Recycling of Materials from Silicon Base Solar Cell Module

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***Abstract* — As the growing of photovoltaic (PV) industry, the environmental problems become a new consideration. Therefore, we propose a thermal method to recover materials, such as silicon, glass, and metal from conventional crystalline silicon modules. Two steps heating were used in the thermal treatment process in this study. During the thermal process, the EVA could be burned out and the whole glass plate could be obtained without breaking. The recycle glass could be directly used again as the module component when the temperature was well controlled. The recycle yield of silicon was 62% and the purity of obtained silicon material was ~8N after cleaning by chemical solution treatment. The copper could be recovered in further acid treatment. The recycle yield of copper was 85%. The results show that the recycling of materials from silicon based solar module is promising.**

***Index Terms* — silicon, recycle, module, solar cell.**

I. Introduction

Silicon is the most widely used material in photovoltaic (PV) industries for making solar panels that convert solar energy into electricity. In 2011, the global solar PV installations rise by 24% to reach 24 GW, up from 19 GW in 2010 [1]. Out of which, the majority was still silicon wafer-based solar cells. The PV modules are designed to generated clean, renewable energy without pollution and have a long lifetime over 20 years. Therefore the waste from used module and PV scrap will astonish growth after 25 to 30 years. It is important to develop a PV recycle process to solve the coming waste problem [2]-[3].

There was already a technique to recycle the CdTe modules [4]. The recycle process of CdTe modules includes crushing, chemical etching, glasses separating. The glasses could be used again by re-melting and the metallic materials, such as Cd and Te, were recover from the etching chemical solution. However the recycle of crystalline Si solar module still not universal because the difficult of EVA removing [5]. The EVA is a thermal-set polymer and can not be melting; therefore the residual choice is thermal cracking or chemical decomposition. During thermal cracking, the EVA could burn out but the glass plate usually breaks in the furnace. It makes difficult to separate the glass and residual solar cell. The chemical process takes time up to several days. Therefore, it is not a promising process to remove EVA [6]. Far now only the recycle of silicon material was promising. The chemical treatment process was already widely used to remove the cell structure, such as metal electrode and anti-refractive coating layer, on the silicon base solar cell and recycle the pure silicon materials [7].

II. Experimental

6-inch single-crystalline and multi-crystalline silicon wafers were used in this study. After solar cells were fabricated, solar cells were sealed individual as conventional solar module structure glass/EVA/cell/EVA/backsheet with 20cm (length) × 20cm (width). The backsheet material here we used was DuPont™ Tedlar®. Fig. 1 shows the solar module we used in this study. The solar module was heated in a furnace to separate each component with a varied temperature profiled. The glass was first recovered after thermal treatment. The ribbons were separated from solar cell surface and recover the inside copper by removing the lead/tin (Pb/Sn) alloy skin with acid etching. The cell structure (emitter layer and back side field layer) was further removed the by chemical treatment until clear silicon chips was got.

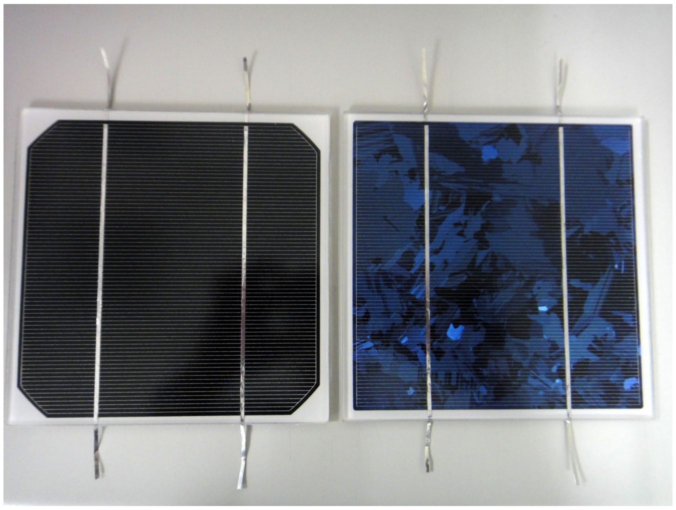

Fig. 1. Silicon solar modules used for the recycle process.

To evaluate the metal content in silicon, high resolution glow discharge mass spectrometry (GDMS, model VG9000) was carried out for bare wafer and recover silicon chip. To observe the differences of transmission between bare glass and recover glass, the UV/VIS spectrometer (Perkin Elmer Lambda 750S) was utilized.

