile in the depletion region, active region for resistive switching, and role of oxygen vacancies in improving the conduction in a-STO films were decently demonstrated. When using in situ nanoindentation coupled with nano-ECR for such studies, it is essential to consider the possibility of densification and then crack formation under compression on the thin a-STO layer, allowing both electrodes to form a conducting channel. In addition, the I-V curves recorded at  $P_{\text{max}}$  can have the contribution from the contact area change due to creep. Therefore, the measurements can be conducted in the steady-state creep region, where the strain versus time plot becomes nearly linear. The application of 10 V on metals at the contact diameters of 100-130 nm (that too for a highly conducting VC tip) results in a big damage to both surface and tip due to the local melting of the surface due to Joule heating  $(I^2 R)$ .
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**Figure 25.** In situ conductive nanoindentation shows the electrical transport behavior and structural deformations in a-STO/Pt stacks of 60 nm. a) The *I*-V curves of 60 nm a-STO films show an increasing current trend with increasing indentation load. b–d) Residual indent impressions (around the electrical contact area) under different  $P_{max}$  after ten high-voltage sweep cycles under increasing  $P_{max}$ . The scan area is 1  $\mu$ m<sup>2</sup> in (b) and 5  $\mu$ m<sup>2</sup> in both (c) and (d). e) The *I*-V curves of nondeformed and deformed regions ( $\approx$ 5 mN, after sweep cycles). f) Schematic diagram of formed filaments because of migration of oxygen vacancies around the nanocontact area. Reproduced with permission.<sup>[309]</sup> Copyright 2014, John Wiley and Sons.

## 3.3.5. Electromechanical Dynamics of Nanocrystalline (nc)-Pt Thin Films

Platinum thin film as a contact electrode plays a huge role in the MEMS/NEMS industry. However, the characterization of Pt thin films has always neglected factors such as surface roughness, grain morphology, the effect of substrates, the texture of the film, as well as the formation of pile-up, which influences the conclusions obtained. Therefore, Nili et al.<sup>[310]</sup> explored the in situ electrical nanoindentation technique to understand the electromechanical dynamics of nc-Pt (111) thin films. The tip area functions for different depths were utilized to avoid geometrical irregularities in the conductive Berkovich tip (274.6  $\mu\Omega$ ). The Pt thin films of thickness 200 nm, with 20 nm thick TiO<sub>2</sub> (adhesion layer), were deposited on thermally oxidized Si

substrates. An insulating adhesion layer helped to get the inherent properties solely from Pt thin films with electrical measurements. The in situ electrical measurements were carried out by applying a constant bias of 1 mV during indentation with a d*P*/d*t* of 10  $\mu$ N s<sup>-1</sup> for loads up to 500  $\mu$ N (**Figure 26**a). To avoid the thermal drift and heating of the sample, for loads above 500  $\mu$ N, the constant bias and d*P*/d*t* applied were 0.5 mV and 100  $\mu$ N s<sup>-1</sup>, respectively (Figure 26b). The voltage was swept between ±1 mV during the hold segment (1 s) at *P*<sub>max</sub> to understand the *R*<sub>c</sub> behavior.

The *I* versus *h* and the  $\rho$  versus *P* graphs are shown in Figure 26. Even at low loads (<50 µN) and at tiny areas of contact (<8 nm), the  $\rho$  was observed to be high due to the high resistivity at the indenter's tip, friction between the indenter tip and sample contact, and the scattering effect due to the surface roughness of

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**Figure 26.** In situ conductive nanoindentation results (*P*, *I* vs *h*) obtained on nc-Pt films at a) low loads and b) high loads. c) The variation of resistivity with varying load. d) The  $P-\rho-h$  curves show that films' resistivity rises at higher loads where pile-up deformation starts to appear. Reproduced with permission.<sup>[310]</sup> Copyright 2014, AIP Publishing.

films (Figure 26c). After this initial stage, the  $\rho$  decreased abruptly, which marked the beginning of the plastic deformation. Instead, when the d*P*/d*t* was increased to 100 µN s<sup>-1</sup> for higher peak loads (>1000 µN), the discontinuity in *R* was not observed as the plastic deformation occurred rapidly.

The *I*–V curves obtained at loads from 50 to 5000 µN showed Ohmic behavior, which confirmed the existence of a metallic contact between the indenter tip and the Pt thin film. It was assumed that to analyze the actual contact area (at the nanoscale), a variable resistivity profile dependent on load and depth was necessary, and an empirical relation between  $R_c$  and the  $\rho$  profile of the indenter was established. Thus,  $\rho$  versus  $h_c$  was studied (Figure 26d). The initial high resistivity was attributed to the surface roughness; however, after 25 nm depth, the average resistivity was close to the theoretical average resistivity (16.5  $\mu\Omega$  cm). From the electromechanical studies (Figure 26a,b) under 50 µN, pure elastic nature was observed on loading. Whereas the current was increasing gradually by increasing the A<sub>c</sub> on loading, a different trend was observed during unloading. Therefore, the friction effects and thermal drifts are the reasons for the flow of higher magnitude of currents through the nanocontact area during unloading and inelastic slipping of the nanocontact at the grain boundaries, respectively.

At the beginning of plastic deformation, the sharp drop in the resistivity profile and the increase in the electrical contact area with increasing penetration depth are due to the flattening of grains. However, the increase in resistivity at higher loads irrespective of the rise in  $A_c$  is due to an increase in the dislocation density in the Pt film due to plastic deformation. Also, the

threshold for load/depth for the increase in resistivity and that for the increase in pile-up deformation were observed to be the same (Figure 26d).

This is a thorough study on the evolution of nanoscale contact resistance at the contact of nanocrystalline Pt films (dominantly (111) oriented) and a ceramic pyramidal conducting VC tip. Almost all the possible parameters that can affect the electromechanical behavior of the films at a fine length scale were considered. An empirical equation relating to the measured  $R_c$  and the  $\rho$  profile of the indenter was derived. However, surface roughness effects and electron scattering at grain boundaries at shallow depths cannot be accounted for in this model. The increase in resistivity at higher depths was due to an increase in dislocation density due to severe plastic deformation. Grain size measurement would be useful in understanding the specific mechanism of dislocation-based activity that caused an increase in resistivity. In an earlier study, the mechanism of evolving plasticity in Pt films was observed to be fully dislocation activity enabled in grain sizes >10 nm, partial dislocation plasticity between 10 and 6 nm grain sizes, and grain-boundary-mediated plasticity in d < 6 nm grains.<sup>[311]</sup> Further, the nature of deformation of the polycrystalline Pt films was found to be grain size dependent. While the thinner Pt films (75 and 100 nm) exhibit brittle behavior, the 250 nm film was reported to exhibit dual brittle/ductile character, and 400 nm films were ductile in the tensile testing measurement of free-standing Pt samples.<sup>[312]</sup> Though the experiment types are completely different, there could be a possibility of an increase in the resistivity due to nanoscale fracture (along with plastic deformation as evident from pile-up formation) of the Pt SCIENCE NEWS \_\_ www.advancedsciencenews.com

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films because the dislocation density at that fine scale may not result in such a large difference in the resistivity. The initial high resistivity up to 8 nm depth (i.e., in purely elastic contact) is due to the surface roughness ( $\approx$ 3 nm) of the films and possibly the electron scattering at the grain boundaries.

#### 3.3.6. Investigation of Tip-Sample Contact during Slip

Intermittent plastic flow associated with dislocation avalanches (slip events) in crystals during nano- and micromechanical testing is well understood with in situ advanced experimental techniques and modeling, but the relationship between the slip and the dislocation velocities remains unexplored. Sparks et al.<sup>[313]</sup> put effort into understanding the dislocation dynamics during slip events using a nanoindenter coupled with in situ electrical measurements on single crystals of Au columns ([001] compression axis), dc-Si, Ni<sub>3</sub>Al, and Vit105 bulk metallic glass (BMG) (Zr<sub>65.7</sub>Cu<sub>15.6</sub>Ni<sub>11.7</sub>Al<sub>3.7</sub>Ti<sub>3.3</sub>).

The nanoindenter was modeled as an undamped linear harmonic oscillator (LHO) to evaluate the values obtained during the slip events. It was concluded that during the slip event, the force between the indenter tip and the sample does not fall to zero at any point. The peak velocities ( $V_{\text{Peak}}$ ) of the tip during the slip events on various samples were also measured and compared with the fast fracture case in Si, where the indenter tip loses its contact with the sample. In the fracture case of Si, the  $V_{\text{Peak}}$  obtained was several orders of magnitude higher than those of other samples, thus confirming the indenter movement with sufficient velocity by maintaining contact with the sample refers to the slip event. From the *P*–*h* measurement during the slip event and its comparison with loading and unloading in the elastic regime, the effective stiffness during the slip event was to be lower than the axial quasi-static stiffness. This confirmed that the slip event was accompanied by plastic deformation rather than dislocation rearrangement.

The nano-ECR technique was utilized to investigate whether the tip-sample contact was maintained during the slip event. A discontinuity in current flow characterized the loss of contact of the tip with the sample. Figure 27a shows the P-I-h curves obtained at 3 mV in the displacement control mode. A plastic flow was noted after the initial elastic response until  $300 \,\mu N$ ( $\approx$ 90–100 MPa). For every displacement jump, a drop in the current was also observed, which coincided with elastic unloading during each event. This confirmed that the relation between I and P could be utilized to understand the deformation related to the  $A_c$  and  $R_c$ . Microstructural events can also be identified by a change in current, as such events alter the sample's resistivity. The displacement jump at  $\approx$ 25 nm was accompanied by no significant drop in current, indicating that the slipping crystal was in contact with the tip (Figure 27b). The study on the current before and after slip events revealed that even though the absolute value of current changes after the event, the slope of the P-I



**Figure 27.** a) The *P*–*h* and *I*–*h* curves obtained from the Au column (in h-control mode), recorded using the in situ nano-ECR technique. b) A zoomed-in view of the first pop-in event at the initial penetration depths in the *P*–*h* data shown in (a). c) The *P*–*h* and *I*–*h* data of an Au column (obtained in load-controlled mode). d) The *P*–*I* curve during, before, and after the slip event shown in (b). e) The inset of (c) shows the SEM image of the Au column after in situ conductive nanoindentation. The slip is evident. All the current measurements were conducted at a constant bias of 3 V. Reproduced with permission.<sup>[313]</sup> Copyright 2017, Elsevier.





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curve remains unchanged, indicating significant force drops (Figure 27d). The current in the open- (Figure 27c) and closed-loop *P*-controlled modes confirmed that even the current drops, it does not drop to zero, confirming contact of the tip with the sample throughout the slip events. The possibility of current flow in the absence of mechanical contact (tunneling, through plasma generation, etc.) was excluded in this study as such things show an arc (at higher voltages) on the crystal surface and the current signal, which was not observed on the deformed sample (inset in Figure 27c).

#### 3.3.7. Electroplasticity in Metals at the Nanoscale

The influence of the electric field on the plastic deformation of metals is known as electroplasticity.<sup>[314]</sup> This effect was found to affect the flow stress,<sup>[315,316]</sup> stress relaxation,<sup>[317]</sup> time-dependent plastic deformation (creep),<sup>[317]</sup> and dislocation generation and their mobility,<sup>[318]</sup> fracture,<sup>[319]</sup> and fatigue.<sup>[320]</sup> Though several mechanisms such as localized Joule heating at the lattice defect and vacancy migration due to electron wind effects were proposed, the understanding remains poor. Li et al.<sup>[321]</sup> attempted to understand the electroplasticity phenomenon in metals using a JEOL 3010 TEM and a Bruker, Inc. Picoindenter equipped with nano-ECR measurement for controlled in situ electromechanical experiments.

The effects of the electric current on the structure and mobility of dislocations in Al, Ti, and Ni thin foils were studied.

The samples were directly attached to an electrical push-to-pull (E-PTP) device with the help of a focused ion beam (FIB) lift-out (Figure 28a-c) and deformed uniaxially in tension (Figure 28d). After each test, it was possible to correlate the video of deformation with the mechanical and electrical data. Two types of dislocation motions were observed. In the first type, upon current pulsing, the pre-existing dislocations escape from the specimen fast in less than 0.1 s. In the second type, the dislocation moves slowly and remains in the specimen for more than 1 s. It was observed that upon application of the current pulse, large slip traces with dislocations at the edge were triggered; therefore, the displacement was increased. Figure 28e-g shows that the pulsed electric field was sufficient for the dislocations to overcome the barrier and move. It was also confirmed that the dislocations moved faster and longer distances with pulsed electric field triggering than mechanical triggering. It was also predicted that the local Joule heating effect could be analyzed through lattice change measurements with TEM diffraction.

In summary, the nano-ECR studies by various researchers on various metals at the nanoscale reveal the fact that although the dislocations' density does not affect the contact conductance, their movements affect it. Probably, since the metals already have high conductivity, the changes in the conductivity due to dislocation density could be extremely small and difficult to detect. Also, the native oxide formation on the metal surfaces was found to affect the measured contact conductance significantly. Further, the pinholes, the presence of metallic oxide phases,



**Figure 28.** a) A microscopic image of an electric push-to-pull (E-PTP) device and b) a thin Al foil (lift-out). c) To observe dislocations in TEM, the dog-bone shape was modified with a hole for localization of stress. d) Tension test was conducted on the Al foil with a specific load function and current pulse in 160 s. e–g) The dislocation movement in Al when applying an electric current at 42 s (the black arrow in (d)). The motion of dislocation was captured within two frames (at 42.1 and 42.2 s). The TEM images show single dislocation, depinning with the applied current. Reproduced with permission.<sup>[321]</sup> Copyright 2019, Cambridge University Press.



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and the formation of fine-scale cracks affect the contact conductance significantly. Furthermore, surface asperities, changes in the contact area, tip contamination, defect states, dangling bonds on the surface of the oxide layers, electron scattering at the grain boundaries (in case of polycrystalline materials), grain sizes, and thickness-dependent deformation mechanisms in thin metallic films play a major role in determining the conductivity at the nanoscale. In addition, delamination of the films from the substrates, solid-state phase transformations under pressure (if the pressure reaches a threshold to trigger the phase transformations), and Joule heating influence the measured properties. The pressure-induced lattice compression, amorphization during indentation, a pile-up of the deformed materials, tip resistivity, and overall resistivity of the entire circuit dominate while quantifying the electrical conductivity at a small scale.

