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Influence of germanium doping on the performance of high-performance multi-crystalline silicon

Jie Su [a], Genxiang Zhong [b,c], Zhaoyu Zhang [b], Xucheng Zhou [b], Xinming Huang [a,b,*]

[a] School of materials Science and Engineering, Nanjing Tech University, Nanjing, Jiangsu 210009, China
[b] Donghai JA Solar Technology Co., Ltd., Lianyungang, Jiangsu 222300, China
[c] Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

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ABSTRACT

The effect of germanium (Ge) doping on the performance of high-performance multi-crystalline silicon (mc-Si) has been investigated in this work. The Ge doping in the mc-Si ingot could reduce the concentration of FeB complexes and dislocation density, resulting in the improvement of minority carrier lifetime. Due to this reduction in dislocation density, the mechanical strength of the mc-Si wafers was enhanced by Ge doping. The preliminary experimental results showed that the average conversion efficiency of Ge-doped mc-Si solar cells was higher than that of normal undoped mc-Si solar cells under the same solar cell fabrication processes. Consequently, we propose that Ge doping is beneficial for the fabrication of higher performance of mc-Si solar cells.

1. Introduction

Czochralski silicon (Cz-Si) and multi-crystalline silicon (mc-Si) have been the dominant materials for fabrication of photovoltaic (PV) solar cells. However, the mc-Si has a lower quality than Cz-Si because of the presence of crystal defects and impurities such as dislocations and metal impurities. It leads to a 1%~2% difference in their solar cell efficiency [1,2]. To obtain higher conversion efficiency of the mc-Si solar cells, reducing the dislocation density and impurity concentration in the mc-Si wafers has been an important topic of research.

Ge doping is one approach to reduce crystal defects and improve the performance of mc-Si wafers. Many studies have shown the effect of Ge doping on the performance of Cz-Si and conventional mc-Si, but few studies have been carried out on the high-performance mc-Si. In the Cz-Si, Ge doping could restrain the generation of dislocation [3] and promote internal gettering capability for metallic contamination [4]. Moreover, the minority carrier lifetime of floating zone Si (FZ)-Si crystals was improved by controlled Ge doping [5]. In the conventional mc-Si, Ge doping significantly lowered the average dislocation density of mc-Si wafers and resulted in a more homogeneous distribution of dislocations [6]. The mechanical strength of the mc-Si wafers was also improved by Ge doping [7]. In addition, SiGe multi-crystalline with wide distribution of the composition would have wide distribution of the absorption coefficient and could be helpful for new solar cell applications [8,9]. Especially, when Ge content was lower than 5% in the silicon, the conversion efficiency of SiGe multi-crystalline solar cell could be improved [10].

In this article, we reported the effect of Ge doping on high-performance P-type mc-Si. We focused on the distribution of FeB complexes and the dislocation density in the Ge-doped mc-Si versus normal undoped mc-Si. The effect of Ge doping on the mechanical strength of the silicon wafers was investigated in the mc-Si ingot. Finally, the conversion efficiency of the solar cells was obtained as a standard to evaluate effect of Ge doping on the improvement of the performance of the mc-Si.

2. Experimental method

The experiments were carried out with seed-assisted methods to cast a high-performance mc-Si ingot in a Jinggong JJL500 directional solidification furnace. For high-performance mc-Si casting, the commercial raw mc-Si particles with granular shape were used as the seeds; particle sizes ranged from 0.5 to 4 mm. These seed crystals were first closely packed on the bottom of the crucible (830 × 830 × 480 mm^3) with a coated film of Si_3N_4, and the layer thickness of the seeds was about 20 mm. Then, 440 kg solar grade silicon feedstock

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* Corresponding author at: Donghai JA Solar Technology Co., Ltd., Lianyungang, Jiangsu 222300, China. Tel.: +86 13382956166.
E-mail address: huangxm@jasolar.com (X. Huang).

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and 1.14 kg Ge were loaded into the crucible, corresponding to the initial Ge concentration in the silicon melt being $5.4\times10^{19}\text{cm}^{-3}$. In the directional solidification (DS) system, the temperature gradient and melting process were well controlled to preserve the silicon seed crystals with an un-melted height of about 10 mm. The temperature gradient near the seed was about 15～30 K/mm which was higher than that in the bulk silicon melts (5～10 K/mm) by computer simulation [11]. Finally, silicon ingots with a height of 270 mm were obtained.

The ingots were controlled to have a resistivity of 1～2 Ω cm by doping a proper amount of boron-doped silicon mother alloy (the B-doping concentration was about $9\times10^{15}\text{cm}^{-3}$). For further analysis, each ingot was cut into 25 bricks of 156 × 156 mm^2 (Fig. 1 (right)). The concentration of FeB complexes was measured by FeB-pair splitting, according to comparison of the minority carrier lifetime measured by microwave detection of photoconductive decay (μ-PCD) before and after light soaking. It was calculated by G. Zoth et al. [12],

$$N_{FeB} = C_{\mu-PCD}\left(\frac{1}{\tau_{before}} - \frac{1}{\tau_{after}}\right), \qquad (1)$$

where $C_{\mu\text{-PCD}}=3.4\times10^{13}\ \mu\text{s}\cdot\text{cm}^{-3}$. The maps of the minority carrier lifetime were obtained by μ-PCD using a Semilab WT2000 device. Silicon wafers (180 μm thick) were cut from the bricks using a standard wire saw and subjected to further measurements. Laboratory off-line PL instrument (BT imaging, LIS-R1) was used to observe the dislocation distribution in the mc-Si wafers. Several plate samples with dimensions of 30 × 10 × 2 mm^3 were also processed from the ingots at the same position as those samples for mechanical strength measurements. The plate samples were first chemically etched by the white etchant (HNO_3: HF=3:1) to remove the surface damage. Then, the mechanical strength of the chemically etched plate samples was measured with a universal testing machine (SANS-CMT5254) using the three-point bending method.