III. Discussions

Two steps heating profile was used in the thermal treatment process. Tedlar was first separated from the solar module back surface in the first step heating at 330°C for 30 minutes. Then the second heating step was carried out for thermal burning out the EVA and Tedlar at 400°C for 120 minutes. The two steps heating was used for the purpose of recover the no-breaking glass plate. Tedlar have good thermal stability in the range of -73°C to 107°C and loss the strength at 260°C to 300°C. At 330°C EVA is not decomposed yet but Tedlar can be separated first from EVA (as shown in Fig. 2). Therefore during the thermal burning process at 400°C, the glass plate will not breaking due to the deforming of EVA and Tedlar. This makes the recycle process easier when there is no breaking glass. The recover glass plate is clear and complete, so it can be reused directly for solar module encapsulation.

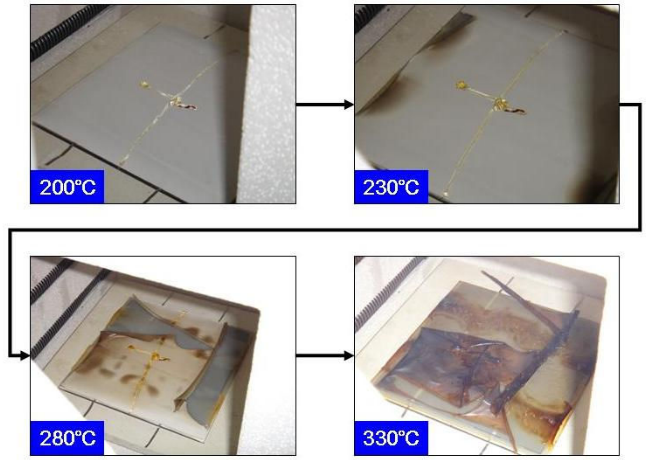

Fig. 2. The Tedlar was separated from EVA during first step heat treatment.

Fig. 3 shows the comparison of the transmission between original glass before used and recovered glass. The transmission from 400 μm to 700 μm was 86% because the surface of glass had roughening structure for the purpose of reduce the light refraction. The curve of recovered glass showed in Fig. 3 was very close to the original glass. It seems the temperature we used in thermal treatment process will not change the penetrability of glass, which was an important factor of glass.

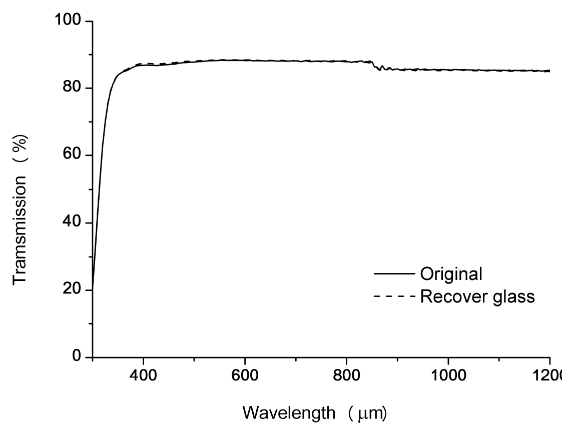

Fig. 3. The comparison of transmission of glass plate.

After the thermal treatment, solar cell chips were obtained. The solar cells were break because of the deforming of EVA. The acid and alkali were used in further chemical treatment process. There are three steps in chemical treatment process. First, the solar cell chips were dipping in $HCl/H_2O_2/H_2O$ = 1:1:5 solutions at 80°C to remove the Al electrode. Second, the 5% hydrofluoric acid was used to remove the SiNx anti-refracting coating layer and Ag contact. Finally, the 25% of NaOH was used to remove the p-n junction and back side field

(BSF) layer, which was form by the Si-Al alloy. Tables I show the impurities content in silicon bare wafer and recover silicon chips. The iron (Fe), nickel (Ni), copper (Cu), and titanium (Ti) were all below the detection limit of GDMS. Only the aluminum (Al) had been detected of 0.07 ppmw in the recycled silicon chips. Since the segregation coefficient of Al is as small as 0.0028, the Al impurities could be easy removed by directional solidification of crystal growth in the future.