Compared to semiconductors, nanoscale plasticity is not that well explored in metals with the help of electrical contact resistance measurement technique. In most cases, an increase in current with increasing penetration depth was observed and attributed to a rise in the contact area. It is observed that this field is still at the nascent stage, and there is considerable scope for exploring nanoscale contact conductance measurement on metals and metal oxides and also there is the need for developing models to understand the electron transport mechanisms and correlation with the defects created by plastic deformation. For example, researchers can still explore by either experiments, modeling, or simulations on the crystallographic orientation dependence of the electromechanical properties, correlate electrical current changes to various plastic deformation mechanisms beneath the indenter (if possible separate individual contributions), correlate the electrical current to the dislocation activities and stress distributions in single-crystalline metals, the effect of deviatoric stress components under the indenter, study the effect of grain size and grain boundary area on the contact conductance in polycrystalline metallic films, friction effects, the role of adiabatic temperature rise during indentation and film-substrate adhesion on the contact current measurement, effect of native oxide on the overall electrical measurement, the work function difference between tip and the sample on the contact conductance, conductivity changes with purely elastic, elastoplastic, or plastic regions, etc. These are important as the dislocations glide only on certain crystallographic planes and in certain crystallographic directions. Further, most of the materials chosen by researchers deform plastically, mostly by the dislocation glide. Still, there are cases in which deformation twinning and possibly (martensitic) phase transformations can contribute to plasticity, although these are relatively unusual. It will be interesting to explore nano-ECR studies on those materials to understand incipient plasticity through electrical current measurement. Further, as Nowak et al.<sup>[173]</sup> suggested, efforts can be made for finding specific conditions and length scales where both combined mechanical–electrical coupling leads to the same effects in metals.

#### 3.4. BMGs

#### 3.4.1. Pt-Based Metallic Glass Thin Films

Pt-based metallic glasses (Pt-MGs) have always been a topic of research in the nano- and microelectromechanical systems industry and in microresonator applications due to their ultrahigh mechanical strength, high glass-forming ability, and high electrocatalytic activity. Further, the contact resistance and electric resistivity of Pt-MG thin films play an essential role in their application as electrodes in energy conversion/storage devices. Thus, Das et al.<sup>[322]</sup> explored the electromechanical behavior of Pt-MG thin films (300 nm thick)/Si substrate using a nanoindenter coupled with in situ electrical measurements. The loading of the P-h curves showed pop-ins due to intermittent plasticity in the form of shear band generation and propagation. Serrations were due to the strain rate divergence between the matrix and shear band nucleus. Nano-ECR experiments were conducted to understand the evolution of the contact resistance of the thin film during deformation.

As shown in **Figure 29**, the increase in *I* with *h* is due to the increased  $A_c$ . For each shear band activity, a simultaneous drop in current was observed due to low electrical conductivity due to electron scattering at the shear band. Compared to crystalline materials, MGs have a high elastic limit. The elastic strain energy that is stored during elastic deformation releases during yielding in the form of heat. In MGs, most of the yielding process localizes in shear bands, and therefore, they act as heat sinks. The temperature rise in heat sinks was considered the reason for the increased scattering of electrons. Moreover, the atomic



**Figure 29.** a) The typical *P*–*h* curve of a Pt-MG thin film showing pop-ins (represented by black arrows) in the loading part; b) the corresponding *I*–*h* plot shows an increase in current with indenter penetration depth. Reproduced with permission.<sup>[322]</sup> Copyright 2015, John Wiley and Sons.



density at these points is low compared to other regions. Therefore, the electron scattering and lower atomic density at the shear band were reasoned for the decrease in electrical conductivity and, therefore, a sharp drop in current.

A drop in electrical current can also be due to the temporary loss of contact. If that is the case, the current should fall to zero, but that is not the case here. The change in the current is relatively small before pop-in and at the pop-in. Therefore, the possibility of temporary loss of contact can be ignored. Thus, the drop in electrical current at the pop-in is due to the high resistivity of the shear band (probably due to the change of resistivity due to a temperature rise in the shear band) due to electron scattering. This indicates a significant change in  $\Delta T$  resulting in increasing the electrical contact resistance that was too significant to cause a drop in conductivity. It is interesting to note that the change in resistivity of the shear band is more dominating the electrical current than the contact area-induced increase in the current.

#### 3.4.2. Nanoporous Metallic Glass (np-MG)

Though the mechanical properties of nanoporous materials are well explored, simultaneous electrical and mechanical responses are scarce. Arora et al.<sup>[323]</sup> studied the electromechanical behavior of a Pd-rich np-MG surface using in situ nano-ECR coupled with the nanoindentation technique. (**Figure 30**) A nanoporous structure of  $\approx$ 500 nm thickness and pore size between 10 and 50 nm was obtained by electrochemical dealloying of Ni–Pd metallic glass.

Figure 30a shows the P-h curves obtained from an MG substrate, nanoporous substrate combination, and nanoporous structure. Nano-ECR experiments were performed by applying a constant bias of 0.1 mV. On comparing the current values at the same penetration depth for both the nanoporous structure and MG sample (Figure 30b), the lower electrical conductivity of the nanoporous structure is evident. The average resistivity for the nanoporous structure was calculated as  $19.65 \times 10^{6} \Omega \text{ nm}^{2}$ , whereas for the MG substrate, it was  $8.86 \times 10^6 \,\Omega \,\mathrm{nm}^2$ . Thus, the average resistivity of the nanoporous structure was 2.2 times larger than that of the MG, which was attributed to the tortuosity of current paths, reduced A<sub>c</sub>, and several conducting channels. This study revealed that the resistivity of MGs could be varied significantly by varying the pore size and volume, which may be helpful in a wide range of applications. It is known that the porosity affects the electrical conductivity due to the nonconducting volume within the pores, limiting the contact area and thus restricting the free flow of electrons. Further systematic studies may help understand the electrical conductivity and porosity relationships (within the elastic limit) in nanoporous MGs and foams.

#### 3.4.3. Structural Evolution Process in BMGs

Though the BMGs are known for their higher mechanical strength, they tend to relax upon temperature or stress, affecting their fatigue performance. Even though macro and microlevel damages in BMGs were well explored, the study on their stress-induced relaxation at the atomic scale was unknown. In





**Figure 30.** a) Representative *P*–*h* curves were obtained from an MG substrate, nanoporous structure, and nanoporous structure–substrate. b) *I–h* curves for the MG substrate and nanoporous structure. The MG substrate and np-structure and substrate combination were indented with 10 mN load, and the np structure was indented with 1 mN load. The np surface layer shows a smaller *I* value compared to the MG substrate for the same  $h_{max}$ . Reproduced with permission.<sup>[323]</sup> Copyright 2015, Taylor and Francis.

this scenario, Liu et al.<sup>[324]</sup> explored and compared the stressinduced structural deformation in fatigue-tested (FT) BMGs and in as-cast (ac) BMGs using in situ conductive nanoindentation. The purpose of the experiment was to utilize the nano-ECR technique to obtain the current, which contains vital information about structural evolution during deformation, and to identify the structural difference between FT and ac-BMGs from the relative resistivity. Cylindrical amorphous rods of  $Zr_{50}Cu_{40}Al_{10}$ with a diameter of 8 mm were chosen for this study. Three micropillars of  $\approx 1 \,\mu$ m diameter and  $\approx 2 \,\mu$ m height were milled (using FIB) out from the ac-BMG and FT samples. Nano-ECR experiments were done with a constant bias of 0.1 V and pressurized up to 1.2 GPa with a holding time of 10 s (Figure 31a).

For all the pressures (0.4, 0.8, and 1.2 GPa), the observed trend in current was the same for the ac and FT samples. For the FT sample, the current observed was low compared to the ac-BMG, SCIENCE NEWS \_\_ www.advancedsciencenews.com

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**Figure 31.** a) The load function and voltage used for in situ conductive nanoindentation experiments. b) The variation of current with time for the ac and FT-BMGs. c) The relative  $\rho$  change of ac and FT-BMGs. d) The total intensity of relative  $\rho$  changes during loading, holding, and unloading segments for ac and FT specimens. Reproduced with permission.<sup>[324]</sup> Copyright 2015, Elsevier.

indicating the higher electrical resistivity of the FT samples (Figure 31b). The electrical resistance of the FT sample  $(9750 \pm 1310 \,\Omega)$  was approximately five times higher than the ac-BMG (2115  $\pm$  58  $\Omega$ ). The calculated change in resistance was attributed solely due to the inherent properties of the sample as the resistance of the conductive tip and that of the sample holder were constant. The inherent resistivity of the BMG was calculated using Pouillet's law:  $R_r = \rho_r L/A$ , where  $\rho_r$  is the inherently reduced resistivity of the sample and L and A are the length and area of the micropillars, respectively, which are extrinsic factors. On calculating the reduced resistivity, there was a rise in value from  $9.1 \times 10^4$  (ac-BMG) to  $53.2 \times 10^4 \,\mu\Omega$  cm in the case of the FT sample, which indicated the increased frictional force experienced by the conducting electrons. The increase in reduced electrical resistivity was due to the increased scattering of the conducting carriers resulting from the irregular atomic arrangement after the fatigue test. The local atomic-scale structural changes did not affect the mechanical properties. The serrations observed in the current curves were due to atomic rearrangements under an applied force. The relative resistivity change  $\Delta \rho_{\rm r} / \rho_{\rm r}$  is plotted against time (Figure 31c).

The negative change in relative resistivity of the FT sample was attributed to a decrease in packing density and an increase in the volume fraction of the loosely packed liquid-like core (LLC) due to the coalescence of LLCs and resembled the structural dilation at the initiation stage of shear band formation. The positive change was explained as an increase in packing density and decreased volume fraction due to the damage recovery. The random change in relative resistivity observed in the fatigue-tested sample confirmed the random variation in atomic packing density. The total intensity of  $\frac{\Delta \rho_r}{\rho_r}$  during loading and unloading is shown in Figure 31d. The relative resistivity change was amplified in fatigue-tested specimens, indicating that the damage and recovery were easier in the FT specimen due to its disordered atomic structure. Thus, through the nano-ECR experiments, it was revealed that the damage at the atomic scale and relaxation induced during the FT-BMG sample could be reactivated by applying external stress. Information from the multiple electrical spikes was sufficient to get information about the coalescence of LLC and the densification of the remaining ones. These details help improve the fatigue performance of BMGs with more homogeneity and few LLCs.

#### 3.4.4. Discrete Drops in Electrical Contact Resistance of BMG

Though the mechanical properties of MGs are well explored using instrumented nanoindentation, the real-time relation between the mechanical and electrical properties and the underlying phenomena remained unexplored for a long time. Singh et al.<sup>[325]</sup> utilized the nano-ECR technique to quantify the plasticity in MGs. A fully amorphous Pd-based BMG (Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub>) sample was chosen for this experiment. Nanoindentation was performed in load-control mode to a  $P_{\text{max}}$  of 9 mN, with a dP/dt of 400 µN s<sup>-1</sup> and a holding time of 10 s at  $P_{\text{max}}$ . A voltage bias of -10 to +10 V was applied for the electrical measurements. The current increases with increasing load due to increased  $A_{c}$  (tip–sample).

The servation observed in both P-h and I-h curves (Figure 32a) was due to the nucleation and spread of a single shear band. Interestingly, the current surge and pop-ins co-occur





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**Figure 32.** The representative a)  $P_{-l-h}$  curves and b)  $l_{-h-t}$  curves obtained using in situ conductive nanoindentation. The inset in (b) shows the amplified view of some part of  $l_{-h-t}$  curves demonstrating the concurrent occurrence of current surges and pop-ins during conductive nanoindentation. c) Schematic illustration shows the plastic deformation of BMGs under the nanoindenter via shear band formation. d) The variation of shear band area estimation from geometrical analysis and from current measurements as a function of *h*. e) The  $l_{-V}$  curves obtained at the  $P_{max}$  show the linear and distorted linear curves from  $Pd_{40}Cu_{30}Ni_{10}P_{20}$  and Vit-1 BMGs, respectively. Reproduced with permission.<sup>[325]</sup> Copyright 2016, AIP Publishing.

at the same indenter penetration depth (Figure 32b). The rise in current was attributed to a rapid increase in  $A_c$  by neglecting the other possibilities such as loss of contact (current drops to zero, but not in this case) and change in the material's resistivity ( $Pd_{40}Cu_{30}Ni_{10}P_{20}$  is a negative coefficient of resistivity material) due to temperature rise (too insignificant) in the shear band. Further, as the indenter penetrates through the sample, the shear

band nucleates at the surface of the contact (Figure 32c). The observed pile-up was also considered to be due to the shear band's nucleation at the free surface.

When the indenter tip reaches the shear offset, the ECR instantaneously drops and results in a surge in current simultaneously with a pop-in event. On plotting, *I*, as a function of the calibrated  $A_c$  function, the slope gives the  $\rho$  of the sample. Thus,

the area of the shear band offset can be calculated. Therefore, the shear band area calculated from the serrations in *I* can be used to adjust the effective  $A_c$ , which is vital in the effective calculation of the mechanical properties of the material. From the plot of shear band offset areas estimated with the geometrical method and nanoECR measurement (Figure 32d), it was observed that both techniques show the same trend. Thus, the reason for serrations in *I* was confirmed to be due to the sudden increase of the  $A_c$  at the shear band offset.

The nano-ECR technique was also proved to be useful in calculating the effective  $A_c$ . The summation of the shear band offset area with the calibrated effective  $A_c$  gives the true effective  $A_c$ . From these area measurements, the plastic strain contributed by the shear band can be calculated using  $\epsilon_{\rm sb} = \sum \Delta A_{\rm sb} / \sum \Delta A_{\rm c}$ , where  $\Delta A_{\rm sb}$  is the shear band offset area and  $\Delta A_{\rm c}$  is the calibrated effective  $A_{\rm c}$ .

However, nano-ECR with the conductive tip can only be used for the Ohmic materials. To prove that, the *I*–*V* curves of Pd-based BMG and Zr-BMG (Zr<sub>41.25</sub>Ti<sub>13.75</sub>Cu<sub>12.5</sub>Ni<sub>10</sub>Be<sub>22.5</sub>) Vit -1 obtained through nano-ECR measurements were compared (Figure 32e) and it was observed that the *I*–*V* curve of the Pdbased BMG was linear due to its Ohmic nature. Therefore, the change in current was related to  $\Delta A_{\rm sb}$  because  $\rho$  is constant. However, in the Zr-based BMG, nonlinear *I*–*V* curves were observed, indicating the Schottky barrier. Therefore, the authors concluded that although the serrations in the current would indicate shear band nucleation, the shear band offset area in the case of non-Ohmic materials cannot be measured through this method.

