

A novel approach for recycling of kerf loss silicon from cutting slurry waste for solar cell applications

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ABSTRACT

A great challenge in recycling of silicon cutting kerf loss is the complete removal of silicon carbide particles. High-gravity centrifugation using a heavy medium with a specific gravity in between that of silicon carbide and silicon is not effective for the submicron particles. In this paper, a novel recycling process for obtaining silicon from the kerf loss powders is reported. The obtained silicon after directional solidification was found to be of solar grade. The average lifetime and resistivity of grown crystal were measured to be 1.02 μs and 0.7 $\Omega\text{ cm}$, respectively, which were close to the original sawing silicon and casted pure Si ingots. The energy conversion efficiencies of the solar cells fabricated from the recycled and pure silicon were found comparable.

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1. Introduction

The photovoltaic (PV) industry is going through a rapid growth. In 2006 alone, the global PV production was over 2 GW. The majority of PV cells are made of silicon, which is mainly produced from the energy-intensive Siemens process [1]. As per current status, the wafer shares more than 65% of the cost for solar cells, but on the other hand, more than 40% of the high-purity silicon is wasted during wafer slicing. The kerf silicon loss is in the form of slurry mixed with the cutting fluid and abrasive silicon carbide (SiC) particles, as well as the worn down metals from the saw wire. Although the kerf loss silicon particles remain in high purity, recycling them from the slurry waste for their reuse has not yet been successful [2]. The major challenges in recycling are the complete removal of SiC particles, which are generally higher in

content than silicon, as well as the metals, whose content is up to tens of thousands of ppm. Since, sizes of the particles are of micron or submicron order, the high-gravity centrifugation is not effective for their removal. Particularly, SiC is highly chemically inert and difficult to be washed away by acid solutions.

In the present work, the silicon slurry waste was obtained from the Chu-Nan's factory of the Sino-American silicon (SAS) products Inc., Taiwan. The slurry, which was produced from cutting of single-crystalline silicon ingot with resistivity in the range of 0.5–5 $\Omega\text{ cm}$, was pre-treated using a centrifuge in order to separate considerably larger SiC particles before arrival into our laboratory. This may be mentioned that before pre-treatment, SiC/Si volume ratio in the waste was ~ 3 which reduced to ~ 1 after the pre-treatment. The as-received slurry consists of 35 wt% SiC, 31 wt% lubricating oil (ethylene glycol), 6 wt% metals from cutting wire, 1 wt% glass from the ingot mounting stage, and 27 wt% kerf silicon fine particles of the order of micron size.

Here, we report a novel process for almost complete removal of impurity contents particularly SiC, hitherto impossible to remove, from the silicon slurry. We have compared the properties of recycled silicon with that of the pure silicon. Our findings show

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that the recycled silicon bears properties of solar grade silicon. This, in turn, establishes the developed process apt for recycling of silicon slurry from kerf loss for PV applications on commercial level.

2. Experimental procedure

The recycling of the as-obtained slurry was carried out using chemical/physical processing steps like chemical treatment, high-gravity centrifugation, high-temperature precipitation technique and directional solidification which are described in detail in the results and discussion part. The slurry was divided into four batches weighing about 550–600 g for the recycling and growth of silicon ingot.

Before recycling of the slurry, particle size measurement was carried out using static light scattering (Beckman, Coulter LS230). The content of SiC (<10.7 wt%) was measured in the powder of the raw material after high-gravity centrifugation using Horiba carbon/sulfur analyzer (Leco, model CS-244). We also carried out density measurement using automatic gas displacement pycnometer (AGDP) (Micromeritics, AccuPyc 1330) for reconfirmation and measurement of higher SiC content. The level of metal impurities in the slurry was measured before recycling process, during recycling process, and also after the crystal growth by a high-resolution glow discharge mass spectrometry (GDMS, Model VG9000). For the measurement, 2 g powder of the material before recycling and during recycling and blocks of size 5 mm × 10 mm × 20 mm, cut from the ingot, from each batch were sent to Shiva technologies, USA for the measurement. For quantitative evaluation of substitutional carbon in the grown ingot, FTIR (Nicolet Magna 550) was used. The carbon content was evaluated at 605 cm⁻¹ corresponding to absorption peak of substitutional carbon in the silicon lattice. For the measurement, vertically sliced crystal wafers of thickness 12 mm from each of the four ingots were used. The same wafers were used for the minority carrier lifetime mapping and resistivity measurement using wafer tester system (Semilab, model WT2000) and sheet resistance measuring system (Keithley, Model RT-70/RG-5), respectively. The measurement was carried out on the whole wafer surface.

