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Multicrystalline silicon crystal assisted by silicon flakes as seeds

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ABSTRACT

The seed assisted growth technology has been used to fabricate the high performance multicrystalline silicon (mc-Si) for photovoltaic application nowadays, which can effectively control the dislocation density by forming uniform and small grains. In this work, we have systematically investigated the effect and mechanism of silicon wafer flakes as the seeds for mc-Si growth. Silicon flakes were put on the crucible bottom as nucleation agents by two different settings, i.e., orderly stacking without interspace and intentionally piling up with interspace. It was found that the numerous small and uniform grains with diameter of ~ 0.5 mm were homogenously formed in the intentionally piled up wafer flake seed layer since the liquid silicon drops flew down and solidified in the interspaces during the melting of polysilicon feedstocks. These small self-formed grains served as new seeds, which were better than orderly stacked wafer flakes as seeds. Minority carrier lifetime and photoluminescence mappings have shown that the initial dislocation density of grains with smaller sizes based on the piled silicon flake seeds was much lower than those without seeds or stacked silicon flake seeds, and meanwhile the dislocation propagation was suppressed by means of smaller grain sizes due to the denser grain boundaries. As a result, the corresponding average conversion efficiency of Al-BSF processed solar cells from the mc-Si assisted by piled silicon flakes as seeds was absolutely 0.29% higher than those without seeds and 0.17% higher to those assisted by stacked silicon flakes.

1. Introduction

Crystalline silicon (c-Si) nowadays occupies more than 90% of the photovoltaic material market [1]. Among c-Si materials, multicrystalline silicon (mc-Si) has become the main stream due to its large productivity and low cost. However, compared to Czochralski silicon (CZ-Si), mc-Si crystal contains more defects like dislocations and grain boundaries (GBs), and therefore the corresponding solar cells have a lower efficiency. In order to improve the quality of mc-Si crystal, various growth technologies have been developed. Nakajima et al. casted mc-Si crystals by dendrite growth technology [2,3], in which the feature was the fast nucleation and growth of grains at the crucible bottom. As a result, the dislocation density in the dendrite grains was quite low, and meanwhile most of GBs were coherent Σ3 GBs with weak recombination activity. However, an unavoidable issue of dendrite growth is the stress induced by the interaction between small branches of the dendrites, which causes the formation and propagation of dislocations with high recombination activities. Later, Lan et al. improved the thermal field and controlled the dendrite growth for the reduction of internal stress [4–6]. They found the small branches of dendrites can be suppressed by optimizing the undercooling, beneficial for the improvement of solar cell efficiencies. Unfortunately, the corresponding technology window for the stress reduction is too narrow, unsuitable for the massive production [6].

During the past decade, it has been recognized that a seed assisting method is a promising route to cast high quality c-Si [7]. Based on this idea, the quasi single crystalline silicon (QSC-Si) with less GBs, also known as mono-like silicon (ML-Si), can be obtained [7–9]. The seeds from CZ silicon crystal cover the crucible bottom in advance. During crystal growth, the seeds are partly melted and allow the silicon crystal to epitaxially grow on them. The solar cells based on QSC-Si have a much higher efficiency than those based on conventional mc-Si. The efficiency improvement of QSC-Si solar cells is mainly attributed to the reflectivity reduction due to the utilization of the pyramid texturization on (100) substrate surfaces [9]. The quality of QSC-Si is much sensitive to dislocations originated from thermal stress and the unavoidable mismatch of the seeds usually multiply along the crystal growth direction [10], the planar density of which could reach 10^6 cm^{-2} at the top of crystal [11]. In the past, we have designed a new setting method of seeds at the crucible bottom to suppress the generation of such

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dislocations [12]. Nevertheless, the QSC-Si is still not ready for massive production, because other issues like high cost must be resolved.

Inspired by seed-assisting growth of QSC-Si, the seed assisted mc-Si (SAMC-Si), also known as high performance multicrystalline silicon (HPMC-Si) technique, has been developed [6,13,14], in which the nucleation agents are induced at crucible bottoms as grain nucleation layer. The SAMC-Si has the feature of uniform and small grains with low dislocation density, which becomes popular in photovoltaics nowadays. The idea is to suppress the dislocation propagation and release the thermal stress by high density GBs. The nucleation agents used for HPMC-Si growth are generally Si/SiO_2 powders or silicon beads [15,16].

In this paper, we have utilized the waste silicon wafer flakes as nucleation layers and found the grown crystal has higher quality. We investigate the effect of the wafer flake nucleation layers on the quality of mc-Si ingots and try to understand the mechanism of defect reduction using this method. It is found that the quality of crystals is strongly dependent on the setting method. The interspaces in the randomly piled flakes can effectively induce heat insulation, increase the vertical thermal gradient in the nucleation layer, and may allow the liquid silicon drops to solidify and to form small bead-like homogeneous seeds with a diameter of ~ 0.5 mm. As a result, uniform and small grains can be easily obtained in the grown crystal with the seed assistance. The seed assisted mc-Si based on this method contains less dislocations and yields higher efficiency solar cells.