In contrast to the metals and crystalline materials, plasticity in metallic glasses is linked to the shear band formation and its propagation. Therefore, the primary things that affect the electrical measurements are the conductivity of the sample, surface roughness, friction between the indenter tip and sample, temperature rise in shear bands, contact area due to shear band formation, and propagation. Although a few metallic glasses (Pd-based) make Ohmic contact, a few form Schottky contact (Zr-based) with the conducting tip. Therefore, the nano-ECR technique can be effectively used for MGs that make Ohmic contact with the indenter tip. Though the authors neglected the change of resistivity with an increase in temperature in the shear band, Das et al.<sup>[322]</sup> observed a current drop during pop-in in a Pt-based BMG, which was attributed to a rise in resistivity with a temperature increase in the shear band. However, in this study, a decrease in resistance (a surge in current) at the pop-in was observed, probably due to the negative coefficient of resistivity (i.e., resistance decreases with an increase in temperature). Unlike crystalline metallic materials (generally, positive coefficient of resistivity), amorphous metallic alloys show both positive and negative temperature coefficients of resistance. However, some reports say that the electrical resistivity of metallic glasses does not change much with temperature ( $\approx 10^{-4}$  K<sup>-1</sup>). Therefore, further systematic experiments on various BMGs (both positive and negative temperature coefficient of resistance) with nano-ECR can clarify this issue in detail. In addition, the scattering of electrons due to amorphous structure, the electron transport mechanism when the MFP matches with the order of interatomic spacing, and the plastic zone size dependence of the electron transport mechanism need to be investigated.

As discussed previously, it is observed that there is still ample scope for exploring nano-ECR on BMGs to understand their electromechanical behavior and electrical transport phenomena of amorphous alloys. For example, Yang et al.<sup>[326]</sup> used a micropillar compression method equipped with nano-ECR to unfold the stochastic inelastic deformation process in a Zr-based MG. The electrical measurements helped to understand how local inelasticity arises within the amorphous structure before yielding. They revealed that the short-lived inelastic events self-organize into subcritical events due to elastic coupling and compete to self-heal and sustain local damage.

#### 3.5. Piezoelectric (PE) and Ferroelectric (FE) Materials

The research community has been using piezoforce microscopy (PFM) and double-beam interferometry (DBI) techniques to characterize piezoelectric thin films. However, the complexity involved in the interpretation of PFM measurements due to the dynamic behavior of the cantilever detection system and its highly sensitive nature to the surface contamination and asperities further the need for advanced sample preparation for DBI measurement. Researchers used alternate techniques such as piezoelectric nanoindentation or in situ electrical contact resistance measurement and direct voltage generation during indentation using a conducting tip. A bottom electrode is the only requirement under the piezoelectric for the measurement. Further, the load applied in nanoindentation can vary from micronewton to newtons, which induces different modes of deformation beneath the rigid indenter (with a reasonably good volume) and allows one to understand the mechanical behavior in a better way. Of course, high-resolution, simultaneous acquisition of topography and piezoelectric response are advantages of PFM. Further, indentation coupled with electrical contact resistance measurement can be used in either direct (generation of electricity upon application of stress) and converse modes (generation of stress upon the application of an electric field). The constitutive equations of direct and converse piezoelectric effect are  $D = dT + \varepsilon E$  and  $X = M_c \sigma + dE$ , respectively. Here, the electrical displacement is *D*, the piezoelectric coefficient is *d*,  $\sigma$  is stress,  $\varepsilon$  is the permittivity of the material, *E* is an electric field, X is the strain, and  $M_c$  is the mechanical compliance<sup>[327]</sup> (usually represented with S, but we already defined the slope of the contact stiffness with S).

#### 3.5.1. Piezoelectric Nanoindentation

The intrinsic electro/magnetomechanical coupling properties and the complex domain structures of ferroelectric, ferromagnetic, and magnetoelectric composite materials result in significant nonlinearity and field dependence of deformation behavior during indentation.<sup>[328–331]</sup> Several researchers have made continuous efforts to develop a measurement method for piezoelectric materials using micro/nanoindentation.<sup>[332]</sup> The contact problem of a rigid circular punch against piezoelectric ceramic half space with axial polarization was the starting point of understanding. Using the Hankel integral, the equations for stress and electric displacement distribution on the polarization direction were derived.<sup>[333]</sup> Fan et al.<sup>[334]</sup> derived relationships between



material constant, stress, and elastic field distribution under elastic deformation.<sup>[334]</sup> They used a potential method to solve the of indentation on problem piezoelectric materials. Giannakopoulos Giannakopoulos. and Suresh. and Ramamurty and co-workers<sup>[335–337]</sup> provided general solutions for elastic indentation of polarized transversely isotropic piezoelectric solids within elasticity. Using conservation of linear momentum and Maxwell's electrostatic equation in cylindrical coordinates, constitutive equations were deduced. New electric boundary conditions were introduced considering the electric properties of indenters. Corresponding dual integral equations for piezoelectric indentation problems with mixed boundary conditions were derived using the Hankel transform/integral. The load, electric charge (macroscopic response), electric potential gradient, and stress distribution (microresponses) were calculated with factors derived from the material constants and geometry of the indenter.<sup>[335-337]</sup> A simplified expression for the profile of a deformed surface and the electrical potential, the electric field effect on the indenter displacement, field singularity, and orientation problems were reported by Liu and Yang.<sup>[338–341]</sup> Wang et al.<sup>[342]</sup> deduced semiempirical formulae that provide good estimates of the indentation responses for the two limiting cases of thin films and bulk (also those in between).<sup>[342]</sup> To solve the constitutive equations of frictionless and friction contact, Kalinin and co-workers and Makagon et al.<sup>[343–345]</sup> proposed new methods and analytical models based on potential theory and different from the Henkel integral and deduced four constants from the elastic tensor, piezoelectric tensor, and dielectric tensor. Also, the indentation response could be captured with the indenter's geometry shape and displacement. These relationships facilitated an analysis of imaging mechanisms of scanning probe microscopy on ferroelectric and piezoelectric materials. The relationships were further developed by considering frictional sliding to interpret various SPM techniques for ferroelectric surfaces.<sup>[343–345]</sup> Giannakopoulos displayed the microcontours of indentation stress and electric potential, and indentation stiffness was calculated using FEM for spherical indentation of various piezoelectric ceramics.<sup>[335]</sup> Later, Ramamurty and colleagues<sup>[346]</sup> showed contours of maximum principal tensile stress and electric potentials showing the difference between poled/unpoled piezoelectric materials and insulating/conducting indenters using FEM spherical indentation studies on transversely isotropic piezoelectric materials. The strength of poled lead zirconate titanate (PZT) was observed to be higher than that of unpoled PZT, and the fracture imitation was switched from Hertzian cracking to subsurface damage initiation after polarization. Suresh and co-workers, Giannakopoulos and co-workers, and Ramamurty and co-workers.<sup>[93,337,347]</sup> performed piezoelectric indentation on PZT and BaTiO<sub>3</sub> and compared the results with the analytical results, which gave related conclusions. However, the analytical model could not describe inelastic deformation (if the load exceeds a certain value) realized from the time-current curves collected from spherical and conical indenters.<sup>[93,337,347]</sup> In 2006. Kalinin and co-workers<sup>[348]</sup> performed nanoindentation experiments and addressed the electromechanical and pressureinduced dynamic phenomena in piezo/ferroelectric materials. They applied the electric potential on the indenter tip, and the backside of the piezoelectric sample and the harmonic



movement were tested. They presented the load dependence of the piezoresponse in single-crystal PZT and BaTiO<sub>3</sub>. Wong and Zeng<sup>[349]</sup> observed local damage and pile-up around the indenter at very low loads when indented on the poled and unpoled states of the Pb(Zn1/3Nb2/3)O3-6%PbTiO3 (PZN-6% PT) single crystal. In the last 20 years, several researchers have performed indentation experiments and developed analytical and FE models to understand the electromechanical properties of thin films and multilayers. The notable observations include the full recovery of PZT with weak hysteresis; however, strong in-plane clamping stress causes incomplete recovery,[350] high residual stress leads to polarization switching, and the domain wall improves the effective piezoelectric coefficient by 35%.<sup>[351]</sup> Cheng and Venkatesh<sup>[352,353]</sup> developed 3D FE models and analyzed the micro/nanoindentation responses of anisotropic piezoelectric materials with bulk, film, nanoisland, and nanowire geometries. They observed that the force/currentdepth curves fit the power law, and piezoelectric nanostructures with higher  $e_{33}$  and  $d_{33}$  have better electromechanical performance, and under appropriate boundary conditions the polarization direction of piezoelectric materials can be determined via analysis of nanoindentation responses. Further, they observed that the mechanical indentation stiffness was more influenced by the elastic properties (dominantly  $C_{33}$  and  $C_{13}$  for longitudinal indentation;  $C_{11}$  and  $C_{12}$  are for transverse), and the electrical indentation stiffness was influenced largely by the piezoelectric properties ( $C_{33}$  and  $e_{33}$ ) (for both insulating and conducting indenters). The percentage of increase in  $C_{33}$  results in the mechanical indentation stiffness increasing by the same percentage. However, the dielectric properties did not influence both the mechanical and electrical indentation stiffness. But  $C_{11}$  and  $C_{12}$ influence the mechanical indentation stiffness by 50% in the longitudinal direction. For an insulating indenter, the influence of  $C_{33}$  on the mechanical indentation stiffness was lower than on that of a conducting indenter.<sup>[353]</sup>

In another study, Cheng and Venkatesh<sup>[354]</sup> developed a 3D FE model to study the electric fields' influence on the anisotropic piezoelectric materials' indentation response. They demonstrated that the electric fields significantly influenced the electrical and mechanical indentation stiffnesses when the field direction was aligned  $||^{el}$  to the poling direction. Whereas the positive *E*-field tends to make the indented material mechanically stiffer, the negative field shows the opposite effect. The effect of *E*-field on the indentation stiffness is similar to the influence of residual stress on the mechanical stiffness (on nonpiezo material), where the compressive stress results in greater resistance to indentation. Further, they demonstrated that in-plane *E*-fields could be used during indentation to identify which domains have poled along specific in-plane directions.<sup>[349]</sup>

*Piezoelectric Contact Stiffness*: Although the Oliver–Pharr method<sup>[16]</sup> based on Hertzian contact mechanics is widely used in interpreting indentation data of nonpiezoelectric materials, in situ conductive indentation data analysis of FE and PE materials requires Hertzian contact mechanics to be extended to materials with strong electromechanical coupling. Kalinin and colleagues<sup>[343]</sup> have done lots of pioneering work in analyzing the problem of piezoelectric nanoindentation involving different geometry indenters. Moreover, the results were used to model

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and offer a quantitative interpretation of electromechanical SPMs on FE materials. Within the assumption of transverse isotropy and cylindrical indenter shape, they interrelated *P*, charge *Q*, indentation depth *h*, and tip potential,  $\psi_0$ 

$$P = \frac{2aC_1^*h}{\pi} + \frac{2aC_3^*\psi_0}{\pi} \quad \text{and} \quad Q = \frac{2aC_2^*h}{\pi} + \frac{2aC_4^*\psi_0}{\pi}$$
(45)

Under purely mechanical loading, the contact stiffness<sup>[134]</sup>

$$S = 2\left(\frac{C_1^*}{\pi}\right) \tag{46}$$

Here,  $C_1^*$  is the indentation elastic stiffness,  $C_3^*$  is the indentation piezocoefficient,  $C_4^*$  is the indentation dielectric constant, and *a* is the contact radius.  $C_1^*$  is a combination of elasticity, PE, and dielectric tensor components rather than just an elastic modulus.

It should be noted that the ratio of *S* to "*a*" is a sizeindependent constant (*S* varies linearly with *a*). These relations provide an extension of the corresponding results of Hertzian contact mechanics and continuum electrostatics to the transversely isotropic piezoelectric medium.<sup>[343]</sup> The  $C_1^*$  for the PE indentation problem is analogous to the  $E^*(=\frac{E}{1-\nu})$  for an isotropic material,  $\frac{C_1}{\pi} \leftrightarrow E^*$ .<sup>[16,355]</sup> Though these stiffness relations were derived for an axisymmetric indenter, using a small correction factor makes them work well even for nonaxisymmetric shapes.

The stiffness relations for an arbitrary indenter shape are given as

$$P = \frac{2}{\pi} \theta(h^{n+1}C_1^* + (n+1)h^n \psi_0 C_3^*) \text{ and}$$

$$Q = \frac{2}{\pi} \theta(-h^{n+1}C_3^* + (n+1)h^n \psi_0 C_4^*)$$
(47)

where h is the total indenter depth,  $\theta$  is a geometry factor  $(\theta = a, \theta = \frac{2}{3}R^{\frac{1}{2}}, \theta = \frac{1}{\pi}\text{Tan}\alpha)$  and  $(n = 0, n = \frac{1}{2}, \text{and } n = 1)$  for a flat indenter, spherical indenter, and conical indenter, respectively.

For spherical indentation, the stiffness relations are

$$P = \frac{4a^3 C_1^*}{3\pi R} + \frac{2aC_3^*\psi_0}{\pi} \text{ and } Q = -\frac{4a^3 C_3^*}{3\pi R} + \frac{2aC_4^*\psi_0}{\pi}$$
(48)

where  $h = \frac{a^2}{R}$ ,  $C_1^*$ ,  $C_3^*$ , and  $C_4^*$  are material-dependent constants. According to Equation (48), a single indentation piezocoefficient relates the *P* and  $\psi_0$ , and *Q* and *h*, similarly to the direct and inverse PE effect in the uniform field case.<sup>[356]</sup> From the *P* equation (Equation (48)), the relationship between *P* and *h* for zero tip bias  $\psi_0 = 0$  can be found as

$$h = \left(\frac{3\pi P}{4C_1^*}\right)^{\frac{2}{3}} R^{\frac{-1}{3}} \tag{49}$$

which is equivalent to the classical Hertzian indentation, where the reduced modulus,  $E^*$ , corresponds to the material constants for anisotropic piezoelectrics  $E^* \leftrightarrow \frac{C_1^*}{\pi}$ .<sup>[16,355]</sup>

For a flat contact  $(R \rightarrow \infty)$ , the second term in the *Q* equation (Equation (48)) relates the indenter charge to the contact area as

$$Q = \frac{2aC_4^*\psi_0}{\pi} \tag{50}$$

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which can be compared with the  $C = 4k\epsilon_0 a$ , the capacitance of the disc on the dielectric substrate, providing correspondence between  $k_{\text{eff}}$  (effective dielectric constant) and  $C_4^*$  as  $k_{\text{eff}} = \frac{C_4}{2\pi}$ . Therefore, the  $C_4^*$  is identified as the indentation dielectric constant (analogous to  $e_{33}$  in the planar case). The second term in the *P* equation (Equation (48)) and the first term in the *Q* equation (Equation (48)) describe the electroelastic coupling in the material; thus,  $C_3^*$  is identified as the indentation piezocoefficient (analogous to  $d_{33}$  in the planar case). In summary, for spherical indentation, the stiffness relations can be interpreted as the sum of elastic, electroelastic, and electrostatic contributions.

