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Microstructure and conversion efficiency of multicrystalline silicon ingot prepared by upgraded metallurgical grade silicon

Pengting Li[a,b], Kai Wang[a,b], Shiqiang Ren[b,d], Dachuan Jiang[a,b], Shuang Shi[a,b,c], Yi Tan[a,b,*], Feng Wang[c], H.M. Noor ul Huda Khan Asghar[e]

[a] School of Materials Science and Engineering, Dalian University of Technology, Dalian 116023, China
[b] Key Laboratory for Solar Energy Photovoltaic of Liaoning Province, Dalian 116023, China
[c] New Energy Materials and Technology Institute Co. Ltd. of Dalian University of Technology, Qingdao 266200, China
[d] School of Medicine, Liaocheng University, No.1 Hunan Road, Liaocheng, 252000 Shandong, China
[e] Department of Physics, Baluchistan University of Information Technology, Engineering & Management Sciences, Quetta 87300, Pakistan

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ABSTRACT

High-performance multicrystalline silicon (HPMC-Si) wafers were produced using upgraded metallurgical-grade silicon (UMG-Si) materials in the seed-assisted growth system at the industrial scale. The HPMC-Si wafers yielded low dislocation density and fine and uniform grain size. We observed that fine grain size suppressed the segregation effect of metal impurities. The effective segregation coefficients of Fe, Al, and total metal impurities approximated 0.265, 0.492, and 0.386, respectively. The concentration of impurities within 10–90% of the solidified fraction in the ingot was relatively uniform based on the improved crystal structure control. The heterogeneous nucleation mechanism of concave and planocera nucleation was discussed intensively. HPMC-Si wafers were obtained under the crystal structure control coupled with behavior regulation of impurity segregation in the seed-assisted growth system. The average conversion efficiency of Al-BSF processed solar cells reached 18.65%.

1. Introduction

Upgraded metallurgical-grade silicon (UMG-Si) has received attention as a low-cost material for high-efficiency silicon solar cells [1–3]. Currently, Siemens process is the most widely used method to produce solar-grade silicon; it is energy-intensive and requires heavy initial investments [4,5]. Various metallurgical technologies, such as directional solidification (DS) technology and electron beam smelting, have been developed to remove silicon impurities [6–8]. Ma et al. proposed a "single-step DS technology" for the preparation of UMG-Si, which can enable the purity and electrical properties of silicon ingot [8]. Li et al. reported that the concentrations of impurities B and P both measure lower than 0.20 ppmw the UMG-Si prepared by coupling of metallurgical methods, whereas the total concentration of total metal (TM) reaches less than 0.23 ppmw [9]. Recent improvements in UMG-Si purification have led to an improvement in feedstock quality. In 2016, Zheng et al. presented an n-type Czochralski (CZ) cell with an efficiency of 20.9% using 100% UMG feedstock [3]. For p-type UMG-Si solar cells, an efficiency of 17.0% was reported in 2010 for multi-crystalline silicon (MC-Si) solar cells, with an average batch efficiency of 16.4% [10]. However, the fabrication of HPMC-Si using UMG-Si has not been reported.

The seed-assisted method in DS has been recognized in recent years as a promising technology for obtaining high-quality MC-Si. The seeds are partly melted and allow the silicon crystal to epitaxially grow on them during crystal growth. The seed-assisted growth technique of HPMC-Si has been developed [11,12]; in this technique, nucleation agents are induced at crucible bottoms as the grain nucleation layer. Therefore, the corresponding improved crystal structures with appropriate crystal orientation, grain size, and dislocation distribution are beneficial not only for the improvement of macrograph properties but also for the realization of high-performance solar cells [13,14]. Wong et al. reported that the (112) to (111) crystal faces are dominant at the low crucible pulling speed, and the percentage of the (100) crystal face is extremely low near the top of the ingots in the seed-assisted system [15]. The defects of silicon ingot can be caused by grain structure, including grain morphologies and lattice orientations [16–20]. Gong et al. verified that the high density of dislocations in silicon can significantly reduce the efficiency of solar cells [18]. UMG-Si usually has more impurities than the silicon prepared by the Siemens process. The effect of seed-assisted method on distribution of impurities during DS has not been reported. On the other hand, the relationship between

* Corresponding author at: School of Materials Science and Engineering, Dalian University of Technology, Dalian 116023, China.

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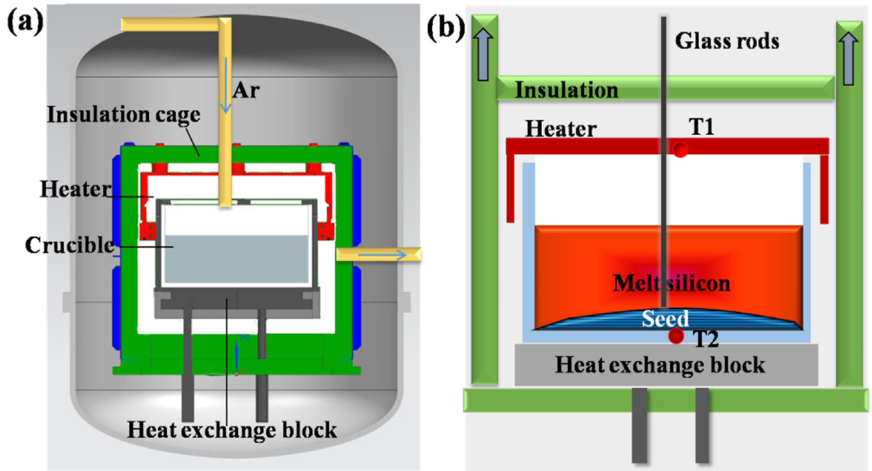

Fig. 1. The schematic illustration of (a) industrial-scale furnace and (b) semi-melting process.

crystal structure and the segregation behavior of impurities remains unelucidated.

