Solar Energy Materials and Solar Cells 171 (2017) 131–135

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

Grain boundary engineering of high performance multicrystalline silicon: Control of iron contamination at the ingot edge

Dongli Hu[a,b], Shuai Yuan[a], Xuegong Yu[a,*], Liang He[b], Yunfei Xu[b], Xueri Zhang[b], Deren Yang[a,*]

[a] State Key Lab of Silicon Materials and School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China
[b] LDK Solar Co. Ltd., Xinyu 338032, PR China

ARTICLE INFO

Keywords:
Multicrystalline silicon
High performance
Iron contamination
In-diffusion
Grain boundary engineering
Nucleation control

ABSTRACT

The high performance multicrystalline (HPMC) silicon material with the feature of small and uniform grains has already been widely adopted in photovoltaic industry nowadays. However, the HPMC silicon ingots still suffer a comparatively lower minority carrier lifetime at the ingot edges induced by Fe in-diffusion. Here, we have engineered the grain boundaries (GBs) to control the low carrier lifetime zone at the HPMC silicon ingot edges, based on the grain nucleation enhanced by silicon powder coating at the crucible walls. The resultant GBs with high density paralleling to the crucible walls can getter Fe impurity, and meanwhile become the barriers for Fe diffusion. Therefore, the detrimental effect of interstitial Fe impurity on the carrier lifetime of edge wafers is sufficiently reduced and the performance of corresponding solar cells is improved. The solar cells have a narrower distribution in the performance, which is beneficial for the stability and durability of solar cells and modules. This growth concept using GBs to control the behaviors of Fe diffused from the crucible walls is interesting for photovoltaic application.

1. Introduction

More than 90% of all commercial solar cells are made from silicon nowadays, which has the mature processing technology, the large abundance in the crust of the earth and the non-toxicity from the environmental perspective. Silicon materials used in photovoltaic industry are generally classified into two kinds, i.e., Czochralski (CZ) silicon and multicrystalline (mc) silicon. Compared to CZ silicon, mc silicon has the advantage of more productivity and lower cost, but contains more impurities and defects. These impurities and defects usually are the recombination centers for carriers and therefore are harmful to the solar cell performances.

The main defects in mc silicon are dislocations and grain boundaries (GBs). Currently, there are various ways to control the generation of these defects in mc silicon. Among them, the nucleation and grain control becomes very important during mc silicon crystal growth. Nakajima et al. have proposed the dendrite casting method to control the orientation of grains in the < 112 > direction and therefore significantly increase the grain size by the introduction of a high initial undercooling [1]. This can result in a high percentage of Σ3 twin boundaries with low recombination activity and the grain size can be up to tens of centimeters. An alternative way to control crystal orientations and GBs is seed-assisted growth, which can avoid the self-nucleation of grains at the crucible inner walls. Quasi-single-crystalline (QSC) silicon ingots can be casted by the traditionally directional solidification method if CZ silicon bricks are used as seeds at the bottom of crucible [2]. Such a QSC silicon ingot is absent of GBs and has the unique < 001 > crystalline direction, which allows the alkaline texturization for the formation of surface pyramids and therefore increases the sunlight absorption [3]. However, dislocations with high density easily generate from the seed joints and multiply along the axial direction of crystal growth due to the high thermal stress, which are even more detrimental than GBs for the efficiency of cast silicon solar cells [4,5]. In order to control the dislocation density, the researchers in LDK Solar Co. Ltd and Sino-American Silicon Products Inc. have firstly used small silicon particles or silicon flakes from broken wafers as seeds to obtain high performance mc (HPMC) silicon ingots, which has the feature of small and uniform grains [6–8]. Compared to the traditional mc silicon and QSC silicon, the relatively denser GBs in HPMC silicon can effectively reduce the thermal stress of ingots and meanwhile act as the sinks of slipped dislocations during the crystal growth, which significantly decreases the dislocation density [6]. Meanwhile, it is reported that the other seeding methods based on SiO_2 particles or notched crucibles has also been developed to grow HPMC silicon ingots [9,10]. Even though the efficiency of solar cells based on HPMC silicon is lower than that of the ones based on QSC silicon, HPMC silicon

---

* Corresponding authors.
E-mail addresses: yuxuegong@zju.edu.cn (X. Yu), mseyang@zju.edu.cn (D. Yang).

http://dx.doi.org/10.1016/j.solmat.2017.06.035
Received 5 January 2017; Received in revised form 5 June 2017; Accepted 19 June 2017

material has been widely adopted in photovoltaic industry by now, due to its simple process and low cost.

However, HPMC silicon ingots still suffer a comparatively lower minority carrier lifetime at the edge with a width of about 2 cm due to Fe in-diffusion from the walls of crucible [11]. After cutting ingots, for example, the ingots from a G6 furnace into 36 bricks with the standard industrial size, 20 bricks coming from the edge region will contain the lower carrier lifetime zone. Many researches have been conducted to find out how this edge zone appears and what is responsible for the degradation of minority carrier lifetime in this region [12,13]. It has recently been recognized that iron contamination is mainly responsible for the carrier lifetime degradation at the ingot edge, instead of substitutional carbon, interstitial oxygen, and dislocations. The Fe impurity is mainly incorporated through the contact of the melt and the crystal with the crucible walls since the crucibles with silicon nitride coating usually contain metal contamination up to several ppm or more. They can form Fe-B pairs with dopant and cause deep level recombination centers for carriers [14]. Due to the small portion of low carrier lifetime edge zone, the non-uniformity in cells may degrade the cell performance during the long-time operation process by introducing heat effect and causing break down in pn junction [15,16]. Phosphorus diffusion gettering during the celling process can remove a portion of these Fe impurities and narrow the low carrier lifetime region [17], but the solar cells based on edge zones still exhibit a lower efficiency than those conventional ones. The utilization of higher pure crucibles or Si_3N_4 coating will unavoidably increase the fabrication cost of HPMW silicon crystals, not practicable for photovoltaic application. Thus, it is still an open question to find a new cost-efficient way to control Fe contamination at the HPMC silicon ingot edges for the improvement and uniformity of solar cell performances.