Nanoindentation Response of PE Materials: The indentation response of PE materials will be influenced by elastic, piezoelectric, and dielectric properties.<sup>[353]</sup> The constitutive relationships for PE materials exhibiting electromechanical (i.e., dielectric and elastic) properties are given by<sup>[357]</sup>

$$\boldsymbol{\sigma}_{ij} = \mathbf{C}_{ijkl}^{E} - \mathbf{e}_{ijk}E_k \quad \text{and} \quad \mathbf{D}_i = \mathbf{e}_{ikl}\varepsilon_{kl} + k_{ij}^{\varepsilon}E_j$$
(51)

The stress tensor is represented by  $\sigma$ , strain tensor by  $\varepsilon$ , *E* and **D** are the electric field and electric displacement vectors,  $\mathbf{C}^{E}$  is the elasticity tensor of C (at constant or E = 0),  $k^E$  is the permittivity sensor of *K* (at constant, or  $\varepsilon = 0$ ), and the piezoelectric coupling tensor is **e**.  $\sigma_{ii}$  (Equation (51)) has a total of 45 constants (21 elastic, 18 PE, and 6 permittivity (or dielectric)) that are independent of material properties. All these independent material properties can influence the nanoindentation response of an elastically anisotropic and PE active material.<sup>[353]</sup> Because of this complexity. the indentation responses were predicted using analytical models (for simple PE materials) and finite-element models (for complex materials). During the indentation process, for PE materials, depending on the electrical boundary conditions, the E-fields/ V generated or electric Q/I generated can be determined.<sup>[353]</sup> If the indentation direction is ||<sup>el</sup> to the poling direction, it is longitudinal indentation. Similarly, if the indentation direction is normal to the poling direction, it is transverse indentation. The relationships between P-h and Q-h for different geometry tips were predicted by the analytical models.<sup>[342]</sup> They are

$$P = \frac{4C_4 \tan \theta}{\pi} h^2; \quad Q = \frac{4C_5 \tan \theta}{\pi} h^2, \text{ for conical indentation}$$
(52)

where  $\theta$  is the apex angle,  $C_4$  and  $C_5$  are complex functions of the dielectric, elastic, and PE properties of the indented materials.

$$P = \frac{8}{3}C_4 R_2^1 h_2^3; \quad = \frac{8}{3}C_5 R_2^1 h_2^3, \text{ for spherical indentation}$$
(53)

where R is the radius of the indenter.

 $P = S_{\rm M} h^{\frac{3}{2}}$ ;  $= S_{\rm E} h^{\frac{3}{2}}$ , for spherical indentation, where  $S_{\rm M}$  and  $S_{\rm E}$  are mechanical and electrical indentation stiffness.

 $P = 4C_4a_0h$ ;  $= 4C_5a_0h$ , for flat indentation, where  $a_0$  is the width of a flat indenter.

In the coming section, we will see examples of how nano-ECR was used to understand the piezoelectric/ferroelectric behavior of materials.



#### 3.5.2. Stress-Induced Depolarization in FE Thin Films

The stability of the polarization state plays a vital role in PE and FE devices in terms of their reliability. Alguero et al.<sup>[358]</sup> utilized the nano-ECR technique to understand the stress-induced depolarization phenomenon in fine-grained ferroelectric Pb<sub>0.88</sub>La<sub>0.08</sub>TiO<sub>3</sub> thin films (mixed <001>, <100> orientations) of thickness 250 and 700 nm deposited on Pt/TiO<sub>2</sub>/Si substrates. Nanoindentation with a 100 µm radius WC-Co metallic spherical tip (as a top electrode) was used to pole the films locally, and the electric current intensity during the depolarization was measured. Even without poling the sample, the depolarization current intensity was measured as 2-4 pC, and confirmed that the spontaneous electric polarization or PE property existed in the film. Poling was done by a  $P_{\rm max}$  of 500 mN with a dP/dtof  $10 \text{ mN s}^{-1}$  and holding time 60 s at  $P_{\text{max}}$ . The poling field was square pulses of height  $150 \text{ kV cm}^{-1}$  and an f = 200 Hz, which was switched on before the application of mechanical load. This poling field was sufficient for 700 nm thickness but not for 250 nm thickness. The effect of positive and negative electric fields and the fields parallel and antiparallel to the direction of initial polarization were studied.

The loading and unloading processes were done in 30 steps with a holding time of 0.1 s at each step, and the current intensity on depolarization was studied (Figure 33a). It was observed that on negative poling, the current intensity increased with loading and reversed its sign-on unloading, which confirmed the presence of the PE contribution. The rise in current intensity upon loading rather than on unloading indicated depolarization during loading. The I<sub>intensity</sub> was increased even after 500 mN indicated unsaturated depolarization on negative poling. In contrast, in the positive poling case, a rise in current intensity was observed on loading, but the reversal of sign was not observed on unloading. Instead, the current intensity showed two maxima at 68 and 310 mN for the 700 nm film and 252 mN for the 250 nm film. It was observed that the current intensity on depolarization upon loading was higher in the case of positive poling rather than negative poling. The maxima in the curve indicate the point at which the rate of depolarization is maximum. It was assumed that if the depolarization was indicating the 90° domain wall motion, the maxima point indicates the threshold stress for such movement. It was concluded that the two maxima points for the thicker film were due to two different sets of domain walls resulting in two threshold stresses. As the substrate's planar stress also affects the domain wall motion, this effect was nearer the substrate rather than at the surface of the fine-grained film.

The relation between the electric charge and the indentation force is shown in Figure 33b. The depolarization charge was observed to be 8.2 and 17 pC for the 250 and 700 nm films, respectively, upon negative poling and -15.6 and -27.3 pC on positive poling. The absolute depolarization value with surface charge density was calculated by understanding the actual  $A_c$  (using *P*–*h* curves). Thus, the absolute depolarization value was calculated as 3.8 and 7.2  $\mu$ C cm<sup>-2</sup> for the 250 and 700 nm films, respectively, on negative poling, and 7.2 and 11.5  $\mu$ C cm<sup>-2</sup> on positive poling. It was concluded that the thicker films and positive poling have a larger depolarization. This was confirmed by increasing the





**Figure 33.** a) Representative *I–P* curves obtained during conductive nanoindentation and b) *P–C* relation during an indentation test for Pb<sub>0.88</sub>La<sub>0.08</sub>TiO<sub>3</sub> films of two different thicknesses poled at different voltages. Reproduced with permission.<sup>[358]</sup> Copyright 2001, AIP Publishing.

electrical poling voltage to 200 and 250 kV cm<sup>-1</sup> for thinner films. A higher depolarization charge was observed in such cases. The uniformity of the depolarization current intensity was measured across the sample. Even though the forces and magnitude of maxima varied across the sample, the depolarization charge was confirmed throughout the sample.

With a large radius spherical tip, the authors showed the polarization and depolarization upon poling and depoling in Pb,  $La(TiO_3)$  films. The variations in maxima values were due to the higher spatial resolution of the technique, fluctuations





in the perovskite structure orientation, and stress at the filmsubstrate interface. It was observed that even with the load of 0.5 N being applied on the 250 nm thin film, the P-h curves showed fully elastic behavior, which ruled out the possibility of the formation of microcracks and onset of plastic deformation, probably due to the presence of only a hydrostatic stress field under the large-diameter indenter, which allows estimation of the surface charge density. However, the contact area contribution on the current increase with increasing penetration depth and the influence of surface asperities (particularly at very shallow depths) on the initial sharp rise of current were excluded from the analysis. The electric breakdown was observed at 300 kV cm<sup>-1</sup>. It would be interesting to perform nanoindentation (also in multicyclic mode) and modeling with varying loading rates, probe the geometry to understand the electromechanical behavior of films and particularly the influence of electric fields on the indentation response of anisotropic piezoelectric materials.

domain processes are different in bulk ceramics and thin films. Nanoindentation, together with the nano-ECR technique, helps to realize a local polarization state, domain processes as well as polarization stability in thin films under high mechanical pressure in real time. Thus, the FE properties of PZT (70 nm thick) and Mn-doped PZT thin films (700 nm thick) were studied by Koval et al.<sup>[351]</sup> using the in situ conductive nanoindentation technique. A WC–Co cermet spherical indenter of 500 µm nominal radius tip was used to study the applied field's effect on the electromechanical response by measuring the transients in electric current during loading and unloading. The experimental setup is shown in **Figure 34**a.

During nanoindentation, a  $P_{\text{max}}$  of 0.5 N was applied in 30 steps, with a dP/dt of 10 mN s<sup>-1</sup> and holding time of 0.1 s at each step. Unloading was also done in 30 steps, like loading. The equation governing the quasi-static charges (*Q*) and the current transients (*I*), when the force is applied in the direction of the poling field, is given by

## 3.5.3. FE, Ferroelastic (FES), and PE Response of PZT Thin Films

FE thin films, particularly PZT thin films, are extensively explored materials in the MEMS industry. The stress-induced

$$\Delta Q = d_{\rm eff} \Delta F \tag{54}$$

$$I = \frac{\Delta Q}{\Delta t} = I_{\rm P} + I_{\rm D}(F) \tag{55}$$



**Figure 34.** a) Schematic of the conductive nanoindentation setup. b) Magnified view of PZT films on Si substrate along with metallic layers and interfaces. The current transient–force curves for the 70 and 700 nm thick films of c) PZT and d) Mn-doped PZT (PMZT). The Q-P hysteresis loops of 70 and 700 nm thick films of the FE e) PZT and f) PMZT thin films. g) The change of Rayleigh parameters with varying *P*. The dependence of the  $d_{eff}$  on the *P* in the loading/unloading cycle for the 70 and 700 nm thick films for h) PZT and i) PMZT. Reproduced with permission.<sup>[351]</sup> Copyright 2005, AIP Publishing.

where  $d_{\text{eff}}$  is the effective piezoelectric coefficient, which includes intrinsic  $d_{\text{eff}}^{\text{in}}$  and extrinsic  $d_{\text{eff}}^{\text{ex}}$  factors.  $I_{\text{P}} = d_{\text{eff}}^{\text{in}} \frac{\Delta F}{\Delta t}$  is the intrinsic current contribution due to the piezoelectric effect and is dependent on loading and unloading rates and  $I_{\text{D}}$  is the extrinsic contribution due to the domain wall (DW) motion and is force-dependent. The  $d_{\text{eff}}$  is not equal to the  $d_{33}$  of the sample as it includes the substrate clamping effects and the effect of the elasto-electric field during spherical indentation.

**1DVANCED** 

The electric current transients developed when the *P* was applied  $||^{el}$  to the poling direction of 70 nm (1 L) and 700 nm (10 L) PZT and Mn-doped PZT thin films are shown in Figure 34c,d. In both cases, as the *P* increased, *I* also increased, and it was more profound in 10 L films. From Equation (55); if  $\frac{\Delta F}{\Delta t}$  is constant, the current transients observed are due to DW motion. Thus, the rise in current with *P* was attributed to the extrinsic contribution by 90<sup>0</sup> DW motion.

On unloading, it was observed that the transient current drops to zero for thinner films and not for 10 L films. Local negative maxima were observed at 150 mN in the case of 10 L films and not in the case of thinner films. Hence, the thickness dependence on current transients during unloading and asymmetric current curves during loading and unloading were attributed to the clamping stress in the plane of the film. In the case of Mn-doped PZT films, the observed rise in current transients was greater than that of PZT films. As doping barely affected the material's intrinsic properties, it was considered that the doped Mn ions softened the DW motion. It was also noted that the unpoled films also produced low-intensity current transients due to the PE effect.

The FES DW motion was confirmed from the nonlinear behavior and hysteresis within the stress range for 1 and 10 L films. (Figure 34e,f). The Q-P hysteresis loop during loading was analyzed using the Rayleigh relation to understand the effect of DW motion on electromechanical properties.

$$Q = d_{\rm init}F + \alpha F^2 \tag{56}$$

where  $d_{\text{init}}$  indicates the initial PE coefficient. The first linear term indicates the reversible component, and the quadratic term indicates the irreversible DW motion where  $\alpha$ , a measure of DW motion (irreversible), is independent of *P*. The ratio of  $\alpha F^2/d_{\text{init}}F + \alpha F^2$  gives the quantitative analysis of irreversible 90° DW motion (Figure 34g). It was observed that the major contribution in thicker films of both compositions was due to the reversible component, and irreversible displacement of 90° DWs was less than 15%–5%. From the Rayleigh graph and the *Q*–*P* loop graph of thicker films, it was realized that on unloading, the FES domains return to their original poling direction, confirmed by the recoverable nonlinear hysteresis in the *Q*–*P* loop.

In the case of 1 L films, on loading  $P_{\text{max}}$  of 500 mN load, the reversible component,  $d_{\text{init}}$ , the coefficient, was decreased after 250 mN to about 80% of its initial value. Also, the irreversible DW displacement had a higher contribution in the case of thinner films, which resulted in increased charge release with force (Figure 34e,f). Also, unloading thinner films resulted in a residual charge at the end of unloading. Even though the dependency of the thickness of the film on force may affect the properties measured, nanoindentation reduced the clamping stress, which was obvious in the increased force-induced charge due to

irreversible DW motion. The defect dipole reorientation, which was observed in doped films with defects, was also considered to affect the FES DW motion.

The effect of force on piezoelectricity was studied (Figure 34h,i). In the case of unpoled films, the initial piezoelectric coefficient before loading indicates self-polarization. As loading increased, the coefficient decreased and returned to zero on unloading, indicating complete depolarization. In contrast, in poled films, the polarization activity increased by about 35% due to the 90<sup>o</sup> DW motion. In thicker films, the clamping effects are less, and thus, the piezoelectric activity increases. In the case of unloading in poled films, the piezoelectric coefficient instantaneously dropped and increased to a different value than loading, indicating no mechanical depolarization took place during maximum loading.

Hence, DW motion induced by an indentation on loading and then switching back to the FE/FES domain on unloading resulted in a highly polarized domain state than that before indentation. The poled PZT and PMZT exhibited high resistivity under stress till 500 MPa, with no evidence of mechanical depolarization.

#### 3.5.4. Piezoelectricity in Sr-Doped PZT Thin Films

Sriram et al.<sup>[359]</sup> utilized the nano-ECR technique to study the inverse piezoelectric response of strontium-doped PZT thin films (see **Figure 35**a).