3. Results and discussion

3.1. The distribution of FeB in the Ge-doped Mc-Si

Iron atoms generally occupy interstitial lattice sites in a silicon matrix. In the P-type conventional mc-Si, positively charged iron ions tend to form FeB complexes with negatively charged boron ions at room temperature [13]. Fig. 2 shows the longitudinal distribution of FeB complexes in the Ge-doped mc-Si ingot and the normal undoped mc-Si ingot after light soaking. The bottom ends and top ends of the two ingots were cut out 45 mm and 20 mm, respectively, for cutting off the lower minority carrier lifetime regions (red-zone) in the results shown in Fig. 2. The concentration of FeB complexes in Ge-doped mc-Si ingot was lower than that in the normal undoped mc-Si ingot. The average concentration of FeB complexes was about $10^{11}\ \text{cm}^{-3}$ in the Ge-doped mc-Si ingot, whereas it was $10^{12}\ \text{cm}^{-3}$ in the normal undoped mc-Si ingot. In the two kinds of ingots, the concentrations of Fe and B were the same in the silicon melt. X. Zhu et al. [14] reported the interstitial iron in the Ge-doped silicon had a higher diffusion barrier than that in the undoped silicon and an extra activation energy of about 0.1–0.6 eV was necessary for the interstitial iron diffusion in the Ge-doped silicon. Ge doping in the mc-Si could reduce the probability of the combination of interstitial iron atoms and boron atoms through increasing the diffusion barrier of the interstitial iron in silicon, thus lowered the FeB complexes concentration. On the other hand, the concentration of Ge and B increased with the ingot height. Ge concentration at the beginning of the crystal was $3\times10^{19}\ \text{cm}^{-3}$ and then it increased with crystal growth. The concentration of Ge in the middle and top of ingot were $4\times10^{19}\ \text{cm}^{-3}$ and $8.2\times10^{19}\ \text{cm}^{-3}$ respectively, corresponding to solid fractions of about 50% and 90% in the ingots. The effective segregation coefficient of Ge in the silicon ingot was about 0.56 by preliminary calculation, which was consistent with D. Yang et al.'s report [15]. However, from Fig. 2 it can also be seen that the concentration of FeB complexes didn't show obvious change with the height of ingot in the normal regions, indicating that the concentration of Ge and B didn't have much influence on the concentration of FeB complexes within the present concentration range.

The concentration of FeB complexes was only a very small proportion in the total iron concentration, but FeB complexes cause a lower lifetime than interstitial iron and other Fe-related complexes at the same injection level [16]. In references [17–19] it was also demonstrated that the minority carrier lifetime strongly decreased with increase of FeB complex concentration in the P-type Cz-Si wafers. The minority carrier lifetime of all the silicon bricks without any passivation treatment in the ingots of the Ge-doped mc-Si and the normal undoped mc-Si was obtained by μ-PCD measurements, and the results are shown in Fig. 3 (after cutting off both the bottom ends and top ends). The measurement method is used in industrial production as a standard method. Fig. 3 shows that the minority carrier lifetime in Ge-doped mc-Si ingot is higher than that in the

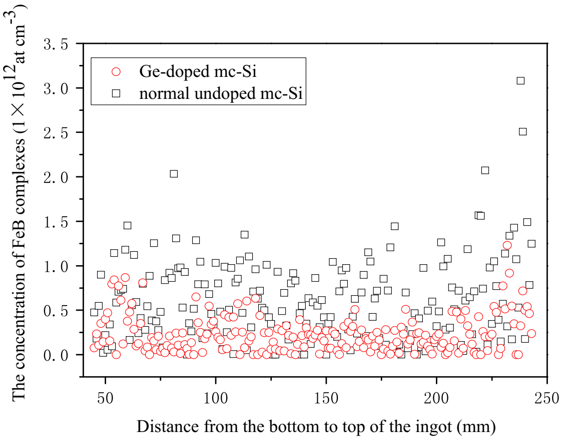

Fig. 2. The distribution of FeB complexes in the Ge-doped mc-Si ingots and the normal undoped mc-Si ingots after light soaking.

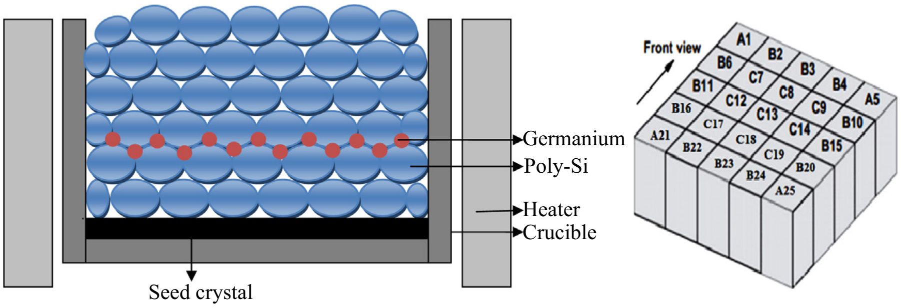

Fig. 1. The loading of seeds and silicon feedstock in the crucible (left) and numbering of bricks from the Ge-doped mc-Si ingots (right).