For fabrication of solar cells, wafers were cut from the center of the grown ingot of the recycled silicon and pure casted silicon. Solar cells with a simple p–n junction without gettering and texturing were fabricated using wafers of size about 15 mm × 15 mm × 350 μm. A phosphorus-doped glass (Honeywell, USA) film was spin coated on the wafer and the n⁺ emitter layer was formed by rapid thermal diffusion at 850 °C for 1 min. The substrates were further etched by a buffered HF solution to remove the glass film from the surface. An antireflection coating of indium–tin oxide of thickness (~70 nm) was formed by sputtering on the wafer surfaces. Finally, the back surface field contact was formed by printing aluminum paste on the back surface and firing at 880 °C. The front metallization was found unnecessary for such small cells.

3. Results and discussion

Fig. 1 shows a typical particle size distribution of impurities in the slurry waste (inset). The major peak around 10 μm particle size is contributed by SiC particles, while the smaller peak is mainly due to Si, but SiC debris and metal powders also share this peak.

For recycling, the as-obtained slurry was first cleaned by using acetone to remove oil, and finally with nitric acid to dissolve the

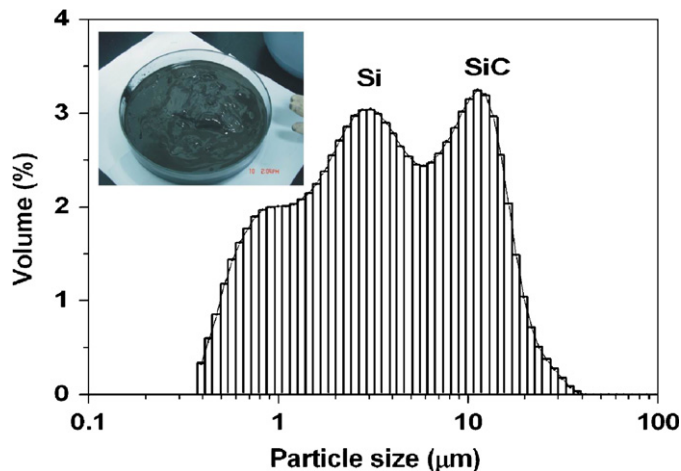


Fig. 1. Particle size distribution of Si and SiC in the as-received slurry. Photograph of as-received slurry shown in the inset.

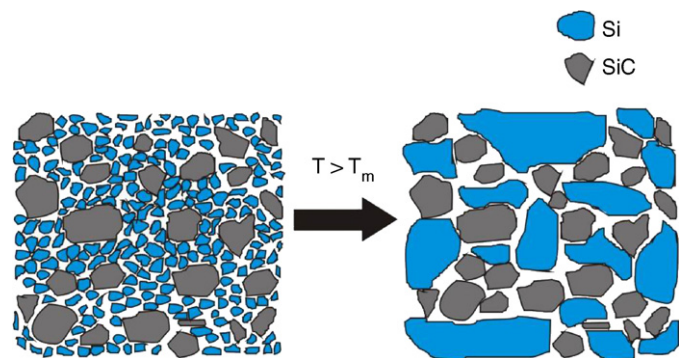


Fig. 2. Schematic illustration of silicon conglomeration during high-temperature treatment.