In this work, we have reported a novel strategy to reduce the low carrier lifetime zone at the HPMC silicon ingot edge by introducing a coating layer of silicon powders onto crucible walls. These silicon powders can control the nucleation of grains at the crucible walls and generate denser grain boundaries, which become vertical at the ingot edges by the hot-zone modification, and therefore barrier the diffusion of Fe impurities towards the ingots. As a result, the minority carrier lifetime at the ingot edges get significantly improved and become more uniform in the whole wafers. The large non-uniformity of solar cells can be effectively avoided, which is beneficial for the stable and durable power out-put of modules.

2. Experimental details

Two HPMC silicon ingots with a weight of 510 kg were casted by a DSS furnace (GTAT Co. Ltd) using the same thermal field structure and growth parameters except for the coating conditions of crucibles, labeled as ingot A and B here, respectively. Both the crucibles were first coated with Si_3N_4 powders at the bottom and the inner walls. Then, the crucible used for ingot A was subjected to the silicon powder coating at the bottom. However, the crucible used for ingot B was subjected to the silicon powder coating at both the bottom and the inner walls. After crystal growth, the ingots were cut into bricks and subsequently sliced into the wafers or the samples for different characterizations. The solar cells were fabricated using the wafers from side bricks of ingot A and ingot B based on the traditional Al-BSF process.

The grain size and grain boundary density of ingot edge were observed by an optical microscope after wet etching in a HF and HNO_3 ($HF:HNO_3 = 1:3$) mixture solution. The Fe concentrations in the samples were characterized by inductively coupled plasma mass spectrometry (ICP-ms) and secondary ion mass spectroscopy (SIMS) techniques. The carrier lifetime mappings of samples were performed by microwave photoconductance degradation technique (MW-PCD, Semilab WT-2000). The Photoluminescence (PL) and Electroluminescence (EL) signals were recorded by a system (BT imaging, LIS-R1). The efficiencies of the solar cells were carried out at 25 °C, 100 mW/cm^2 by a HALM equipment (H.A.L.M Electronic GmbH).

Fig. 1. Optical image of the crucible with silicon powder coating for ingot B.

3. Results and discussion

Fig. 1 shows an optical image of the crucible for Ingot B. It can clearly be seen that a uniform layer of silicon powders is coated at the bottom and the inner walls of crucible. The thickness of silicon powder layer is 0.5–0.7 mm, observed by a scanning electron microscope (SEM). It should be mentioned that the silicon powder layer at the crucible bottom has widely been used to control the initial nucleation of HPMC silicon for the achievement of small and uniform grains in photovoltaic industry, as applied for ingot A. Here, the utilization of silicon powder layer at the crucible inner walls is expected to control the initial nucleation of grains for the edges of Ingot B.

For the conventional HPMC silicon, the edge and edge-close part of side bricks usually contain a relatively high concentration of Fe impurity, which usually exhibit a red zone in the minority carrier lifetime mapping by MW-PCD technique, as schematically shown by Fig. 2. Fig. 3 compares the distribution of grains in the edge parts obtained from ingots A and B. Note that the microscopically convex front of solidification is important for the growth of HPMC silicon, but the solidification front very near the inner crucible is concave due to the wetting of Si_3N_4 or silicon powder coating layer for melt silicon and high undercooling here. Therefore, the initial growth direction of grains is vertical to the crucible walls, and late on the grains will continually grow along the direction vertical to the crucible bottom. Compared to the Si_3N_4 coating layer, the utilization of silicon powder coating layer can largely reduce the wetting angle with the melt silicon, and therefore enhance the grain nucleation rate at the inner walls of crucible. As a result, a larger number of small grains and therefore denser GBs will be generated near the crucible wall for the ingot B (Fig. 3b). With the grain growth, these GB with higher density tends to become upright by the temperature gradient, parallel to the crucible wall.

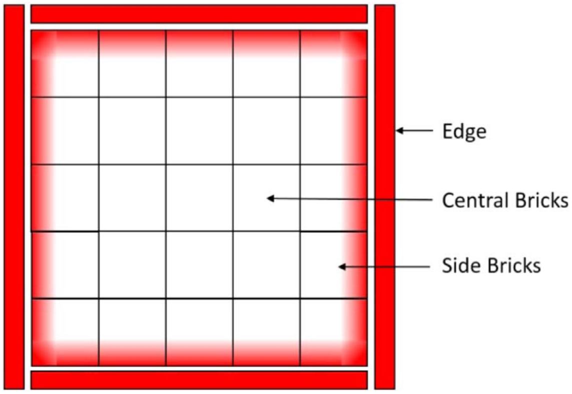

Fig. 2. Scheme of bricks and edges cutted from a HPMC silicon ingot.