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Recycling of silicon scraps by SiC absorption with Al addition in multicrystalline silicon

Shiqiang Qin[a,b], Pengting Li[a,b], Shuang Shi[a,b], Shutao Wen[a,b], Dachuan Jiang[a,b], Yi Tan[a,b,*]

[a] *School of Materials Science and Engineering, Dalian University of Technology, No. 2 Linggong Road, Ganjingzi District, Dalian, Liaoning Province 116023, China*
[b] *Key Laboratory for Solar Energy Photovoltaic System of Liaoning Province, Dalian 116023, China*

A R T I C L E I N F O

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A B S T R A C T

A new method for SiC elimination from multicrystalline silicon with Al addition by using the chemical reaction between Al and SiC is conducted in this study. Inclusion-free region is obtained when Al addition content increases to 5.4% and 7.9%. SiC particles tend to pile up around Al during the process and precipitate at ingot bottom. Furthermore, Al-Si alloying occurs at the inclusion-free region. The electron probe micro analysis mapping illustrates the existence of carbon in the precipitated Al which indicates the occurrence of chemical reaction between SiC particles and Al during the process. The results can be an effective way to eliminate SiC for silicon scraps recycling.

1. Introduction

The recycling of silicon scraps from solar-grade silicon refining industry is an urgent topic to be investigated since the numerous silicon wastes during the refining process in recent years. The aggregation of SiC inclusions on the top of the silicon ingot makes the certain region unavailable to be applied to produce silicon wafer. The existence of SiC becomes hard inclusions which can cause lattice distortion and Ohmic shunts in solar cells, which is very harmful to cell performance. It can also make the wire saw break down during silicon wafer sawing and even scrap the silicon ingot [1]. Therefore, the top part of the ingot has to be cut and become silicon scraps. If tons of these wastes can be recycled, it will tremendously save resources and reduce production costs.

In recent years, efforts have been made by researchers to separate SiC from silicon. Investigation of the SiC inclusions behavior in silicon with a variety of routes and methods are also conducted, such as electron beam melting [2,3] and electro-magnetic induction [4–6]. The electron beam and electro-magnetic can affect carbon migration during melt process due to the effect of the different physical properties between silicon and silicon carbide. Besides, separation of silicon and SiC from sawing waste is also conducted to recycling sawing wastes [7–10]. However, few chemical methods are considered to be applied in the recycling process.

In this paper, a new route is proposed to remove SiC inclusions from silicon by Al addition as a fact of the chemical reaction between Al and SiC under high temperature. The migration of SiC with Al addition during melt process is investigated.

2. Experimental

The raw material used in this study is multicrystalline silicon which has a content of 5% SiC inclusions embedded in it which has a size of 15 μm. They were washed with alcohol and cleaned in a supersonic wave cleaner to remove contamination and then dried sufficiently in a drying oven. 35 g inclusion-enriched silicon is put into four Al_2O_3 crucibles during melt process which has 2.8%, 4.1%, 5.4% and 7.9% addition of Al, respectively. A vacuum resistance-heated furnace which has a vacuum of lower than 5×10^{-3} Pa is applied to melt silicon with a holding time of 10 min at the temperature of 1450 °C and then with furnace cooling to room temperature. Four silicon ingots are obtained and the element distribution of the longitudinal sections is observed by electron probe micro analysis (EPMA) mapping analysis.

3. Results and discussion

Fig. 1 shows the macro morphology of the ingot longitudinal section after melt. Obvious SiC enrichment region is formed according to the morphology images. The enrichment region boundary is bumpy at ingot bottom with 2.8% Al addition as shown in Fig. 1(a). And there are also some enrichment regions that distribute sporadically. As Al addition increases, the enrichment part at ingot bottom becomes flat while it still exist enrichment regions at the other part. With Al addition increases to 5.4%, no SiC enrichment region is found except the ingot bottom. Finally with 7.9% Al addition, the precipitated SiC enrichment region

* Corresponding author at: School of Materials Science and Engineering, Dalian University of Technology, No. 2 Linggong Road, Ganjingzi District, Dalian, Liaoning Province 116023, China.
E-mail address: lnsolar@dlut.edu.cn (Y. Tan).

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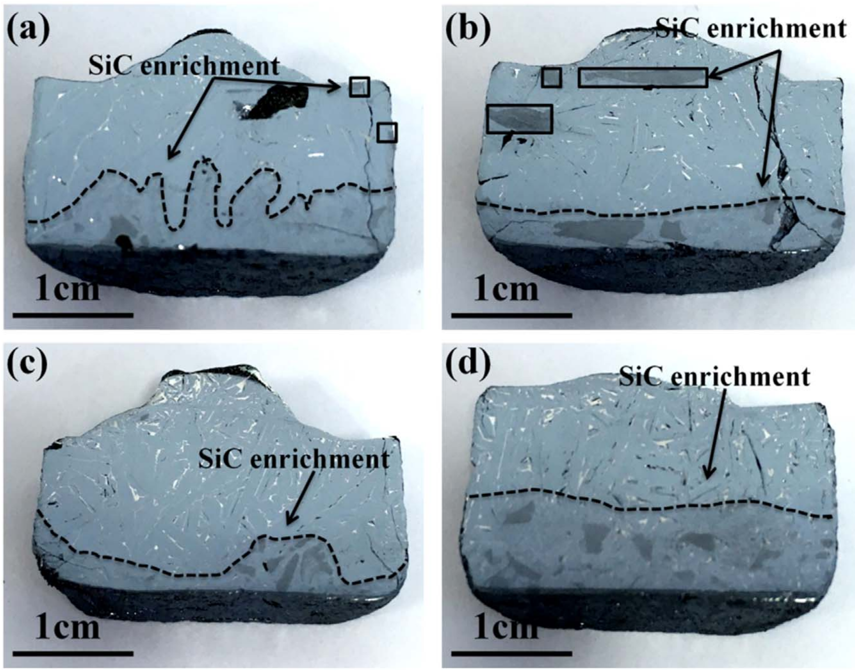