metal particles followed by centrifugation at 3300 rpm (2100G) for 60 min to remove the cleaning liquid. In order to reduce the content of SiC particles, a high-gravity centrifugation was carried out using a centrifuge. A heavy fluid with specific gravity between that of Si (2.33) and SiC (3.2) was added into the above-cleaned slurry and centrifuged at 3300 rpm (2100G) for 60 min. During centrifugation, SiC settles down to the bottom and Si floats on the liquid surface. The floating material, consisting of mainly Si, was taken out and cleaned with acetone and deionized (DI) water to get the raw material. The results obtained from Horiba carbon/sulfur analyzer and density measurement show that SiC concentration after high-gravity centrifugation in the raw material is still 7–15 wt%. In order to reduce the SiC content further, repeated high-gravity centrifugation was performed and concentration measurement was done using the above techniques. However, even after three times of centrifugation, SiC content remained almost same, i.e. about 10 wt% in the raw material. It is concluded that it is impossible to remove SiC particles completely from the slurry by centrifugation process only. It may be due to very small particle size of SiC remaining in the raw material. Therefore, in order to remove SiC content further, we have developed a new method of high temperature (HT) treatment.

For HT treatment, the Si/SiC powder was first palletized. The pellet was placed in a silicon nitride coated quartz crucible of inner diameter 46 mm and was subjected to the HT treatment at about 1470 °C for several hours in argon atmosphere using an induction furnace. Due to difference in the melting points of the constituents, Si started oozing out of the material in the form of

clusters during HT treatment. The formation of clusters is schematically shown in Fig. 2. Once the cluster formation was over, the material was cooled down. The silicon clusters and SiC could now be easily separated by simple water cleaning because Si clusters were non-adherent to the SiC particles. Fig. 3 shows the collected clean Si conglomerate after the HT treatment and water cleaning. Further, most of the other impurities were segregated towards the surface of the Si conglomerates during the cooling down stage. These impurities were washed away from the conglomerate skin using hydrofluoric acid. The silicon was further cleaned by DI water and used for crystal growth by directional solidification using a silicon nitride-coated quartz crucible.

During crystal growth, the crucible lowering speed was kept at 10 mm/h and temperature gradient was about 20 °C/cm. Ingot of 46 mm diameter and 30 mm height was grown from the recycled silicon using directional solidification. This is to mention that the directional solidification is also known to remove the impurities, including SiC, having low segregation coefficients and different melting points [3,4]. To verify the result, the wafers of grown ingot were inspected by SEM and no SiC particles were observed in the microstructure. This shows that the almost complete removal of SiC is achieved by the proposed process.

Further, the initial amount of slurry taken was ~500–600 g, as mentioned above, consisting ~135–162 g of silicon. After casting, silicon ingots weighing ~60–70 g were obtained. Thus, the overall yield of the recycled silicon was found to be ~45%.

Table 1 shows a typical GDMS result of the average values of the impurity in slurry at different stages of recycling. The results clearly show that most of the metal impurities except, iron, aluminum, calcium, magnesium and copper, were almost removed after the cleaning. The acid treatment was found to be effective in reducing the metallic impurities by a factor of around two or for some metals even more. Residual impurities were further reduced by HT treatment as shown in the table. But some impurities like iron, copper, chromium and aluminum were still present in the material well beyond their acceptable limits. Since the segregation coefficients of the iron, copper, chromium and aluminum are very small, i.e. 6.4×10^{-6} , 8×10^{-4} , 1.1×10^{-5} and 2.8×10^{-3} , respectively, these impurities could well be reduced to the acceptable limit after directional solidification. Other small impurities like Ni, Zn, Pd, Co, Ti, Ca, Mg were also removed to their values, well below the acceptable limit, for solar cell applications as shown in the table. But, the content of phosphorous was reduced to 1.1–1.7 ppmw only in the grown crystal by directional



Fig. 3. Photograph of cleaned silicon conglomerates after high-temperature treatment.