An inbuilt mapping software with the nanoindenter was utilized for positioning the metallic tip precisely for area scan and line scan to study the piezoelectric response. The peak-to-peak voltage of 10 and 32 V applied on the top of the Al electrode resulted in a peak-to-peak thickness variation of 4.34 and 13.97 nm, respectively. This was accompanied by the  $d_{33}$  measurement, which was 434 and 437 pm  $V^{-1}$ , respectively. Mapping over an area of  $80 \times 80 \,\mu\text{m}^2$  over the Al electrode showed areas (Figure 35b) with a high piezoelectric response with  $d_{33}$  varying from 458 to 608 pm V<sup>-1</sup>, with an average of 545 pm  $V^{-1}$ . Piezoelectric response on a line 1250  $\mu$ m, at intervals of 250 µm, showed (Figure 35c) that the piezoelectric effect was constant over the electrode area and decreased when the tip was moving away from the electrode area. To validate the method, a-SiO<sub>2</sub> was used in place of PSZT, and the  $d_{33}$  response was studied, which resulted in a nullifying reaction. Therefore, the thickness variation was confirmed to be due to the piezoelectric response of the film. The  $d_{33}$  magnitudes of PSZT were also measured using AFM to confirm the results, and the nano-ECR technique was proven to be successful in understanding the piezoelectric response of thin films.

#### 3.5.5. Energy Generation Characteristics of PE Thin Films

It is imperative to understand the influence of mechanical pressure on the voltage and current changes and the associated geometric parameters on PE materials for better design of devices. Bhaskaran et al.<sup>[9,360]</sup> utilized nanoindentation to study the in situ *V* and *I* generation of piezoelectric thin films and nanoislands. PSZT films of composition (Pb<sub>0.92</sub>Sr<sub>0.08</sub>)(Zr<sub>0.65</sub>Ti<sub>0.35</sub>)0<sub>3</sub> were deposited on metalized Si substrates. The voltage generated

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and the transient current generated during the nano-ECR measurements are shown in **Figure 36**. On increasing the *P* from 0.1 to 1 mN, the generated V was observed to be 4–23 mV. A linear relation between force and the generated voltage was observed (Figure 36a). On 200 and 400 nm nanoislands, the generated voltage was about 4 and 22 mV for 0.1 and 2.5 mN, respectively, in both cases. The same results were obtained for 700 nm PSZT thin films, thus confirming that planar geometry does not influence the generation of voltage.

The variation of current with the applied force (Figure 36b) showed an increase from 40 to 180 pA, indicating the dependence of geometry on the current generation. It was predicted that the increased current densities in nanoislands are due to the restricted geometry leading to a lack of surrounding material for the generated current leakage. The improved piezoelectricity in the films was attributed to the size-dependent flexoelectric effect (i.e., enhancement of the piezoelectric effect with increased strain gradients at nanoscale due to the size of nanostructures). Further, as the film thickness increased, the width of nanocolumns also increased, and greater grain size resulted in greater voltage generation.



**Figure 35.** a) Schematic of the conductive nanoindentation experimental setup to study the piezoelectric response of Sr-doped PZT films. b) Mapping of the PE response of a PSZT thin film for 32 V. c) Variations in piezoelectric response with distance from the top AI electrode for a peak voltage of 32 V. Reproduced with permission.<sup>[359]</sup> Copyright 2007, AIP Publishing.

**Figure 36.** a) As the force is increased, the voltage also increased in a similar fashion. b) The P-I-t curves show current transients under an applied load cycle. Reproduced with permission.<sup>[9]</sup> Copyright 2011, John Wiley and Sons.





#### 3.5.6. Large-Field-Induced Strain in Pb-Free PE Materials

The high morphotropic phase boundary (MPB) was observed to exhibit a high electromechanical response in piezoelectric materials.<sup>[361]</sup> This has led to the development of Pb-based perovskites and ceramics based on the MPB. However, the presence of Pb in these materials poses a health risk, which calls for the development of lead-free piezoelectric materials. Zhang et al.<sup>[361]</sup> observed a large electric-field-induced strain (over 5%) in BiFeO<sub>3</sub> (BFO) films due to the moving of boundaries between

the tetragonal-like (T) and rhombohedral-like (R) phase. The conductive AFM confirmed that the  $d_{33}$  of the R phase was 53 pm V<sup>-1</sup>, that of the T phase was 30 pm V<sup>-1</sup>, and for the mixed phase, it was 115 pm V<sup>-1</sup> (**Figure 37**).

To unveil the origin of the large strain in the BFO films, the authors carried out in situ TEM experiments coupled with electrical contact resistance measurement equipped with a BDD tip. Stripe-like features (Figure 38a), which indicate the mixed-phase structure, vanished completely upon applying an indentation force of  $30 \,\mu$ N. Figure 38b is due to the pressure-induced phase



**Figure 37.** a) The  $d_{33}$  versus *E*-field curves of T-like, R-like, and mixed-phase BFO thin films, grown by physical and chemical deposition methods (pulsed laser deposition (PLD) and chemical vapor deposition (CVD)), measured in capacitors with a diameter of 32 µm. b) The AFM image shows an *E*-field-induced PT between the mixed phase and T-phase. The mixed-phase to pure T-phase conversion, when subjected to a field of +1500 kV cm<sup>-1</sup>, is shown with a blue square area. The recovery of the mixed phase from the pure T-phase is represented by a red square upon application of  $-600 \text{ kV cm}^{-1}$ . c) The as-grown film across the PB; d) switched by a positive *E*-field (in  $0.5 \times 0.5 \text{ µm}^2$  area); and e) the same area poled by a negative electric field. The scale bar in all AFM images is 500 nm. f) The line scan across as-grown, switched, and recovered film regions. g) The variation of surface displacement with switching sequence. Reproduced with permission.<sup>[361]</sup> Copyright 2011, Springer Nature.





**Figure 38.** Bright-field (BF) TEM images a,c) before and b,d) after application of *P* and *E*-fields by the nanoindenter. The insets show SAD patterns indicating reversible phase transformations between the mixed and pure T-phase under the mechanical field and the *E*-field. Reproduced with permission.<sup>[361]</sup> Copyright 2011, Springer Nature.

transition to the pure R-phase. The selected area diffraction (SAD) patterns provide evidence for the reversible transformation upon removal of pressure. Such phase transformation was shown to be driven by the *E*-field also (Figure 38c,d). Interestingly, upon application of a *V* of up to +20 V, the reversible motion of the phase boundary was observed in real time (Figure 38d). In addition, the split spots of (011) were replaced by a single spot, and they reemerged upon returning to 0 V, indicating the reversible phase transition. Further, due to phase interconversion in an applied field, a large piezoresponse was observed, confirmed by the localized nanoscale switching dynamics analysis.

## 3.5.7. In Situ Multifield Nanoindentation

Multiferroic materials have unique properties, among which the ability to control nano/microelectromechanical properties under

the influence of an external *E*-field and magnetic fields is the most attractive one. Zhou et al.<sup>[362]</sup> developed a multifield nanoindentation apparatus (**Figure 39**a) to study the mechanical properties of materials in an electrostatic, magnetostatic, and electromagnetic field. The indentation *P*–*h* curves in the presence of electric, magnetic, and electromagnetic fields are shown in Figure 39b–e.

Instead of the nanoindentation apparatus equipped with nano-ECR, where only an electric field can be applied, this machine can apply simultaneous electric and magnetic (*M*) fields and measure the mechanical properties. The magnetic module consists of a permanent magnet (PM), soft magnetic (SM) materials, and a magnetic field measurement system (Gaussmeter with a Hall-effect magnetometer). In addition to the magnetic module, it has an electric module, a piezoelectric actuator, and load and displacement sensors. The *M*-field strength was varied by varying the distance between the N and S poles. Once the required *M*-field for the sample was achieved, the movement of the iron poles was switched off, and the *M*-field was kept stable.

The authors have shown the potential of the apparatus by performing experiments on a ferromagnetic (FM) Ni single crystal (Ni-SC), ferroelectric PMN-PT-SC, and a layered magnetoelectric (ME) composite La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>/PIN-PMN-PT and studied their electromechanical, magnetomechanical, and electromagnetic coupling properties, respectively.

In Ni-SC, due to the demagnetization state and the magnetic saturation level, the magnetic field strengths of 0 and 2000 Oe were applied. On applying the magnetic field, it was found that the *E* and *H* were reduced to 38% and -7%, respectively, which was attributed to the magnetic domain switching and domain evolution induced by stress and the external magnetic field, respectively. In the ferroelectric relaxor PMN-PT-SC, which was poled in the in-plane direction, DC voltages of 0 and 160 V were applied. The observed change in the unloading slope with the application of the electric field was attributed to the decrease in stiffness due to ferroelectric domain evolution and the motion of the phase boundary. The electric field influenced *E*, and *H* was found to be -33% and 22%, respectively. The study on the layered ME composite La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>/PIN-PMN-PT proves the potential of the multifield nanoindentation apparatus



**Figure 39.** a) Multifield nanoindentation was developed to study the effect of in situ electric, magnetic, and electromagnetic fields on multiferroic materials' mechanical behavior. b-e) The *P-h* curves of lanthanum strontium manganite (LSMO)/Pb( $In_{1/2}Nb_{1/2}O_3$ )-Pb( $Mg_{1/3}Nb_{2/3}O_3$ )-PbTiO<sub>3</sub>(PIN-PMN-PT) were obtained at b) no field, c) with a 750 V mm<sup>-1</sup> electric field, d) with a 2000 Oe magnetic field, and e) with both electric and magnetic fields of 750 V mm<sup>-1</sup> and 2000 Oe, respectively. Reproduced with permission.<sup>[362]</sup> Copyright 2013, AIP Publishing.



to reveal the electromagneto-mechanical properties of the sample. The sample consists of two parts, one, the magnetic layer LSMO, which was 350 nm thick and has strong electromagneticstructural coupling properties; second, the ferroelectric layer PIN-PMN-PT substrate, which was 0.4 mm thick. LSMO acted as the top electrode during the indentation experiments, and the voltage drop happened between the ferroelectric substrate. The electric field and the piezoelectric effect are sufficient to create the misfit strain between the magnetic and ferroelectric layers. Due to the electromagnetic coupling properties of the component layers, a significant change was evident in P-h curves in the presence and absence of the external field (Figure 39b-e). From the P-h curves, it was revealed that the external fields influenced the stiffness, irreversible energy loss, and indentation work of the sample. However, due to the high noise level during testing, this apparatus was efficient in measuring the electromagneto-mechanical behavior of only bulk samples but not of thin films.

# 3.5.8. Tunable Mechanical Properties of Relaxor FE Single Crystal Using an Electric Field

Zhou et al.<sup>[363]</sup> designed a multifield nanoindentation system through which *E*-field-tunable mechanical properties of a relaxor ferroelectric material (a tetragonal 0.62PMN-0.38PT crystal) were studied. The crystal poled with upward initial polarization direction (inset of Figure 40a) and 5 mm (l)  $\times$  5 mm (w)  $\times$  0.2 (t) mm pieces were cut along the thickness [001] direction. During the nanoindentation process, the applied voltage was in the range of -200 to +200 V. As shown in Figure 40a, with an increase in the electric field from negative to positive, it was observed that the  $h_{\text{max}}$  and final depth ( $h_{\text{f}}$ ) were decreased, and the indentation curves were influenced. Using the methodology proposed by Oliver and Pharr,<sup>[16]</sup> the *H*, stiffness (S = dP/dh), effective elastic modulus (E<sub>effective</sub>), and energy dissipation during indentation, and their variations to the electric field, were calculated (Figure 40b-e). The increase in H with an electric field (Figure 40b), decrease in dP/dh and  $E_{\text{effective}}$ , and energy dissipation with an increase in the amplitude of the electric field (Figure 40c-e) irrespective of its sign were clearly observed. From these observations and the linear fitting method, equations to establish the relationship between these physical quantities with electric fields were formulated.

The authors explained the process of domain switching with simultaneous mechanical loading and application of an electric field and proved the electrically tunable mechanical properties (**Figure 41**A(a)–D(d)). On applying the compression stress in the initial polarization direction, the domains switch to 90<sup>°</sup> in the in-plane direction, causing depolarization, whereas the positive voltage always tries to stabilize the initial polarization direction (Figure 41A,B). Thus, the competition between the mechanical stress and the electric voltage resulted in increased average stress and, thus, in increased *H*. In contrast, the negative voltage destabilizes the initial polarization direction and hence, results in decreased stress leading to decreased *H* (Figure 41A(a), B(b)). The work done by the negative voltage was irreversible, and the loading work was more in the case of negative voltage compared to positive.



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**Figure 40.** a) The *P*–*h* curves at various electric potentials. b–e) The electric-field- dependent (b) *H*; c) dP/dh; d) *E*<sub>effective</sub>; and (e) energy dissipation. Reproduced with permission.<sup>[363]</sup> Copyright 2014, AIP Publishing.

Similarly, from the unloading, *S* and  $E_{\text{effective}}$  were measured. The removal of mechanical compression resulted in the domain switching in the direction of the *E*-field, leading to an additional spontaneous strain with the elastic strain (Figure 41B(b),C(c)). Thus, a higher electric field resulted in larger second domain switching and stress, leading to a decrease in the  $E_{\text{effective}}$  and *S*. The same trend was followed in the dissipation energy as it was influenced by domain switching and reversible and irreversible work.

The electrical field tunable relationship from the linear fitting of the curve in Figure 41e is given as follows

$$\frac{H}{E_{\text{effective}}} = k(1-\eta) + l = -dkE + (k+l-k\eta_0)$$
(57)

where  $\eta$  is the energy dissipation, k and l are the fitting parameters, and d depends on the sign of the electric field. Hence, the equations for  $E_{\text{effective}}$  (effective modulus) and H were proposed as





**Figure 41.** A–D, a–d) Schematic representation of the domain switching process under the combined action of mechanical force and *E*-fields (+ve or –ve); and the corresponding potential well structures. e) *E*-field tunable scaling relationship among *H*, *E*, and indentation work. The solid triangles (black) are the experimental data obtained at various *E*-fields. Reproduced with permission.<sup>[363]</sup> Copyright 2014, AIP Publishing.

$$E_{\text{effective}} = \frac{[k(1-\eta)+l]\pi S^2}{4P_{\text{max}}} = \frac{[-dkE+(k+l-k\eta_0)\pi S^2]}{4P_{\text{max}}}$$
(58)

$$H = \frac{[k(1-\eta)+l]^2 \pi S^2}{4P_{\max}} = \frac{[-dkE + (k+l-k\eta_0)^2 \pi S^2]}{4P_{\max}}$$
(59)

where *S* is the stiffness. Through this method, the  $E_{\text{effective}}$ , *H*, and indentation work were calculated without the error of determining the actual  $A_c$  with the Oliver–Pharr method.<sup>[16]</sup>

The influence of the flexoelectric effect on mechanical properties was also studied. The previous studies proved that the influence of size on the elastic modulus was an aftereffect of the flexoelectric effect. Along with that, the authors proved that the elastic modulus varying with the electric field was also indicative of the flexoelectric effect. From the equation for the free energy of the ferroelectrics, it was proved that the difference between the domain switching during the mechanical unloading process in the presence of positive and the negative electric field was due to the flexoelectric coupling energy. It was also explained that when the electric field was applied in a direction opposing the initial polarization direction, the barrier to cause ferroelastic switching was less, and hence more domains were switched in case of positive voltage. Thus, during unloading, there were more ferroelastic domains to switch back in negative voltage, leading to more significant mechanical deformation.