In this paper, HPMC-Si ingot was prepared using UMG-Si materials and the seed-assisted method. The crystal structure of the silicon ingot was characterized with respect to the crystal faces, dislocation density, and grain size. The heterogeneous nucleation mechanism of planocera and concave nucleation was discussed intensively. HPMC-Si wafers were obtained through the crystal structure control coupled with behavior regulation of impurity segregation. Then, solar cells with high conversion efficiency were prepared using HPMC-Si wafers.

2. Experimental procedures

HPMC-Si wafers were grown by industrial-scale DS furnace (GT450) in this experiment. The induction heating and directional cooling system of this furnace is shown in Fig. 1(a). The heaters provide heat for the hot-zone, in which the heat is preserved by the insulation cage. The heat exchange block was installed beneath the crucible to take heat away from the hot-zone. The flowing inert argon gas was applied to purify the growth environment in the furnace. The furnace operated at a low pressure of about 60,000 Pa. About 800 kg UMG-Si feedstock materials were loaded into the crucible. As shown in Table 1, the concentrations of Fe, Al and TM in UMG-Si materials are 0.344 ppmw, 0.252 ppmw and 1.239 ppmw, respectively. The inside of crucible with the inner dimensions of 1040 × 1040 × 480 mm^3 was covered with the Si_3N_4 coating to prevent impurity dissolution. The used silicon seeds were broken monocrystalline silicon wafers with a size of about 2 mm, the height of the broken silicon wafers was about 20 mm. During the semi-melting process, the temperature gradient and melting process were well controlled to preserve the silicon seed crystals with an unmelted height of about 10 mm, just as shown in Fig. 1(b).

After the completion of the process of solidification and cooling, the silicon ingot was cut into 36 bricks. The experimental samples for the measurement of electrical performance and impurity concentration were taken from the longitudinal cross sections of bricks No.19 to No.24, as shown in Fig. 2(a). Wafers were sliced from the blocks along the growth direction by wire sawing process and the sampling diagram is shown in Fig. 2(b). The wafer had a cross-section area of 156 × 156 mm^2 and a thickness of about 180 µm. The presence of a large number of gaps in the seed region can absorb infrared light, which will appear in the imaging system with black shadows as shown in Fig. 2(c). There was no black shadow in the crystal growth process above the red lines of this ingot, which proved that the UMG-Si does not contain insoluble particles such as SiC and Si_3N_4.

The impurities concentration was determined by inductively coupled plasma mass spectrometer (ICP-MS). The crystal faces of a silicon wafer was measured by a detection method which abbreviated as Rotary Reflection Method [23]. The minority carrier lifetime mapping of the bricks was performed to define defect development by microwave photo conductance decay equipment (WT-2000). Then, the bricks were cut into wafers and corresponding photoluminescence (PL) mappings were measured by a PL equipment (BT imaging, LIS-R1) to characterize the dislocation distribution of HPMC-Si wafers. The area ratio of dislocations of the wafers was qualitatively characterized by the software ImagePro-Plus. The standard screen-printed Al-back surface field (Al-BSF) solar cells were fabricated and the conversion efficiency of solar cells was measured by a solar cell I-V tester from H.A.L.M Elektronik GMBH.

3. Results and discussion

3.1. Crystal structure characterization and analysis

The crystal structure was characterized in 156 × 156 mm^2 silicon wafers from bricks grown in the seed-assisted system. In order to obtain high-performance solar cells, the control of dislocation, crystal orientation, and grain size is extremely important. The average grain sizes of ingots at the bottom, middle, and top measured 3.47, 6.64, and 8.23 mm, respectively. Grain sizes presented a relatively homogeneous distribution at different solidification fractions, although the average values increased along the solidification fraction, as shown in Fig. 3. The results are consistent with those of a previous paper [12], which reported that seed induction at the beginning of crystal growth limits the grain size, resulting in relatively uniform grain sizes.

The crystal faces of silicon wafers were measured using an abbreviated rotary reflection method [21]. The detection method uses a camera shooting device to irradiate the silicon wafer in a rotating manner at different angular directions and obtains the corresponding

Table 1
The concentration of impurities in UMG-Si materials (ppmw).

Element	B	Ni	Cu	V	Ti	Mg	Fe	Al	Sum
Concentration	0.075	0.008	0.018	0.069	0.032	0.085	0.344	0.252	1.239