Table 1

Level of metal impurities measured by high-resolution glow discharge mass spectrometry (GDMS)

Element	Concentration (ppm w)			
	Original slurry	After acid treatment	After HT treatment	After directional solidification
Fe	3000	370	75	< 0.05
Ni	12	9	6.5	0.07
Cu	450	65	35	2.4
Zn	180	1.1	0.2	< 0.05
Pb	0.1	0.22	< 0.05	< 0.05
Cr	11	30	12	< 0.1
Al	37	100	35	< 0.05
Co	0.73	0.29	0.05	< 0.01
Ti	16	13	8	< 0.01
Ca	290	430	3.5	< 0.5
Mg	130	360	1.6	< 0.05
B	0.3	1.5	0.65	0.49
P	7.3	4.3	5.9	1.7

solidification. It is known that the complete removal of boron and phosphorous from the slurry is not possible either by chemical cleaning or by HT treatment, but they can be reduced only slightly through directional solidification because of their high segregation coefficient (0.35 and 0.8, respectively, for phosphorous and boron) [5–7]. The source of phosphorous content in the slurry was identified to be the glass mounting stage during wafer slicing, which contained about 2.4 wt% of phosphorous inside. Apparently, in the acid washing stages, the glass was not completely removed. It is believed that this problem can be avoided by replacing the mounting stage by graphite. Because of the existence of phosphorous, the grown ingot turned into *n*-type near the top portion of the crystal during growth because of the fact that the segregation coefficient of phosphorous is smaller than boron. Further, the table shows the average copper content to be 2.4 ppmw. The copper is well-known for killing carrier lifetime, as well as it quickly diffuses into the bulk. However, it is known that in directional solidification, impurity content varies along the length of the crystal being small at the beginning and more towards the end of the crystal growth. Therefore, copper content is expected to be within the acceptable limit for solar cell applications in the middle or lower part of the crystal.

The FTIR results show that the content of the substitutional carbon in the wafer of grown Si ingot is 4.86 ppma, which is well within the range (0.5–5 ppma) of acceptable limit for solar cell applications.

The resistivity was found to increase from 0.5 Ω cm at the bottom to 1.4 Ω cm at the center and then decreased again to 0.5 Ω cm at the top of ingot. The minority carrier lifetime was also found varying from 0.45 to 1.5 μs and decay again to 0.7 μs along the crystal growth. This may be attributed to the charge compensation as a result of the coexistence of phosphorous and boron. The average minority carrier lifetime and resistivity for the grown ingot of recycled silicon were found to be 1.02 μs and 0.7 Ω cm, respectively, while those of casted pure silicon were found to be 3.6 μs and 4.1 Ω cm. The lower resistivity and lifetime of recycled silicon ingot in comparison to the casted pure silicon may be due to phosphorous residues in the crystal.

Solar cells were made taking at least five wafers of size about 15 mm × 15 mm × 350 μm from each of the four grown Si ingots. Because of the impurities segregation, the solar cell energy transfer efficiency was found to vary according to the wafer position in the crystals being the lowest impurity in the wafer from the bottom of the ingot. The best energy conversion

efficiency (η) of the solar cells made from the recycled silicon was found to be 11.6% ($V_{oc} = 503$ mV and $J_{sc} = 37.2$ mA/cm²), which was comparable to that of casted pure Si ingot ($\eta = 11.3\%$, $V_{oc} = 513$ mV, $J_{sc} = 28.9$ mA/cm²). It may be mentioned that the solar cell fabrication process was not optimized therefore; efficiency of the fabricated cell was not so high. Further, the surface texturing and passivation were also not considered during the cell fabrication. Above results show that recycled silicon possesses properties of solar grade silicon and may be used for solar cell applications.

4. Conclusion

To summarize our results, the kerf loss silicon was successfully recycled by a novel process discussed above to obtain solar grade silicon. The overall yield of the recycled silicon was ~45%. Most of metal impurities in the slurry waste were removed by the recycling process. Most importantly, SiC particles were almost completely removed from the slurry by HT treatment which is reported for the first time herein. The average minority carrier lifetime and resistivity of the grown crystal were found to be slightly lower than those of original sawing Si and casted pure Si ingots. The efficiency of fabricated solar cell was found to be comparable with the one from the pure Si crystals. The recycling and characterization results show that the proposed process is apt

for recycling of kerf loss silicon. Further to add, the discussed process can be scaled up for the commercial production, but with certain limitations. During chemical/physical treatment, prolonged use of acid may have corrosive effect on the centrifuge surface. Therefore, use of Teflon made disk centrifuge may be used on commercial level.

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