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Formation mechanism and properties of twinned structures in (111) seeded directionally solidified solar grade silicon

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ABSTRACT

The growth structure of photovoltaic multicrystalline silicon formed by directional solidification presents a high fraction of Σ3 and higher order twins. Previous studies proposed that these complex structures are formed by a succession of 2D nucleation events of Σ3 twins on {111} growth facets at the triple line formed by their intersection with the crucible wall, another crystal, or the surface. In this work, we report the reproducible formation of multiple twinned domains inside solar grade Si single crystals grown by directional solidification above a (111) seed. These domains start on a Σ3 twin nucleated inside the crystal bulk, and systematically develop into similar twinned structures characterized by a ternary arrangement of grains in Σ3, Σ9, and Σ27 relationship. The mechanism of formation of the initial twin nucleus is discussed, and a scenario is proposed for the processes of subsequent multiple twinning. The growth competition between twin grains is shown to promote the appearance of incoherent twin boundaries, and dislocations near grain boundaries and in the twin grains themselves. The electrical activity of Σ-boundaries is measured, and the correlation between the structure of the defects and the resulting detrimental electrical activity is then discussed.

1. Introduction

A large fraction of the grain boundaries present in photovoltaic multicrystalline silicon (mc-Si) grown by directional solidification from the melt are twin boundaries, especially Σ3 [1,2]. The unique property of the perfect Σ3 (111) coherent boundary is its very low boundary energy [3], with which is associated a negligible electrical activity [4]. Perfect Σ3 (111) boundaries are thus acceptable defects in mc-Si growth as they are less harmful to the photovoltaic properties of the material than random boundaries. However, successive twinning events result in higher-order Σ9 and Σ27 boundaries that are more recombination active, and may act as sites for dislocation nucleation [5,6]. These twinning phenomena also play a major role on the overall mechanism of selection of the grain structure of multi-crystalline silicon [7]. A way to improve the control of the grain structure consists in using heterogeneous nucleation sites at the bottom of the ingot. The material obtained by this technique, known as High Performance multicrystalline silicon (HP-Si), shows a reduction in the area occupied by grains in $\Sigma 3^n$ relationship and much lower intra-grain dislocation densities [6]. Indeed, the random boundaries nucleated at the bottom of the ingot can better accommodate the thermo-mechanical stress in the ingot, thus improving the material quality [6]. With the aim of further improving the material quality to approach that of single crystals, another route has been recently developed which consists in growing quasi-monocrystalline ("monolike") ingots by directional solidification starting on a pavement of monocrystalline seeds that are placed in the bottom of the crucible [8]. This creates a

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single crystal or, more often, large crystals separated by grain boundaries parallel to the growth direction, the characteristics of which are determined by the relative misorientations between seeds [9]. The possibility of choosing the growth direction in this process allows a better control of the optical reflectivity, the <100> direction giving the lowest reflectivity with the standard basic surface texturing etch. However, this requires elimination of the twins which have be reported to be able to propagate from junctions between seeds or at crucible walls (see for instance [10]). For all the above reasons, there is a strong interest in understanding the processes of formation of the different twin boundaries and their associated electrical activity. The possibility of choosing the arrangements of the seeds makes monolike growth ideal for this. An example is the work of Trempa et al. [10], where nucleation of twins near the crucible wall was studied for different growth orientations. Another example was recently published by Autruffe et al. [11], who investigated dislocation generation from artificially created $\Sigma 3^n$ grain boundaries.

It is well accepted that, thanks to their very low energy, Σ3 (111) boundaries are formed by two dimensional nucleation on the (111) growth facet [12–14]. However, thermodynamic considerations indicate that the probability of forming such a twinned nucleus on the facet at the typical undercoolings at which these facets grow (1 °C–10 °C according to the data compiled in Ref. [14]) remains very low, except at particular favourable sites such as the triple line (TPL) formed at the intersection of the facet with the crystal surface or another grain [13,14]. Using the criterion developed by Voronkov [15] for the anchoring of facets at the solid-liquid-vapor triple junction during Czochraski growth, Hurle [13] showed that nucleation at this site could explain the high twinning frequency in III-V compounds; Duffar and Nadri [14] subsequently extended the approach to the case of directional solidification of multicrystalline silicon. More specifically, these last authors developed criteria for the occurrence of facets at grain boundary triple lines, and found, for particular facet orientations, nucleation probabilities in qualitative agreement with observed twinning frequencies. The mechanism was recently confirmed by Tandjaoui et al. [16] who, thanks to *in situ* synchrotron X-Ray imaging, directly observed twin nucleation at grain boundary grooves in silicon. It is also worth noticing that the same mechanism was found in molecular dynamics simulations by Pohl et al. [17]. In addition, numerous studies mention possible effects of impurities on the nucleation of Σ3 twins [3]. In particular, it has been argued that carbon, which is one of the main contaminants of solar grade silicon, might play a role through the formation of SiC precipitates. Such precipitates, when located at the twin boundary, causes a reduction in the grain boundary energy [18,19].

