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Experimental study of grain boundary orientations in multi-crystalline silicon

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ABSTRACT

Some peculiarities of straight and zig-zag grain boundaries in multi-crystalline Si ingots were analyzed by Scanning Electron Microscopy-Electron BackScatter Diffraction (SEM-EBSD) and Three Dimensional (3D) grain boundary reconstruction.

In the cases where straight grain boundaries were perpendicular to facing {111} planes in the two neighboring grains, they were found parallel, within the measurement accuracy, to the bisector of the two facing {111} planes. This is in agreement with the theory predicting the existence of Facetted–Facetted grooves during the growth of multicrystalline Si. Another grain boundary was corresponding to the predicted Facetted–Rough groove.

It was found that the zig-zag grain boundaries were successively composed of {111} twin planes and $(\bar{4}11)/(011)$ planes, so that the two grains are always in Σ3 relationship. The phenomenon leading to the formation mechanism for these boundaries remains a subject for research.

1. Introduction

The grain structure of multi-crystalline Si ingots impacts the conversion efficiency of photovoltaic cells, because grain boundaries are places where lattice defects interact with minority carriers [1,2]. Furthermore, grain boundaries act as getters attracting impurities, which have the drawback of increasing the grain boundary effect on electronic carriers but the advantage of cleaning the surrounding grains. These effects have gained importance since the use of less and less pure silicon raw material by the industry [3]. It is therefore important to know how the ingot growth parameters impact the grain structure of the multi-crystal.

Recent research works, based on classic kinetic and thermodynamic considerations and on a review of the literature concerning growth, grains and twins in silicon [4], gave the following results [5,6,7]:

- Under usual ingot growth conditions, the solid–liquid interface morphology is rough, excepted on the {111} planes, where it is facetted. It follows that the grain–grain–liquid triple line that surrounds a grain during growth is facetted in certain places that depend on the crystallographic orientation of this grain.
- The undercooling of the facet increases with growth rate. Under a small temperature gradient, a large undercooling gives a large facet. Then, when the growth rate is high and the temperature gradient small, the solid–liquid interface can be totally facetted, while under low growth rate and large gradient, facets are very small.
- Depending on the morphology of the grain–liquid surfaces, the grain boundary groove can show three different morphologies that impact the grain boundary growth direction (Fig. 1):
  - Facetted–facetted, in which case the grain boundary is a plane that follows the bisector of the two facets (Fig. 1(a)). This case is referred as Facetted groove.
  - Rough–rough, with grain development controlled by kinetic factors, as classically known in metallurgy (Fig. 1(b)).
  - Rough–facetted in which case the grain boundary is a plane that follows the direction of the {111} facet (Fig. 1(c)). This case is referred as Mixed groove.

Such theoretical expectations, while coherent with numerous experimental facts [8], have to be confronted with the observation of grain boundary directions in various configurations. Consequent upon these findings, this paper presents multi-crystalline silicon ingot characterizations performed in order to:

- Study several grain boundaries, appearing as straight lines on metallography, in order to check if they correspond to the

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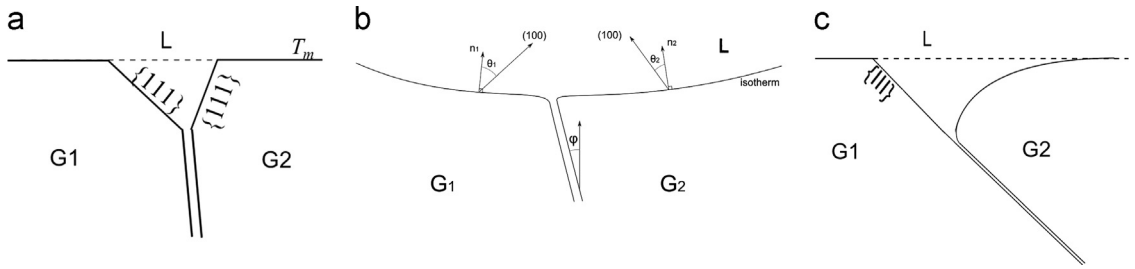

Fig. 1. Morphology of the grain–grain–liquid triple line groove and direction of grain boundary growth. (a) Facetted groove, (b) Rough groove, and (c) Mixed groove.

Facetted groove shown in Fig. 1(a). More precisely: does the crystallographic orientations of the two neighboring grains show facing {111} planes at the grain boundary? And does the grain boundary follow the bisector of these two planes?
- Show a particular result concerning the Mixed groove as shown in Fig. 1(c).
- Study the particular case of zig-zag grain boundaries, often found in multi-crystalline silicon.