## 3.5.9. Piezoelectricity in P(VDF-TrFE) Core-Shell (C-S) Structures

Choi et al.<sup>[364]</sup> utilized the nano-ECR technique to study the piezoelectric generation efficiency of poly(vinylidenefluoride-trifluoroethylene) (P(VDF-TrFE)) C-S micropillar structures. The platinum-coated polyurethane acrylate (PUA) micropillar (Young's modulus  $(Y) \approx 1.6$  GPa) was used as the core, and nanoscale thick P(VDF-TrFE) ( $Y \approx 1.5$  GPa) was deposited on top of the core as the shell, thus forming vertically aligned P(VDF-TrFE) C-S micropillars. The converse piezoelectric effect of the C-S micropillar was realized from obtaining the displacement of the micropillar as a function of applied V under stress. A conducting tip of diameter 8.3 µm was used to compress the micropillar of diameter 5.4 µm (Figure 42a). The converse piezoelectric effect (Figure 42b,c) was studied from the voltagedisplacement relation. A trapezoid load function was used with a peak load of 100 µN (Figure 42d). At 28.6 s, a voltage of 5 V was applied for 10 s to study the displacement change during the hold segment at  $P_{\text{max}}$ . At 100 µN, the displacement changes for the P(VDF-TrFE) film were measured as 0.2 and 0.37 nm for C-S micropillars. (Figure 42b).

The effective converse PE coefficient was calculated as  $d_{33}^{\text{eff}}$ 

$$d_{33}^{\text{eff}} = \frac{\text{displacement (pm)}}{\text{applied voltage (V)}} = \frac{\text{ds}}{\text{dV}}$$
(60)

 $d_{33}^{\rm eff}$  was measured as 40 ± 2 pm V<sup>-1</sup> for the P(VDF-TrFE) film and 74 ± 2 pm V<sup>-1</sup> for the C–S micropillar (Figure 42c).

To study the enhancement of the PE coefficient in C–S micropillars, the load was varied (200, 500, and 1000  $\mu$ N) on the micropillar, and the effective  $d_{33}$  was measured. It was observed that the PE coefficient varied from 76 ± 2 to 96 ± 5 pm V<sup>-1</sup>, and the PE coefficient exhibited by the C–S micropillar was 1.85 times larger than that of the films. The two reasons for the enhancement of the piezoelectric coefficient were considered as: 1) The total effective PE coefficient includes the contribution from both the core and the shell, which includes the sidewalls; 2) the geometric strain confinement (GSC) effect in P(VDF-TrFE) C–S micropillar structures. The charge generated by the shell was 0.0126 pC, which was four times greater than that of the core (0.0032 pC). Thus, it was proved that the vertically aligned





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**Figure 42.** a) Schematic of the in situ conductive nanoindentation on a P(VDF-TrFE) thin film and a C–S micropillar for studying converse PE effects. b) The change in the displacement (at 26.8 s) of the P(VDF-TrFE) film and the C–S micropillar at 5 V. c) The  $d_{33}$  of the P(VDF-TrFE) film and the C–S micropillar at 5 V. c) The  $d_{33}$  of the P(VDF-TrFE) film and the C–S micropillar. d) The applied *P* and *V* as a function of time. Reproduced under the terms of the CC BY 4.0 license.<sup>[364]</sup> Copyright 2015, Y. Y. Choi et al., Nature Research Journals.

P(VDF-TrFE) C–S micropillar structures could overcome the lack of stiffness in the P(VDF-TrFE) material.

#### 3.5.10. PE Response of $Sc_xAl_{1-x}N$ (0001) Thin Films

To understand the influence of growth conditions on the morphology and structure of PE thin films and improve their efficiency for application in sensors and actuators requires an in-depth understanding of their electromechanical properties. Žukauskaite et al.<sup>[365]</sup> demonstrated the direct and converse piezoelectric effects of wurtzite  $Sc_xAl_{1-x}N$  (0001) thin films using nano-ECR equipped with a conductive BDD Berkovich tip of resistivity 3  $\Omega$  cm, and the results were comparable with double beam interferometry (DBI) and piezoresponse force microscopy (PFM).

 $Sc_xAl_{1-x}N$  (0001) thin films of thickness 250–500 nm were deposited on an  $Al_2O_3$  substrate with TiN as the back electrode. Wurtzite AlN was considered as the reference sample, and Sc concentrations of x = 0.1, 0.2, and 0.3 were tested. In the case of direct PE measurement configuration (**Figure 43**a), loads in the range of 0.1–11 mN were applied, and the voltage generated was measured as a function of *P* and *h*, whereas in the converse effect (Figure 43b), a dc voltage of +40 V with a constant load of 10 µN was applied, and the displacement was measured. As shown in Figure 43c, with the load increasing from 0.002 to 11 mN, the generated peak voltage was also increasing up to x = 0.2. The experiments were repeated with multiple loading/unloading cycles, and the results were observed to be the

same, confirming that deformation during voltage generation was elastic.

The bowing behavior in curves was attributed to the local structural changes. It was confirmed that the generated voltage had increased by +10% for x = 0.1 and +15% for x = 0.2 on comparing with the reference sample (Figure 43e,f). On further increasing the Sc concentration, a decrease in voltage generation was observed, which was attributed to the degradation of the microstructure. From the results, it was confirmed that *E* and *H* also influence voltage generation. Hence, the complex strain produced in the sample by the indenter tip and the plastic deformation during direct measurement resulted in the insufficiency of the common elastic theory to calculate the piezoelectric coefficient; therefore, converse measurement was performed.

In the converse measurement, a voltage was applied, and the small displacement was measured under a low load (Figure 43g, h). The trend was the same as that of the direct measurement. With the application of +40 V, the displacement was increased up to x = 0.2 and decreased at x = 0.3. The results obtained from the converse piezoelectric measurements using nano-ECR were fast, reproducible, and more sensitive than the DBI and PFM.

#### 3.5.11. BaTiO<sub>3</sub> Nanoparticles in a Polymer Matrix: PE Response

The low electrical output is a common problem in particle– polymer composite nanogenerators due to electrical disconnection between the randomly dispersed nanoparticles and energy loss during traveling through highly insulating polymers.<sup>[366]</sup> www.advancedsciencenews.com

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**Figure 43.** Schematic of the in situ conductive nanoindentation setup to measure a) the direct and b) the converse piezoelectric effect. c) The solid gray line represents an applied load (in triangular loading/unloading function), and dotted curves represent generated voltage for  $Sc_xAl_{1-x}N$  films with *x* value varying from 0 to 0.3. at  $P_{max} = 11 \text{ mN}$ . d) The black dotted curve represents generated voltage and displacement curves in aluminum nitride (AIN) reference samples. The generated voltage for various  $Sc_xAl_{1-x}N$  films with *x* = 0.1, 0.2, 0.3 during a direct measurement with the application of e) load and f) displacement at different  $P_{max}$ . g) The voltage-dependent surface displacement changes in AIN and ScAIN films during PE nanoindentation. h) Relative PE response with varying Sc concentration in  $Sc_xAl_{1-x}N$  (0001) films (converse measurements). Reproduced with permission.<sup>[365]</sup> Copyright 2014, John Wiley and Sons.

The proper alignment of these particles together with a closer arrangement would result in shorter pathways for efficient energy transfer, and the stress-induced geometric structure will result in zero energy loss. Vertically aligned (200) cubic BaTiO<sub>3</sub> nanofibers in the poly(dimethylsiloxane) (PDMS) polymer matrix were shown to exhibit a higher piezoelectric response.<sup>[367]</sup> Therefore, the authors utilized a high-power electric field of  $32.5 \text{ kV cm}^{-1}$  to align the spherical BaTiO<sub>3</sub> nanoparticles vertically in the polymer matrix. The distinct transformation of (200) cubic BaTiO<sub>3</sub> under the given electric field caused the piezoresponse. Through various characterization techniques, it was confirmed that the BaTiO<sub>3</sub> nanopillars in the polymer matrix (A-BTOP) had a higher piezoelectric response (3 V and 650 nA) and improved transparency due to reduced light scattering than nonaligned BaTiO<sub>3</sub> particles in the polymer matrix (NA- BTOP) (0.6 V, 48 nA). When the electrical field was applied to randomly oriented BaTiO<sub>3</sub> spherical particles, they got polarized and

attracted to the oppositely charged longitudinal end of other spherical particles, thus forming a nanopillar inside the polymer matrix. These chains were sensitive to the mechanical bending motion, and they were touching the top and bottom of the PDMS matrix, and hence both the electrodes.

The nano-ECR technique was utilized to investigate how effectively the electron transfer happens and compare the electrical current generation in A-BTOP film and NA-BTOP films. A VC tip was utilized to measure the generated current (**Figure 44**a). The *P*–*h* curves recorded for both aligned and nonaligned films are shown in Figure 44b. From the *I*–*h* curve, in the case of the A-BTOP film, it was observed that the release of the load resulted in a sudden increase in current, and the generated output current was consistent at 0.08 nA (Figure 44c), whereas in the case of the NA-BTOP film, no change in output current was observed at this depth (Figure 44d). The sudden increase in the current was attributed to energy storage during loading and



(a)

(b) 1.5

Force (mN)

-13



Figure 44. a) Diagram of conductive nanoindentation setup for measuring the direct PE effect of a single BaTiO<sub>3</sub> agglomerate. b) P-h curves of aligned BTOP and nonaligned BTOP films. The insets show indented positions. c) I-h-t curve of the aligned BTOP film. The h-t function is represented by trapezoids. A sudden increase is evident during load release. d) I-h-t curve of the nonaligned BTOP film with no evidence of current rise. Reproduced with permission.<sup>[366]</sup> Copyright 2017, John Wiley and Sons.

4000

holding. As the BaTiO<sub>3</sub> nanopillars were located directly under the polymer matrix surface, it was predicted that the generated current could easily be transferred to the indenter tip.

1000

2000

Displacement (nm)

3000

## 3.5.12. Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> Film with Polarity-Dependent Resistance-Switching Property

The phase-change memory (PCM) devices suffer from two major drawbacks for their potential use. They are 1) device failure due to repeated switching, which results from the crystalline and amorphous phase density difference; 2) larger energy consumption due to the process of melting the crystalline bits and quenching into the amorphous phase by an intense pulse while writing. In this scenario, it was suggested that the polarity-dependent resistance (PDR) switching can overcome the problem. Therefore, Liu et al.<sup>[368]</sup> developed a Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> (GST) film with PDR switching property and studied the electromechanical properties using a corroded tungsten tip (5.32  $\Omega$  cm) attached to the nano-ECR measurement system. A force of 2 mN was applied continuously to ensure the consistent contact of the tip and the sample.

It was observed that the negative pulse resulted in reduced depth compared to the positive pulse, which was attributed to the ionic diffusion rather than the melting of the sample by an electrical pulse because Joule heating does not depend on the polarity (Figure 45). The bilayer effect (formation and extermination of bilayer defects) in the GST sample was identified as the reason for the PDR switching, which resulted in a volume change of 1.19% compared to the pristine GST sample.

In summary, it is realized that nano-ECR coupled with nanoindentation has been utilized very well to obtain a comprehensive understanding of the nanoindentation response of mostly isotropic and rarely anisotropic PE materials. Most of the studies were limited to observing piezoelectricity (either by the direct method or by the converse method) during indentation on PE materials,

understanding stress-induced depolarization in FE thin films, investigating the PE, FES, and FS response of various materials during indentation, unraveling the origin of large-field-induced strain in Pb-free PE material and electric-field-tuned mechanical properties of reflexor FE material. However, it is essential to keep more efforts to establish nano-ECR coupled with nanoindentation as an efficient technique to characterize piezoelectric, ferroelectric, and ferroelastic materials of different dimensions at different length scales. Experimental attempts should be made to understand the role of indenter geometry and the conductivity of the indenter on the response of anisotropic or isotropic PE materials. Further, the effects of surface asperities, loading and unloading rates, electric fields on the indentation response of PE materials and comparing the geometry-dependent indentation responses require more focus. It is observed from the aforementioned studies that the results were not linked to the nanoscale plasticity in PE materials because most of the authors used very large spherical indenters for being within the elastic region to avoid complexity in the analysis. As PE materials are being widely applied in energy-harvesting devices, the apriori prediction of electric current, mechanical properties, fracture, and fatigue using FE simulations will help to design better materials for next-generation device applications. Because of the complexity involved in such analysis, the commercially available models only deal with the elastic deformation of PE materials. Therefore, new elemental models and constitutive equations involving low-dimension effects and plasticity are required.

10

3 4

Time (s)

#### 3.6. Carbon Nanotubes (CNTs)

#### 3.6.1. Contact Behavior between Indenter Tip and CNT Turf: Time Dependence

CNT turfs are the new attraction in the electronic industry due to their higher electrical and thermal conductivities. Therefore, it is

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**Figure 45.** a) The variation of *h* as a function of *t* with changing polarity; b) a magnified view of (a), and the inset shows the voltage swept between -1.2 and +1.2 V as a function of time. Reproduced under the terms of the CC BY 4.0 license.<sup>[368]</sup> Copyright 2019, B. Liu et al., AIP Publishing LLC.

essential to know the mechanical properties in-depth, particularly the turf transfer, compression behavior, viscoelastic (VE)/ viscoplastic (VP) properties, and the time-dependent (TD) behavior. Qui et al.<sup>[369]</sup> made efforts to explain the mechanical properties of a vertically aligned CNT turf, particularly the elastic and adhesive properties, using nanoindentation. The *P*–*h* curves obtained from the nanoindentation experiments depend on the contact between the tip and the sample. The tip–sample adhesion, as well as the friction between them, altered the results. Along with this, in the case of the CNT turf, TD contact behavior was observed, which again altered the result. Thus, the authors explained the TD properties and the adhesive properties of the CNT turf with the help of depth-control nanoindentation coupled with nano-ECR and in situ TEM indentation.