As they have much higher interface energy than the coherent Σ3 boundary, Σ9 and Σ27 twins are considered to result from successive events of nucleation of the coherent Σ3, which finally lead to complex multiple twinned structures. The elementary processes by which the formation of these multiple twinned domains occur are difficult to follow in a multi-crystalline growth structure. One such process may be the encounter of two grains previously nucleated with a Σ3-type relationship from the same grain as has been observed in *in situ* experiments on thin samples in Ref. [7]. In a *post mortem* study performed on bulk multi-crystalline samples [2], the different multiple twinned structures were observed and discussed in terms of the associated reduction of the grain boundary energy (for instance, the dissociation of the high energy Σ9 (221) boundary) but their relation with the instantaneous growth front morphology was not discussed. Other open questions concern the mechanism which control the crystallographic orientation of the twin boundary planes as well as the crystallographic distortions and dislocation densities at these boundaries, all parameters which play a determining role in their electrical activity [20].

In the present paper, a very reproducible process of formation of multiple twinned domains observed during monolike growth of solar grade silicon in the <111> direction is reported. These multiple twinned domains were observed several times in two distinct ingots grown with the same seed orientation, feedstock, and cooling rate. The possible mechanisms of initiation of these domains are discussed on the basis of the characterization of the initial interface by HRTEM and Atom Probe Tomography. The subsequent steps of multiple twinning are thoroughly investigated by EBSD on successive horizontal cross sections. Synchrotron X-ray White beam Topography and Rocking Curve Imaging are then used to characterize the dislocation network and lattice distortions associated with the formation of these twinned domains. Lastly, the electrical activities of the different twin boundaries are measured using Light Beam Induced Current (LBIC) and calibrated Photoluminescence imaging, and the correlations between the structural characteristics of the defects and the resulting detrimental electrical activity are discussed.

2. Experimental procedure

2.1. Crystal growth

A <111> monolike Si ingot with a diameter of 158 mm and a height of 100 mm was grown by directional solidification in a laboratory furnace devised for seeded growth [21]. For this, a circular (111)-monocrystalline seed (154 mm in diameter and 20 mm thick) was extracted from a Czochraslki ingot and placed in the bottom of a cylindrical Si_3N_4-coated silica crucible so as to cover the crucible base. The crucible was then filled with Solar Grade (SoG) silicon feedstock previously characterized by Glow Discharge Mass Spectrometry (GDMS): dopant concentrations were 0.65 ppm wt B and 1.4 ppm wt P; the only metallic element detected apart from Ge was Al at a level of 0.02 ppm wt, the other metallic elements being below detection limits of 1 ppm for Ta, 0.05 ppm wt for Fe, and lower than 0.01 ppm wt for the other elements. As for the concentrations of the light elements O and C, which depend on the growth environment, these were directly measured in the solidified ingot by FTIR. The O content, which results from the balance between the inward O flux from the oxidised crucible coating and the outward flux from the melt surface into the argon flow, was around 3×10^{17} at/cm^3. The C concentration profile, which mainly results from the contamination by the CO vapours present in the furnace atmosphere, and the segregation due to rejection by the advancing front, was found to vary from 1×10^{17} at/cm^3 at the top of the ingot to 4×10^{17} at/cm^3 at the bottom of the ingot, which means that the liquid remained under-saturated in C during most of the crystallisation, the saturation value being in the range 4×10^{17} at/cm^3 to 6×10^{17} at/cm^3. In contrast, it is known that, due to the contact of the Si melt with the Si_3N_4 crucible coating, the liquid ahead the front is slightly super-saturated in N during the whole crystallisation process, and that, depending on growth conditions, Si_3N_4 particles may precipitate inside the liquid or at the growth front [22].

The ingot was grown from the bottom (where the seed crystal was located) towards the top. Here, seeding is controlled thanks to a system for tuning heat extraction from the bottom of the crucible. The heating arrangement simultaneously provides top and lateral heating, which causes a change in the shape of the isotherms from concave towards the melt in the lower part to convex in the upper part of the ingot. This change in curvature occurs at around 25% of the height of the ingot, as revealed by the shape of iso-resistivity curves viewed on a peripheral vertical section of the ingot (Fig. 1) (Iso-resistivity curves represent instantaneous shapes of the