The next part will present the experimental methodology used in order to study grain boundaries found in several industrial and laboratory ingots. Results will then be presented and commented as function of the different configurations encountered.

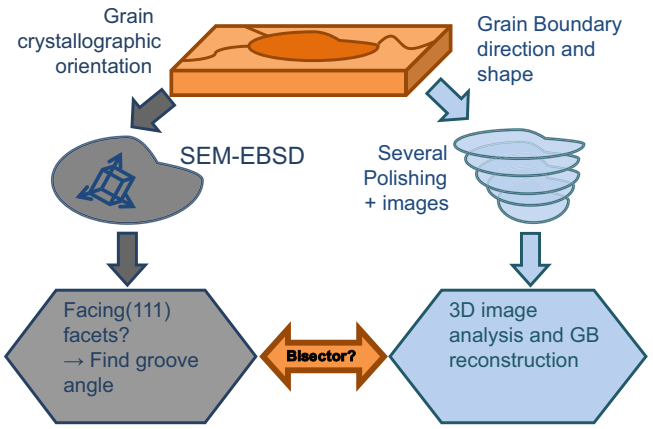

Fig. 2. Experimental methodology used for grain boundary (GB) characterization.

2. Experimental procedure

2.1. Principle

Checking the position of the {111} planes in the grains necessitates knowing the absolute orientation of their unit cell in the sample. For this purpose, SEM-EBSD analysis of the sample surface will be used. Additionally, flatness and orientation of the grain boundary will be measured by reconstruction of the grain boundary from metallography taken at increasing depths under the sample surface, obtained by successive grinding and polishing. Therefore the samples follow two parallel treatments, as shown in Fig. 2.

2.2. Sample selection and preparation

Eight samples were taken from multi-crystalline photovoltaic silicon ingots solidified in industrial (4 samples) or laboratory (4 samples) furnaces. Growth rates were ranging from 2 to 8 $\mu m\,s^{-1}$, temperature gradients from 5 to 12 $K\,cm^{-1}$ and the raw material was of various purity, from waste Si of electronic industry to Ultra Metallurgical Grade Si. Metallography showed that all ingots were presenting straight grain boundaries, twins (which are related to facet existence [6]) and some zig-zag grains elongated along the growth direction. Therefore it is considered that the obtained results could represent a general grain boundary behavior, regardless the precise growth conditions or material purity.

From these ingots, samples $3.5\times1\times2\ cm^3$ were cut with a precise diamond saw in order to secure the orthogonallity of the faces, a necessary condition for later proper grain boundary reconstruction. The analyzed faces were perpendicular to the growth direction. A top slice, 1 mm thick, was cut for SEM-EBSD analysis (Fig. 3(a)). Mechanical polishing was done on abrasive discs and by the use of diamond solutions from 9 μm to 1 μm until a homogeneous surface is obtained. After this, the samples were etched to reveal the grains into an aqueous solution of NaOH 10 $mol\,l^{-1}$, heated to 60 °C for 8 min. Scanning the samples with a regular office scanner (256 gray levels on 600 dpi) gave the most homogeneous images, compared to optical microscope or camera (Fig. 3(b)). Afterwards, the samples were mirror polished again by the use of colloidal silica solutions to get a passivized surface. In order to keep trace of the grain positions before introducing the sample in the Field Emission Gun-Scanning Electron Microscope (FEG-SEM) chamber, micro-indentation marks were performed on the pieces for precise adjustment under the field emission gun.

This polishing procedure was used repeatedly, to trace the grains in the other bulk of the sample. They were polished parallel to the surface by using a specifically designed tool. Ten to twenty pictures were taken at each depth for the reconstruction of the grains. In this, for each polishing, 400 μm was removed, precisely measured with a calliper. They were then etched following the above procedure and scanned pictures were taken.

2.3. Crystallographic orientation

The characterization tool is composed of a FEG-SEM, a low light camera on which a phosphorus screen is attached, a camera control unit (CCU), a TV monitor and a computer to index the EBSD patterns. After tilt compensation correction, the EBSD absolute angle resolution is typically obtained with an accuracy of 1° by using a FEG-SEM. During the automated scan, the electron beam was moved 2 mm from each point along the indented marks at a step size of 50 μm, *x*-size of 2300 μm and *y*-size of 2400 μm, magnification of 29× and working distance between 11 and 12 mm. At each point, the computer captures and indexes the pattern and stores the crystallographic data and the corresponding location and this data is then saved on the computer for indexing to determine the grain orientations.

From the EBSD measurements, the map of grains was obtained and typical results are shown in Fig. 4. The color indicated in the legend represents the plane orientation of each grain. Furthermore the three Euler angles were obtained for each grain.