TABLE I
IMPURITY CONTENT OF SILICON MATERIAL MEASURED BY GDMS (UNIT:PPMW)

Element	Concentration	
	Si bare wafer	Recycle chip
B	0.06	0.05
P	<0.01	0.07
Al	<0.01	0.07
Fe	<0.01	<0.01
Ni	<0.01	<0.01
Cu	<0.01	<0.01
Ti	<0.005	<0.005

The ribbons need further cleaning after the thermal treatment. The out surface of recycled ribbons is Pb/Sn alloy and need to be removed for recycling the copper inside, which is more expensive than Pb and Sn. The recycled ribbons were dipping in nitric acid and sulfuric acid to remove the Pb/Sn skin. Finally the clean Cu could be obtained (as shown in Fig. 2).

Table II shows the material yield of the recycle process. The recycle yield of glass is almost 100% because the glass was no breaking and kept complete as original. The recycle yield of silicon is 62%, which is base on the textured silicon weight inside the module. The 38% silicon loses during NaOH etching, which is using to remove the p-n junction and BSF layer. The Cu recovery yield is about 85% and the losing is due to the acid etching process for remove the Pb/Sn alloy.

TABLE II
RECYCLE YIELD OF SOLAR MODULE RECYCLE PROCESS

Process	Component	Weight (g)	Recycle yield
Begin	Module	263.28	
Thermal treatment	Glass plate	210.5	100%
	Cell chips	10.44	
	Ribbons	2.51	
Chemical treatment	Si chips	6.28	62%
	Copper	1.63	85%

The overall recycle process in this study was shown in Figure 4. The recycle of silicon based solar cell was different with the recycle process of CdTe soalr cell, which uses crushing as the first step. In this case, the module structure was separated by thermal treatment in first step. This will prevent the glass plate from breaking. Another advantage is the total process time of thermal treatment was shorter than chemical process, which needs several hours to several days [6]. In this case, the process time for decomposing the EVA and Tedlar was shorter than 3 hours. However the treatment of gassing was the problem of this recycle process. The burning of EVA and Tedlar produced heavy smokes, which were noxious and harmful, and the gassing can not be emitted into the air. Therefore, the treatment of wasting gas was important else the air pollution will become coming environment problem.

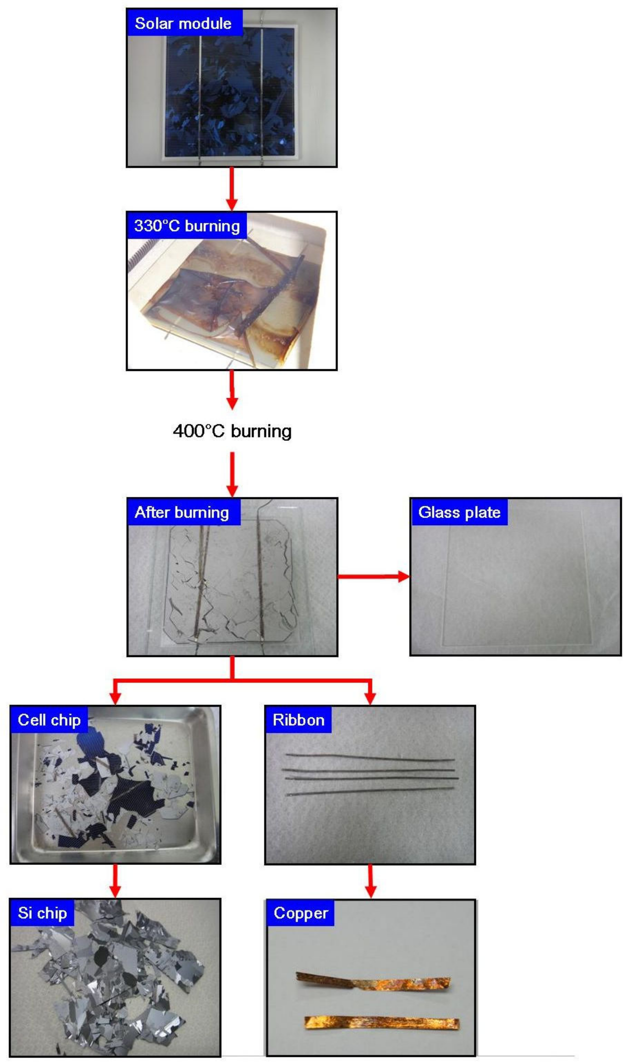

Fig. 4. Recycle process for solar module in this study.

IV. CONCLUSIONS

In this work, thermal treatment and chemical treatment were used to recycling the materials from silicon base solar module. Two steps heating were used in the thermal treatment process. The results showed that the glass plate could be recovered without breaking and could be directly used again as the module component when the temperature is well controlled. The silicon and Cu could be also recovered after chemical treatment. The recycling of materials from silicon based solar module is promising.

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