CNT turfs of 100  $\mu$ m height and 200  $\mu$ m diameter were chosen for the experiment. A nanoindenter equipped with a Berkovich diamond tip was utilized to understand the tip–sample interaction. From the initial *P*–*h* curve, the negative load/pull-off load on unloading was observed, attributed to the adhesion between the sample and the tip. As the unloading rate increased, an increase in negative load was also observed. From the increase in *E* of the CNT turf up to 75% with an increase in the holding ADVANCED ENGINEERING MATERIALS www.aem-journal.com

time and constant  $A_c$ , it was predicted that the CNT turfs' stiffness was time-dependent. Two reasons were assumed for the increased stiffness on unloading: 1) More CNTs encounter the tip as the time increases, and therefore, a larger force will be required to retract the tip (could be either due to increased adhesion or tube–tube interaction); 2) the same number of tubes was in contact with the tip, but their adhesive force increases with time. To understand the underlying phenomena, the nano-ECR technique was used.

The current flow was measured upon applying a fixed voltage of 1 V. As shown in **Figure 46**a, an increase in the current was observed with increasing *h*, which was attributed to the increase in the  $A_c$  as well as an increase in the number of CNTs form to contact with the tip. However, during the holding time at the  $h_{\text{max}}$ , it was observed that the load decreased due to the turf creep, whereas the depth and the current remained constant. The constant current at  $h_{\text{max}}$  confirmed that a constant number of CNT channels were involved in electron transport between the Si substrate and the tip.

To study the mechanical response of the CNT turfs on compression, in situ TEM indentation was carried out (Figure 46b–e). The CNT turfs were transferred to a silicon wedge and the sample was compressed using a diamond tip to realize the tube–tube interaction (Figure 46b). The tubes were compressed to half their total length with a holding time (20 s), and the length and angle of tubes before and after releasing the tip were compared. The TEM images before, during, and after the compression show no difference in projected length and angle of tubes, and hence no slip or glide of the tubes was observed (Figure 46c–e).

Therefore, by combining the in situ TEM results with the nano-ECR results, the study confirmed that, with the increase in time, there was no increase in the number of CNTs encountering the tip; rather, the adhesion of tubes to the tip increased, which was attributed to the increase in the bonding of each tube with the tip. Hence, the number of CNTs in contact with the tip remained constant at constant displacement. The absence of sliding of tubes confirm that sliding is not the primary mechanism of viscoelastic behavior and time-dependent deformation during contact loading. Therefore, it was assumed that either the tubes or entanglement between the tubes could be the reason for the permanent deformation observed under contact loading.

# 3.6.2. Electromechanical Characteristics of a Cellular Assembly of CNTs

Entanglement of CNTs resulting in cellular assembly is a highly attractive area of research as they have huge potential in strain sensing as well as cellular foaming. There have been many studies on the local transport properties in individual CNTs using SEM, STM, and AFM. However, the underlying transport mechanism in CNT cellular assembly was not explored. Kiran et al.<sup>[370]</sup> utilized nano-ECR coupled with the nanoindentation technique to reveal the electromechanical properties of the cellular assembly of CNTs to understand the local transport properties of CNTs. CNT mats of  $\approx 2 \text{ mm}$  were indented with a BDD tip in the depth control mode. The indenter was penetrated to  $h_{\text{max}}$  of 500–2000 nm with dh/dt of 50 nm s<sup>-1</sup>. Initially, the voltage





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**Figure 46.** a) The *P*–*h*–*I* versus time curves obtained using in situ conductive nanoindentation on the CNT turf. At the hold segment, the current remained constant while the load relaxed. b) Schematic drawing of tip–CNT bundles interaction on a Si wedge. c–e) TEM images of CNTs before, during, and after the test. The measured distances and angles of tube contact remained the same before and after the test. Reproduced with permission.<sup>[369]</sup> Copyright 2011, IOP Publishing.

was kept constant at 2 V, and *P*–*I*–*h* was measured up to 500 nm depth. The *I*–V characteristics were measured by sweeping the voltage between -2 and +2 V for 2 s at  $h_{\text{max}}$ . The cellular assembly possesses both high density as well as porous regions and exhibits different electromechanical characteristics, as shown subsequently.

From the calculated *E*, it was observed that the *E* of the denser region  $(13.2 \pm 1.8 \text{ MPa})$  was two times higher than that of the porous region  $(6.8 \pm 2.7 \text{ MPa})$  (dense region  $= 0.47 \text{ g cm}^{-3}$ , porous  $= 0.26 \text{ g cm}^{-3}$ ). Further, the viscoelastic nature of the CNT assembly was identified from the hysteresis and the complete recovery on unloading. However, a negative load/pull-off load was observed during unloading due to the sample–tip interaction (van der Waals).

Similarly, from the *I*-*h* curves, it was observed that the current in the case of the denser region gradually increased, whereas it showed a negligible change in the case of the porous region (**Figure 47**b,c). In the denser region, at a fixed voltage of 2 V, the current increased to a maximum of  $9 \,\mu\text{A}$  at  $h_{\text{max}}$ . However, on unloading, the current decreased to  $3 \,\mu\text{A}$ (Figure 47b), which was attributed to the lesser compressive force during unloading and therefore a lesser number of current-conducting channels in contact with the tip. In the case of maximum loads  $\leq 4 \,\mu$ N obtained at the porous region, no significant change in current (before and after loading) was observed, whereas for the denser region ( $P_{\rm max} \leq 10 \,\mu$ N),  $\Delta I = 1.5 \,\mu$ A (Figure 47d). Though the current does increase with loading in both cases due to an increase in the  $A_c$ , the significant change in the current observed ( $\Delta I$ ) at the denser region was due to more CNT conducting channels crossing each other and forming tunnel barriers in the microstructure. Hence, it was confirmed that the density of the CNT assembly determines the transport properties.

A nonlinearity in the I-V curves was observed in the porous region, whereas in the case of the denser region, the initial nonlinearity at zero bias was changed to linear on increasing the voltages (**Figure 48**a,b). Nonlinear I-V curves indicate non-Ohmic contacts. Here, the nonlinearity was attributed to the complex electron transport through the metallic percolation path in the dense and porous region. Further, it was observed that the current in the case of the denser region was higher during forward bias (Figure 48a) than reverse bias, whereas for the porous region, it was observed to be vice versa (Figure 48b), which was attributed to the widening of the barrier and hence







**Figure 47.** a) SEM image showing the cellular structure of CNTs. The black circles represent structural porosity. P-I-h curves from b) the dense and c) the porous regions at a constant bias of 2 V. d) The difference in currents (at zero depth) before and after the test versus peak load shows a greater difference for the dense region than the porous region. Reproduced with permission.<sup>[370]</sup> Copyright 2013, IOP Publishing.



**Figure 48.** a,b) I-V curves measured between -2 and 2 V for dense and porous cellular CNT regions, respectively. The Ohmic response from the Cu reference sample is shown as the inset in (a). c) The dI/dV versus V plot shows the differential conductance behavior of pure Cu and the dense and porous regions of the sample. d) The log–log plot (for positive bias alone) of (c) for the dense region. The power-law fit to the data points is shown. The inset of (d) shows dI/dV versus V for the dense region for the negative bias. Reproduced with permission.<sup>[370]</sup> Copyright 2013, IOP Publishing.



confirmed the barriers across crossed CNTs. The initial nonlinearity observed in the case of the denser region was attributed to fewer surface contacts. The weak connections between the crossed CNTs were studied by analyzing the nonlinearity in the variation of differential conductance (dI/dV) versus V and compared with those of Cu, which showed complete Ohmic behavior (Figure 48c). The nonlinear curves refer to the non-Ohmic and tunneling property of CNT–CNT contacts. Further, in the case of the denser region, an asymmetric minimum of differential conductance was observed at zero voltage, whereas in the case of the porous region, zero conductivity was observed at zero bias, which was attributed to the electron– electron interaction and diffusive conductivity in the denser region as well as weaker contacts and in turn poor conductivity in the porous region.

The power-law behavior of dI/dV versus V on the log–log scale helped in understanding the mechanism of electron tunneling in the denser region (Figure 48d). It was predicted that when the electrons tunnel into the Luttinger liquid (LL) from the exterior cells of nanotubes, the conductance exhibits a power law. Here, in the denser region, the matching of the exponent (0.24)with the theoretical value during forward bias confirmed the bulk-bulk electron tunneling in the LL and, during reverse bias (0.60), confirming the end-end electron tunneling into the LL. Similarly, the resemblance of the exponent in the porous region (0.82) to the theoretical value was assumed to be due to the extrinsic defects in CNTs. The inverse relation between the number of conducting channels and the exponent confirmed the higher conductivity in the denser region compared to the porous region. The higher conductivity of the denser region above Cu during compression was attributed to more CNTs in contact and lowered the barrier to tunnel the charge carriers as compression increased. Thus, the electron transport mechanism in the denser region under compression was confirmed to be an end-end and bulk-bulk electron tunneling.

Similar work, but on arrays of vertically aligned CNTs (also known as turfs), was performed by Bahr and colleagues to study the mechanical and electrical properties using the nanoECR technique.<sup>[371]</sup> They found that although the elastic properties did not vary significantly, the electrical properties varied substantially within a turf due to the local contact behavior. In contrast to the aforementioned study, a decrease in electrical current with increasing contact area was observed for a penetration depth of 200 nm with strong adhesion of the CNTs to the tip at the beginning. The current values are of the order of  $10^{-8}$  A, probably due to either there being no electrical contact, bending of the tubes, or a very limited number of conducting channels for the current flow. However, with the depth increasing to 500 nm, the current started rising above 300 nm, indicating an increase in the contact area between the tip and the turf. At higher penetration depths, as expected, the current increased with increasing contact area. However, several current drops with increasing depth in the I-h curve indicate the contact formation and loss between the tip and the CNTs.

It is seen that the contact area largely determines the contact conductance between CNTs and the conducting tip.<sup>[372]</sup> It is also possible to form a Schottky contact if the CNTs contact the non-active (low-boron-doped) sites on the tip. This issue can be resolved to an extent if VC tips are used. Further, contact

resistance depends on the contact length for side contacts.<sup>[373-376]</sup> Furthermore, the work function, which is close to 3.9 eV for BDD, downshifts to 0.3 eV when applied to intense electric fields.<sup>[377,378]</sup> which can also influence the contact resistance. However, this is an unlikely cause for the nano-ECR measurements where the voltage can be a maximum of 10 V. In addition, a thin vacuum gap between the tip and carbon (if the cohesion is stronger) can affect the conducting properties. The contact resistance would go down if more CNTs made contact with the tip.<sup>[379,380]</sup> or even if the contact area is smaller. More importantly, the local chemical contamination on the CNTs (such as oxidation) acts as a tunnel barrier and is known to significantly vary the contact resistance. Furthermore, the contact resistance depends not only on the tip-CNT contact, but also on the CNT-CNT contact, chirality, angle between two CNT axes, and the force applied on the contact beneath the indenter. Interpreting which one of these parameters dictates the contact resistance through the nanoindentation coupled with nano-ECR experiment alone is quite difficult as many parameters vary at a time. Therefore, complementary modeling provides more insights into the contact conductance at the nanoscale, details on the individual contributions, and quantification of resistance terms.

#### 3.7. Polymers

# 3.7.1. Electromechanical Characterization of the Metal-Coated Polymer Particles

Micron-sized polymer sphere (MPS)-based conductive adhesives play an important role in electronic materials. MPSs come into action when they are compressed and are known for their low cost and high mechanical durability. However, their adhesive properties are closely related to mechanical properties such as fracture resulting from increased and prolonged stress. Hence, it is crucial to know the electromechanical characteristics of MPSs to reveal their ideal deformation range with minimum resistance and stable structure without fracture. Bazilchuk et al.<sup>[381]</sup> characterized MPS-based conductive adhesives electromechanically using flat punch nanoindentation coupled with the nano-ECR technique (**Figure 49**).

The experimental setup is shown in Figure 49a. The total measured resistance of the MPS particle was given by

$$R_{\text{measured}} = R_{\text{tip}} + R_{\text{contact tip-MPS}} + R_{\text{shell}} + R_{\text{contact MPS-substrate}} + R_{\text{substrate}}$$
(61)

The Määttanen model of the shell resistance was given by

$$R_{\rm shell} = \frac{\rho}{\pi t} \ln \tan \frac{\pi}{4} (2 - \varepsilon) \tag{62}$$

where *t* and *e* are the coating thickness and strain of the crosssection area of the deformed sphere, respectively. Therefore, it was confirmed that the shell resistance was independent of particle size, whereas  $R_{\rm tip}$  and  $R_{\rm substrate}$  were independent of the particle deformation.

Experiments were done on 10–100Ag (Figure 49b) ("10" indicates the core polymer diameter in micrometers and "100" indicates the coating thickness in nanometers, and Ag

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**Figure 49.** a) A schematic diagram showing the in situ conductive nanoindentation setup for measuring the electromechanical properties of MPS. The MPS particle b) before and c) after test. d) The *P* and *I* function for measuring the electromechanical properties of MPS. e) The variation of *R* and nominal strain as a function of indentation load and unload. f) The *R*-strain characteristics of 30–100Ag and 10–100Ag MPS particles. The inset shows a magnified view of the 30–100 Ag curve. g) The variation of *R*, at 10 mN load applied on 10 and 30 µm MPS particles, with different thicknesses. The *R* values were measured at 40% and 5% strain for 10 and 30 µm MPS particles. h,i) Comparison between *R*-strain characteristics of 10–200Ag and 10–200Ag and 10–200Ag and 30–270Ag. The particle–particle variability is represented by the error bars. j) Comparison between *R*-strain characteristics of 10–140Ag and 10–120Ni/30Au. Reproduced with permission.<sup>[381]</sup> Copyright 2016, AIP Publishing.

represents the metallization of coating) samples by applying load up to 12 mN with dP/dt of 2 mN s<sup>-1</sup> and holding time 2 s with a source current of 1 mA. (Figure 49d) The possibility of the influence of Joule heating was neglected with repeated experiments.

SEM before and after indentation is shown in Figure 49b,c, and the *R*, nominal strain versus force in Figure 49e. The resistance decreases with increasing *P* due to an increase in  $A_c$ . However, during unloading, the resistance increased



gradually due to the elastic recovery, keeping the tip and sample in contact.

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The effect of particle size on the electromechanical properties was studied by analyzing the resistance–strain behavior of 30–100Ag and 10–100Ag samples (Figure 49f). As the shell resistance was independent of particle size, it was concluded that the total resistance depends only on  $R_{\text{contact tip}-MPS}$  and  $R_{\text{contact MPS}-\text{substrate}}$ , which, in turn, depends on the  $A_{\text{c}}$ . The increase in the  $A_{\text{c}}$  was predicted to be the square of particle size. As the contact area increased, the resistance decreased, thus a low resistance observed in 30–100Ag sample at the very low strain compared to 10–100Ag sample. From Figure 49f, the high error bars at low strain indicate the initial deformation, where the nanocontact asperities play a dominant role.

