Materials Science in Semiconductor Processing 53 (2016) 1–7

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

# SiC sedimentation and carbon migration in mc-Si by election beam melting with slow cooling pattern

Shiqiang Qin [a,b], Dachuan Jiang [a,b], Pengting Li [a,b], Shuang Shi [a,b], Xiaoliang Guo [c], Guangye An [c], Yi Tan [a,b,*]

[a] School of Materials Science and Engineering, Dalian University of Technology, Dalian 116023, China
[b] Key Laboratory for Solar Energy Photovoltaic System of Liaoning Province, Dalian 116023, China
[c] New Energy Materials and Technology Institute Co., Ltd. of Dalian University of Technology (Qingdao), Qingdao 266000, China

ARTICLE INFO

*Article history:*
Received 29 February 2016
Received in revised form
20 May 2016
Accepted 3 June 2016
Available online 9 June 2016

*Keywords:*
Silicon carbide
Silicon
Solar energy material
Electron beam melting

ABSTRACT

The development of photovoltaic industry demands great amount of multicrystalline silicon. Carbon and SiC in silicon need to be contained in a limited amount since they can cause great adverse affect to solar cells. The behavior of carbon and its precipitation SiC in silicon by electron beam melting (EBM) with a slow cooling pattern was investigated in this study. SiC is found to sedimentate to ingot bottom after EBM. The presence of $Si_3N_4$ can be heterogeneous nucleation agent for SiC to nucleate continually and both of them precipitate to the ingot bottom. The comprehensive effect of slow solidification condition, temperature gradient and melt convection causes the sedimentation of SiC. It is also found that oxygen plays an important role on the migration of the dissolved carbon. The formation of carbon-oxygen complexes tend to migrate to ingot top since oxygen can transfer from silicon melt to vacuum environment during EBM.



## 1. Introduction

The growing demand of solar-grade silicon is driven by the development of solar cells industry which can alleviate energy shortage. Silicon takes up most of the photovoltaic market as a commonly used raw material for solar cells [1]. Metallurgical method which focuses on removing impurities such as Fe, Al, Ca [2,3] and B, P [4,5] is proved to be an effective and energy-saving way to produce solar-grade silicon. In addition, the light element like C, N, O and their related impurities have lots of adverse effects on silicon quality [6,7]. During the directional solidification process which is one of the key links in metallurgical route, inclusions will segregate to the top of the ingot with metal impurities and then be cut off to obtain inclusion-free silicon. There are nearly 120,000 t of this kind of silicon is wasted due to the high content of inclusions, mainly SiC and $Si_3N_4$. To recycle these silicon wastes may tremendously save resources and reduce production cost. One of the most detrimental second phase particles embedded in mc-silicon is silicon carbide. When carbon which derived from the graphite heaters using in the process exceeds its solubility in silicon, silicon carbide will precipitate [8]. The major concern of SiC that presents in solar-grade silicon is that it can cause conspicuous effect on the mechanical and electrical performance of silicon material, such as wire break while wafer sawing and severe ohmic shunts that will degrade the performance of solar cells [9]. Therefore, to study carbon behavior in silicon has significant value for solar-grade silicon industry.

Considerable efforts have been made to study the behavior of SiC in silicon. Research like separating silicon and silicon carbide from sawing waste [10–14] and remove SiC from silicon ingot [15] are conducted. Several methods have been proposed, such as Al-Si alloy and electro-magnetic induction [16,17]. In our previous work, electron beam melting (EBM) was used to understand carbon migration in multi-crystalline silicon [18]. EBM will affect impurity migration during the process since the advantages of high temperature, high vacuum, high temperature gradient and strong ability of melt stir and convection it possesses. In this paper, a slow cooling pattern was applied during electron beam melting to have a better understanding on carbon distribution behavior in mc-Si.

## 2. Experimental

The raw material used in this study is multicrystalline silicon that derived from directional solidification with SiC and $Si_3N_4$

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

http://dx.doi.org/10.1016/j.mssp.2016.06.002
1369-8001/

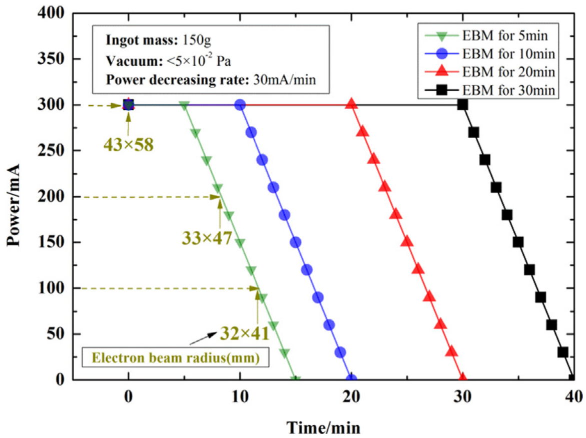


**Fig. 1.** Power decreasing pattern during EBM.

embedded in it. They were washed with alcohol and cleaned in a supersonic wave cleaner to remove any possible contamination and then dried sufficiently in a drying oven. 150 g as-cleaned silicon was placed in a water-cooled copper crucible with a circulation water cooling system in an electron beam melting furnace and then melted using a 30-keV electron beam that has circular scanning pattern at 300 mA with a vacuum $<5\times10^{-2}$ Pa for 5 min, 10 min, 20 min and 30 min, respectively. After melting, the electron beam power was reduced with a uniform rate of 30 mA/min and shrink electron beam scanning radius properly to obtain slow cooling pattern, as shown in Fig. 1.