Fig. 1. Macro morphology of the silicon ingot longitudinal section after melt. (a) With 2.8% Al addition. (b) With 4.1% Al addition. (c) With 5.4% Al addition. (d) With 7.9% Al addition.

account for nearly 50% of the longitudinal section with a flat interface. For the non-enrichment region, obvious Al-Si alloying phenomenon occurs, and the alloying extent increases with the increasing Al addition.

The electron probe micro analysis mapping of the silicon ingot top of the longitudinal section is conducted to further investigate element distribution as shown in Fig. 2. The mapping clearly illustrates that Al-Si alloying phenomenon occurs during melt and the extent increases with the increasing of Al addition. Furthermore, Al precipitate at grain boundary and carbon precipitate along with it. It is a common chemical reaction that SiC particles react with Al and produce Al_4C_3 during fabrication of Al matrix composites reinforced with SiC particles according to the following reaction [11]:

$$4Al+3SiC \rightarrow Al_4C_3+3Si$$

It was reported that this reaction would proceed at temperatures above 850 °C [12]. And the melt temperature 1450 °C is much higher than that. When silicon is melted at the melt point, the SiC particles inside the melt will react with Al. SiC is consumed continually until Al reacts completely. After reaction, Si precipitates inside Al to form eutectic silicon when the solidification process begins. And more primary Si is generated since more Si-Al melt exists during cooling process with more Al addition.

The enlarged Al-Si alloy region of the ingot upper part is shown in Fig. 3. The black phase in the Al-Si alloy is found to be Al-C binary phase and SiC as shown in Table 1, and SiC phase size is much smaller than raw particle which is about 15 µm. It can be indicated that the reaction of Al and SiC performed in Al melt after wetting.

From the Al-Si binary diagram shown in Fig. 4, the solidification status of Al-Si hypereutectic is explained as following:

I.The precipitation of primary Si ($T_{liquidus}$-$T_{eutectic}$): The supersaturated Si precipitated as primary phase, the process can be presented as follows:

$$L \rightarrow L_1+Si$$

As the segregation coefficient of C $k(C) < 1$, the free C during Al and SiC reaction will segregate to Si-Al alloy rather than Si solid phase. As the reaction consume Al, the rest liquid Al during solidification is calculated as 2.4% , 2.7% , 2.6% and 6.1%, respectively. The contents of 2.4% and 6.1% are used to calculate the content of primary Si *ω(Si)* and the rest liquid phase *ω(L)*. The solidification routes are shown in the binary diagram which are A-B-C-D and A′-B′-C′-D′ correspond to 2.4% and 6.1% Al contents.

For the content of 93.9%Si-Al alloy:

$$\omega(Si) = \frac{FC}{FG} = \frac{93.9\% - 12.2\%}{100\% - 12.2\%} = 93.1\%$$

$$\omega(L) = \frac{CG}{FG} = \frac{100\% - 93.9\%}{100\% - 12.2\%} = 6.9\%$$

For the content of 97.6%Si-Al alloy:

$$\omega'(Si) = \frac{FC'}{FG} = \frac{97.6\% - 12.2\%}{100\% - 12.2\%} = 97.3\%$$

$$\omega'(L) = \frac{C'G}{FG} = \frac{100\% - 97.6\%}{100\% - 12.2\%} = 2.7\%$$

II. Si-Al eutectic reaction ($T_{eutectic}$ = 850 K): When the temperature reaches to 850 K, the rest liquid will have the eutectic reaction. The eutectic Si precipitated from liquid L_1, the reaction formula is shown as follows:

$$L_1 \rightarrow Al_{eut}+Si_{eut}$$

A process of liquid-solid transformation will occur, so the segregation of free C between eutectic Si and L_1 can occur. As the segregation coefficient of C is less than 1,it will precipitated to liquid rather than eutectic Si. The calculated contents of eutectic Si and Al is as follows:

For the content of 93.9%Si-Al alloy:

$$\omega(Al_{eut}) = 6.9\% \times \frac{FG}{EG} = 6.9\% \times \frac{100\% - 12.2\%}{100\% - 1.65\%} = 6.2\%$$

$$\omega(Si_{eut}) = 6.9\% \times \frac{EF}{EG} = 6.9\% \times \frac{12.2\% - 1.65\%}{100\% - 1.65\%} = 0.74\%$$

For the content of 97.6%Si-Al alloy:

$$\omega(Al_{eut}) = 2.7\% \times \frac{FG}{EG} = 2.7\% \times \frac{100\% - 12.2\%}{100\% - 1.65\%} = 2.4\%$$

$$\omega(Si_{eut}) = 2.7\% \times \frac{EF}{EG} = 2.7\% \times \frac{12.2\% - 1.65\%}{100\% - 1.65\%} = 0.29\%$$

III. Solid Si-Al phase solidification ($T_{eutectic}$- T_{room}): After eutectic reaction, no liquid exists. When the alloy solidified to room