Figure 49g shows the effect of coating thickness on the resistance of 10–XXAg, and 30–XXAg samples at maximum strain (to avoid the influence of nanocontact asperities). From Equation (62), the shell resistance is inversely proportional to the coating thickness. However, a deviation from ideal behavior was observed. When the thickness of the Ag film reduces below 52 nm (which is the MFP of bulk silver), higher resistance was observed. As discussed in the earlier sections,  $Holm^{[207]}$  showed that the contact resistance is a function of applied *P* and *H*. The hardness for a thicker metal shell increases in the contact region; therefore, the *P* required will be high for a given strain. This causes an increase in the contact area, therefore reducing the contact resistance.

Figure 49h,i shows that the resistance decreased with increasing coating thickness, and the higher resistance for thin coatings was attributed to the inhomogeneous surface with nanoscale asperities. The effect of metallization (i.e., Ag, Au, and Ni) was analyzed using the stress-strain measurements, which showed higher stiffness for the 10-120Ni/30Au samples than for the 10-140Ag sample due to the higher mechanical stiffness of Ni compared to Ag. However, on increasing the P, the pop-in in 10-120Ni/30Au indicates the brittle nature, and a further decrease in stiffness indicates the crack developed by the fracture. Nevertheless, the 10-140Ag sample exhibits the ductility of the Ag coating. The effect of metallization on the particleto-particle variation is shown in Figure 49j. At higher strain, the resistance of 10-140Ag becomes lower than 10-120Ni/ 30Au due to the lower resistance of bulk silver compared to bulk Ni and Au.

The authors explored all the possibilities that affect the electromechanical properties of MPS during conductive nanoindentation. The surface asperities and surface scattering<sup>[382]</sup> dominate the resistance measurements at lower shell thickness. Also, the metallization with different elements with different mechanical stiffness affects the contact resistance. Earlier results show that the experimental measurements of resistivity of epitaxial Ag films on mica fit well to Fuchs–Sonderheimer theory for electron scattering in thin films.<sup>[383]</sup> However, in this case, for MPS, the specular reflection of a large number of electrons dominates due to the Ag-conducting polymer interface being more conducive to a specular reflection of electrons than the metal-thin-film case.<sup>[384]</sup> The shear sliding of the MPS and friction during indentation can cause a change in the resistance measurement. The lateral expansion of the particle (which can cause a nonlinear increase of  $A_c$ ), the interface characteristics between the shell and polymer, pressure-induced electrical resistivity changes (due to rise in adiabatic temperature during indentation) within the metallic film, contamination-caused impurities in the coating, inhomogeneous surface, chemical composition, polymer cross-linking density, loading and unloading rates, particle sizes, and grain boundary scattering also affect the resistance measurement. The spreading resistance, which is higher for thin films, also contributes to the total resistance measurement. To understand the role of the polymer-metal shell interface on the contact conductance, an independent measurement on Ag particles alone and the polymer core alone and comparison with MPS would be helpful in decoupling the resistance terms. Further, analytical modeling, FEM studies, and MD simulations combining the elastic-plastic and viscoelastic nature of deformation can better explain the plastic and fracture behavior of the MFPs coated with nanoscale metals and the evolution of the contact resistance. Readers are suggested to read the original work by the authors to get more information on the experimentation and analysis.

## 4. Conclusion

We reviewed the development, methodology, models for quantifying resistance components and contact area, electron transport at different depth regimes, progress, and applications of in situ electrical contact resistance measurement coupled with the nanoindentation technique, which offers simultaneous quantitative electromechanical properties of electronic materials in numerous geometries and length scales (from nm to bulk). To the best of our knowledge, we have covered most of the research articles published so far that use nano-ECR coupled with nanoindentation in quantifying the electromechanical properties and providing insights into the nanoscale plasticity/indentation-induced deformation mechanisms of a wide variety of electronic materials, aiming to deliver a state-of-the-art review that helps researchers from multidisciplinary areas. After reviewing a good number of published articles, it is observed that the nano-ECR is a versatile tool that has aided researchers to investigate, understand, and quantify the electromechanical behavior/properties of materials in a quantitative, accurate, convenient, straightforward, and simple way, which otherwise may be impossible through conventional methods. Furthermore, it is a robust technique that can be used to indent soft, hard, and superhard materials with conductive rigid indenters of different geometries with forces ranging from micronewtons to several newtons, which may be difficult with AFM-based conductive indentation as the surface topography significantly influences the electrical properties<sup>[385]</sup> and with the limitations of force and displacement ranges. In addition, analysis of the electromechanical data obtained from the *P*–*I*–*h*, *R*–*h*, *I*–*V*, and *P*–*I*–*t* curves is relatively easy due to the availability of the well-established tip area calibration models for different tip geometries. Further, tests can be done to obtain the current-depth curves along with P-h curves by providing a fixed voltage to the conducting stage, which unravels the real-time mechanical deformation of the samples beneath the indenter, and I-V curves at any point on the P-h curve can be measured by varying the voltage anywhere between -10 and

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+10 V, which allows understanding the pre- and postdeformation characteristics of a material.

Though in situ nano-ECR coupled with nanoindentation was developed to detect pressure-induced phase transformation during loading and unloading in Si,<sup>[28]</sup> it is evident from Section 3 that this tool was used on most electronic materials with different dimensions such as other semiconductors, metal oxides/composites, metals/interfaces, piezoelectric and ferroelectric materials in bulk and thin-film form, amorphous metallic alloys, carbon nanotubes, fuel cells, photovoltaic cells, and polymers. With the help of this tool, several new insights were gained in the area of indentation-induced phase transformations, deformation mechanisms beneath the indenter, thin-film fracture, homogeneous nucleation of dislocations, self-healing mechanism in nanobelts, structural evolution in BMGs, deformation transients, tip-sample electrical contact characteristics, fatigue, diode characteristics, external-field-dependent mechanical behavior of materials, tunneling effects, piezo- and ferroelectric response in direct and converse methods, resistive switching, contact behavior between tip and CNTs, etc. We highlight a few observations subsequently.

The electromechanical characterization using nano-ECR coupled with nanoindentation is a versatile tool for providing an in-depth understanding of the small structural changes associated with nanoscale deformation and studying the mode of plastic deformation in semiconductors and nanosized samples of Si, GaAs, and InP crystals.<sup>[171,172]</sup> It has provided evidence for the self-healing mechanism of elastically and plastically nanodeformed ZnO belts by measuring the electric current on the damaged areas.<sup>[277]</sup> In addition, this technique helped researchers to analyze the time-dependent electrical-mechanical coupled behavior of individual nanomaterials such as ZnO nanorods, particularly the creep mechanism.<sup>[386]</sup> Further, it could manipulate the energy bandgap in 2D TMD and Os and aid in studying the charge transport mechanism and electromechanical properties of a complex system at the nanolevel, thus opening a window to broader applications in the field of electronics, optoelectronics, and NEMS.<sup>[196]</sup>

Further, the in situ conductive nanoindentation measurement technique assisted in calculating the quantum tunneling barrier height that leads to the quantum tunneling/percolation model of conductive nanocomposites such as nickel nanostrands to better understand the electronic properties,<sup>[289]</sup> aided to realize the electrical contact properties at the metal interfaces, particularly at NiCr/TiW films and Sn/SnO<sub>2</sub>/W structure,<sup>[296]</sup> detected the delamination process in quasi-static and oscillating dynamic experiments showing the simultaneous pop-in and the sudden drop in current were indicative of the delamination process in Ti<sub>x</sub>N<sub>y</sub> film,<sup>[306]</sup> and effectively characterized the MIM device (with conductive indenter as one contact) (Nb/Nb<sub>2</sub>O<sub>5</sub>/BDD tip) to understand the real-time asymmetry and nonlinearity behavior of the device.<sup>[308]</sup>

Furthermore, this versatile technique helped in unraveling the influence of substrate, indenter geometry, and pile-up formation, loading rate, and contact depth on the electromechanical properties of Pt thin films at elastic and plastic nanocontacts under various loads and  $A_{cr}^{[310]}$  understanding the dislocation dynamics (slip events), contact issues during slip in materials such as single-crystal Au columns, Si, Ni<sub>3</sub>Al, and Vit105 BMG, where

it could trace the slipping crystal without losing mechanical contact,<sup>[313]</sup> recognizing the localized strain field and lattice change around deformations and the effect of the electric field on plastic deformation in metals such as Al, Ti, and Ni,<sup>[321]</sup> explaining the electron scattering due to localized heating in shear bands,<sup>[322]</sup> and unravelling the electromechanical behavior of nanoporous metallic glass materials such as Pd-rich nanoporous metallic glass surface and the momentarily atomic-scale evolution under stress in BMGs such as  $Zr_{50}Cu_{40}Al_{10}$  and  $Pd_{40}Cu_{30}Ni_{10}P_{20}$  for improving the fatigue performance.<sup>[323–325]</sup>

In addition, nano-ECR coupled with the nanoindentation technique provided deep insights into the non-180° domain wall dynamics in lanthanum-modified lead titanate thin films and threshold stress for depolarization,<sup>[358]</sup> facilitated the study of the local polarization and stability of polarization in FE thin films such as PZT and Mn-doped PZT for the better design and fabrication of MEMS,<sup>[351]</sup> utilized the inverse PE effect to quantify the  $d_{33}$  of Sr-doped PZT and Sc<sub>x</sub>Al<sub>1-x</sub>N (0001) thin films without the need to go to the popular piezoelectric force microscopy (PFM),<sup>[359,365]</sup> and aided in confirming high electrical field induced strain of 5% in BFO films, which is higher than the conventional PE materials and comparable to SMAs. In addition, it provided an in-depth understanding of the real-time phase transformation behavior under pressure and electric field and assisted in unraveling the origin of such a phenomenon.<sup>[361]</sup>

Furthermore, the nano-ECR technique has shown its ability in identifying vertically aligned P(VDF-TrFE) C-S micropillar structures can overcome the lack of stiffness in P(VDF-TrFE) material and showed that the PE coefficient could be improved by 1.85 times in the case of the core-shell structure compared to films.<sup>[364]</sup> helped in understanding the time-dependent behavior of CNT turfs (nano-ECR coupled with TEM picoindenter) that revealed the adhesive interaction between the tip and the CNT turf.<sup>[369]</sup> and unraveled the mechanism of electron conduction in the cellular assembly of CNTs by identifying denser and porous regions, their viscoelastic nature as well as the identification of the presence of crossed CNTs under compression, their influence on the entire conduction mechanism, and the electron transport system inside a denser region.<sup>[370]</sup> The technique further revealed the range of resistances up to which the conductive adhesive property exists. The significance of the metallization of coating and particle size on mechanical durability of conductive adhesive was detected, therefore paving new pathways to the tuning of mechanical properties for a better adhesive property.<sup>[381]</sup> In addition to the electric field, the multifield nanoindentation showed immense potential in measuring the electric, magnetic, and electromagnetic coupling properties of the samples and their simultaneous influence on mechanical properties. Therefore, it opened a wide window to the design of new materials that can work on electric and magnetic fields.[362,363]

Although significant efforts have been made by researchers in improving the nano-ECR measurement system, development of highly conductive and rigid ceramic tips, and analytical models for data analysis, more studies (experimental, simulations, and modeling) are needed to develop an in-depth understanding of the electron conduction mechanism at the nanocontacts (e.g., metal–semiconductor and metal–oxide). Before forming a contact at the tip–sample interface, the detailed electron transport mechanism during initial contact and contact at different



depth regimes (i.e., ballistic and diffusive) must be explored to improve the understanding of the evolution of the contact resistance at the nanoscale. Furthermore, more studies are desirable to understand the effect of the native O<sub>2</sub> layer, surface topography, and tip imperfections (sharpness and roundness issues, etc.) on the nanoscale contact resistance measurement. Also, the tip shape (pyramidal, conospherical, flat punch, etc.) plays a vital role in quantifying materials' electromechanical properties. Therefore, the current line distribution at the tip-sample interface must be understood. Furthermore, the equipment limitations and the validity of the developed models are to be studied. For example, Equation (25) for quantification of resistance terms associated with a nanocontact was valid only for Ohmic contacts. Further, the Joule heating issues (due to the large current passing through the small contact areas of conductors) need to be investigated in detail. It is worth noting here that very recently, Volpi and co-workers<sup>[217]</sup> have addressed some of these issues with the help of custom-built ECR experiments using BDD tips, numerical modeling, and FE simulations. However, as the electrical contact conductance measurements depend on the resistivity of the tip, similar efforts are needed for improving the understanding of the contact conductance metallic/piezoelectric/metal-oxide/ characteristics between semiconductor samples and conducting ceramic tips (such as VC tips of different geometries) as these are known to have higher electrical conductivity than BDD tips, as discussed in the earlier sections.

It is realized that though there are a few ECR studies conducted on metals, some of them focused on quantification of individual resistive terms in the circuit, developing new models for calibrating/monitoring the contact area using electrical current measurement to avoid the Oliver-Pharr approach,<sup>[16]</sup> and a few of them focused on investigating the electrical contacts at the interface and the role of the native oxide on the contact conductance. But there are very few studies that correlate electrical conductivity to nanoscale plasticity. Most of the studies reported an increase in the electric current with increasing contact area. However, there is still scope for an in-depth understanding of nanoscale plasticity in metals through electrical current measurement by conducting nanoECR experiments, modeling, and simulations on different metals at various dimensions. For example, conductive tips with different geometries can be used on different metals with different crystal structures (FCC, BCC and HCP) to understand the physics of size-dependent dislocation-mediated plasticity and electromechanical behavior. Further, as the dislocations can only glide on certain types of crystallographic planes and in certain crystallographic directions, attempts can be made to use nano-ECR on various crystallographic faces to understand the slip-mediated plasticity and the role of the strain field around the indenter. Furthermore, metals with different extent of surface roughness can be created, and nano-ECR measurements can be recorded on them to understand the role of surface asperities to establish a relation between surface roughness and electrical contact conductance.

We also noticed that nano-ECR coupled with nanoindentation was used well on different materials with different dimensions but rarely utilized on devices. Therefore, this technique can be extended to test devices and characterize layered dichalcogenide materials, organic semiconductor crystals, charge transfer complexes, electrically conductive metal–organic frameworks, conducting polymers, metal-particle-filled polymers, polymer adhesives, etc. for their electromechanical properties.

We tried our best to cover most of the aspects of the nano-ECR characterization of a wide-range of materials covering both background physics and practical issues involved in the use of the equipment and interpretation of the experimental data. We hope that this comprehensive Review provides a reasonably good knowledge of the conductive nanoindentation, the combined electrical and mechanical properties of bulk and small-volume materials at the nanoscale and deep insights into the nanoscale contact mechanics that are essential for designing miniaturized smarter electromechanical devices.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# Keywords

electromechanical properties, in situ electromechanical characterization, mechanical deformation, nanoindentation, nanoscale electrical contact resistance, nanoscale plasticity

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