2. Experimental

Three cast mc-Si ingots were fabricated by using directional solidification furnaces (GTAT Co. Ltd). The size of quartz crucibles with Si_3N_4 coating was 890 × 890 × 480 mm^3. Fig. 1 shows the scheme of the usage of nucleation agents for the growth of mc-Si. Ingot A was grown without nucleation agents as a reference. The nucleation agent used for ingot B and C was mc-Si wafer flakes with the diameter of 0.5–2 cm and thickness of ~ 180 µm. For ingot B, the flakes were compactly stacked at the bottom of the crucible. For ingot C, the flakes were intentionally piled up to obtain interspaces. Note that during the melting stage, polycrystalline feedstocks were fully melted from the crucible top to the bottom, and the nucleation layer for ingot B and C were partially melted so that the solidification started from the unmelt

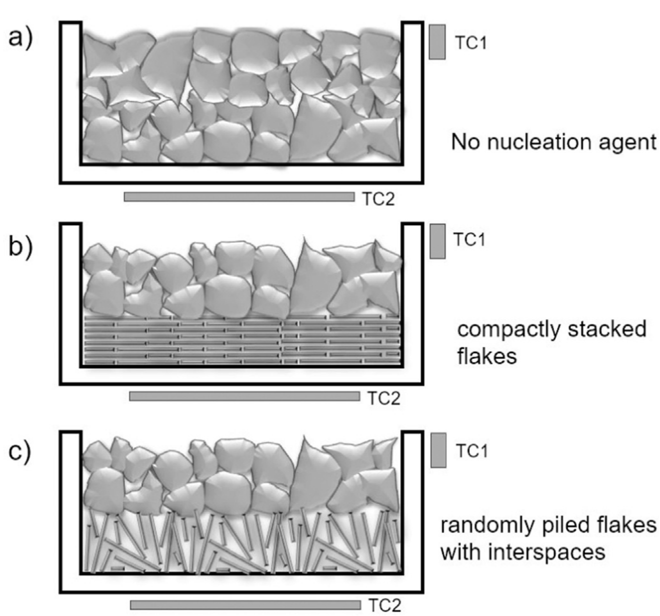

Fig. 1. The scheme of nucleation layer preparation for the growth of (a) ingot A, (b) ingot B and (c) ingot C.

nucleation layer. During solidification, the process parameters of ingot B and ingot C are the same, and the temperature of the heater and beneath the crucible were monitored by two thermal couples (TC1 and TC2) shown in Fig. 1.

After the solidification, the ingots were cut into bricks. The grain structures at the ingot bottom were observed by an optical microscope. The minority carrier lifetime mapping of the bricks was performed to define defect development by a microwave photoconductance decay equipment (Semilab WT-2000). Then, the bricks were cut into wafers and photoluminescence (PL) mappings were measured by a PL equipment (BT imaging, LIS-R1) to characterize planar dislocation distribution. Finally, the standard screen-printed Al-back surface field (Al-BSF) solar cells were fabricated and the conversion efficiencies were measured by a HALM equipment (H.A.L.M Elektronik GmbH).

3. Results and discussion

Fig. 2 shows the optical microscopy (OM) photos of grains near the various ingot bottoms. For ingot A without nucleation agents, which inherently is conventional dendrite growth, the large dendrite grains with a general width of 3–5 mm are found at the ingot bottom growing up vertically along the crystal growth direction, seeing Fig. 2a. For the seed-assisted growth, the mechanism of grain formation is epitaxial growth, which strongly depends on the setting of silicon flake seeds. When the silicon wafer flakes are stacked orderly at the crucible bottom, the width of epitaxially grown grains is close to diameter of the flake seeds, that is, 0.5–2 mm shown in Fig. 2b. However, when the silicon wafer flakes are piled up intentionally to form some interspaces at the crucible bottom, the size of grains in the grown crystal is relatively smaller, seeing Fig. 2c. The inset shows a plane-view OM photo of the grains at the height of the red line in Fig. 2c. It can be observed that a large quantity of spherical grains with a diameter of ~ 0.5 mm exist beneath the interface of crystal and seeds.

Fig. 3 shows the photoluminescence images of the wafers sliced from the bottom parts of various ingots, which can well characterize the dislocation distribution in as-cut wafers [17]. For ingot A, it can be seen that the grain size is not uniform, and meanwhile some large dislocation cluster patterns are generated between the dendrites. For ingot B, the grain sizes of the wafer are relatively small and uniform, close to those of the wafer flake seeds. Note that the PL micrograph in Fig. 3b shows there are a lot of small dislocation clusters in the sample. This indicates that the dislocation generation is still a severe problem for the ingot B with the orderly-setting of wafer flake seeds. However, the grain size is even smaller and more uniform in ingot C and the dislocation clusters are almost invisible, seeing Fig. 3c. It strongly suggests that the dislocation clusters can be significantly avoided by intentionally piling up the wafer flake seeds to obtain interspaces.

The development of defects can be furtherly clarified through microwave photoconductance decay minority carrier lifetime mapping. Fig. 4 shows the lifetime mappings of the brick profiles of (a) ingot A, (b) ingot B, and (c) ingot C. The patterns of low lifetime regions are in correlation with the distribution of structural defects, mainly related to dislocations. It can be observed that the dislocation densities of ingot A and ingot B are much higher, compared to ingot C. The difference is that in ingot A, the lifetime values of some “good” grains are higher compared to ingot B, which suggests that the quality of ingot A based on dendrite growth is more or less better than that of ingot B based on the orderly stacked seeds. It should be noticed that the low lifetime regions related to the dislocation propagation and multiplication are much more continuous in ingot A, compared to ingot B. This phenomenon could be ascribed to large dendrite grains in ingot A, and denser GBs can stop the dislocations propagate in ingot B. Fig. 4c show that the lifetime of ingot C is quite uniform, indicating that few dislocations are generated in the main part of the ingot, except for the top part. This result reconfirms that dislocations can be effectively suppressed in the uniform and small grains of ingot C, which is quite