Partial obtained silicon ingot after EBM was taken to immerse in acid solution of HF:$HNO_3$=3:1 to remove Si to extract SiC and $Si_3N_4$. X-ray diffraction (XRD) was applied to ascertain the structure of SiC and $Si_3N_4$. The element distribution was observed by EPMA. For micro morphology of the samples, a field-emission scanning electron microscopy (FE-SEM) was employed. A Fourier

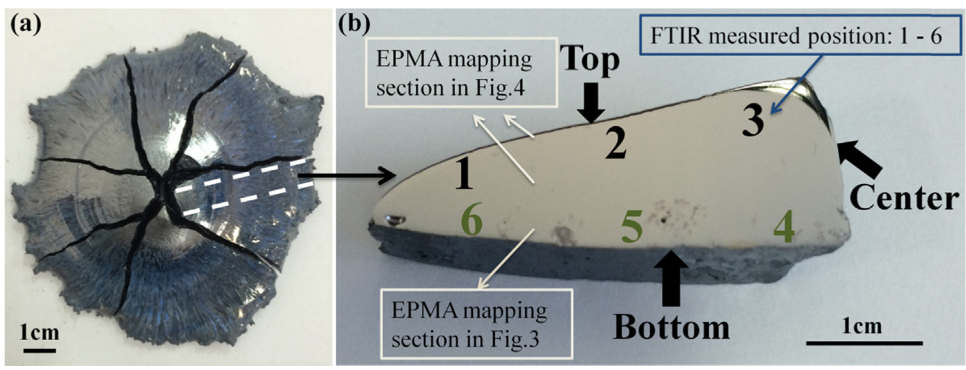


**Fig. 2.** (a) Top view image of the ingot after EBM; (b) Image of the ingot longitudinal after EBM and illustration of EPMA and FTIR measured section.

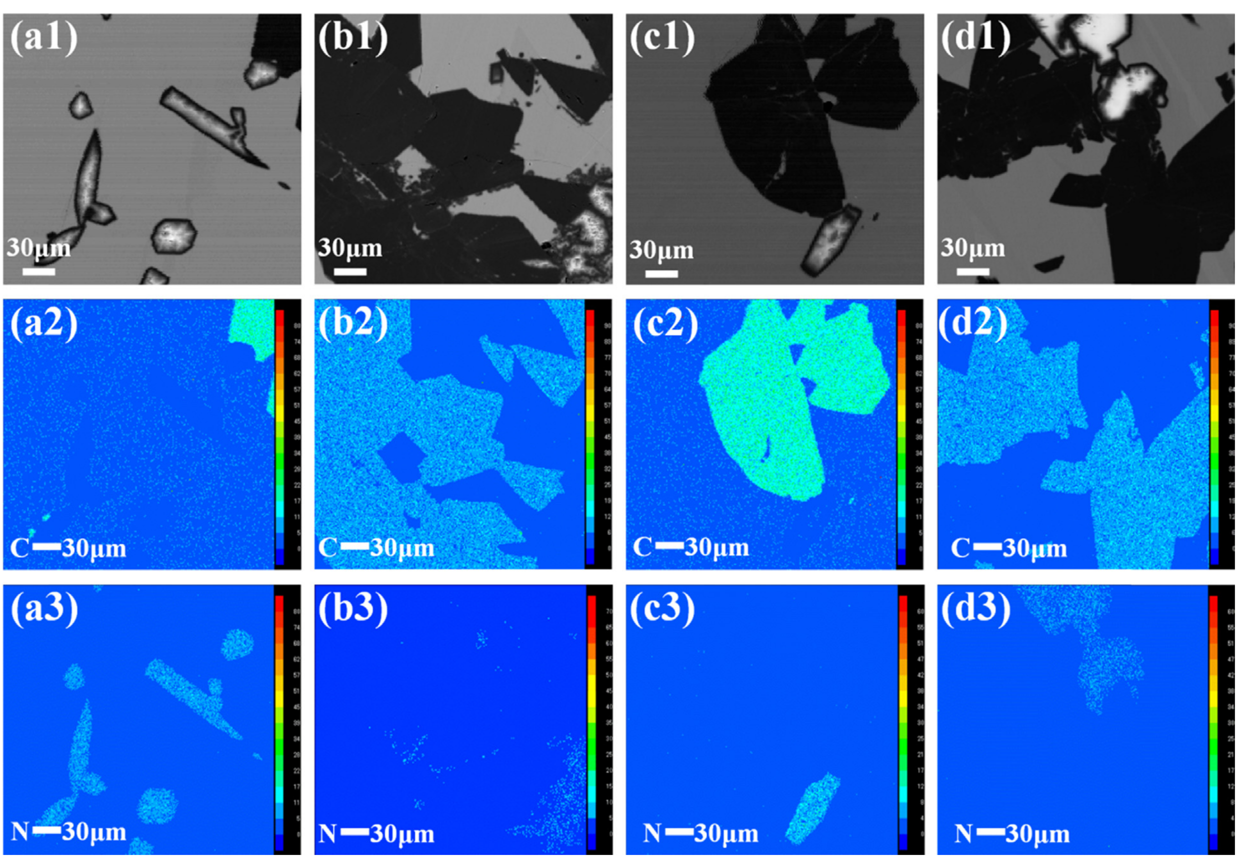


**Fig. 3.** (a1–d1) Typical backscatter images of the ingot bottom after EBM for 5 min, 10 min, 20 min and 30 min, respectively; (a2–d2, a3–d3) EPMA mapping of elements distribution at silicon ingot bottom after EBM.