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Segregation, precipitation and dislocation generation between seeds in directionally solidified mono-like silicon for photovoltaic applications

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ABSTRACT

The generation of structural defects in directionally solidified mono-like silicon on a pavement of seeds has been investigated by synchrotron X-ray imaging, micro-FTIR mapping and electronic techniques. In particular, we analyse the region where the liquid Si penetrates between two seeds and we correlate the segregation and precipitation of impurities with the generation of cascades of dislocations during crystal growth. The solidified silicon grows epitaxially on the seeds without creating any distortion at the interface; however, due to the relative misorientation between the two seeds a highly and inhomogeneously distorted sub-grain boundary is created. Locally distorted zones, in particular linked to precipitates, are detected along and near the sub-grain boundary. The precipitates mainly consist of Si, C, N and O. Dislocations generated in these distorted zones propagate away from the sub-grain boundary towards the un-melted portions of the seeds, but they are blocked by barriers of precipitates formed at the positions of the initial seed surfaces. Higher in the ingot, bunches of dislocations propagate and multiply in the bulk.

1. Introduction

The main challenge of industrial-scale production of photovoltaic devices is the growth of large, high quality Si monocrystals at a much lower cost than that of microelectronics-quality crystals. Directional solidification has become a very promising method for achieving this. With the use of an extended monocrystalline seed, high quality "mono-like" Si ingots [1–3] can be grown. However, multiple seeds are needed in order to grow large crystals, which raises the question of growth at the boundary between seeds. Ideally, silicon grows vertically from the bottom up with the same orientation as the seed layer, therefore creating a single crystal. However, undesirable defects (sub-grain boundaries, impurities and dislocations) occur, often preferentially at the junction of the seeds [4] and extend to the whole ingot during the growth process, having a serious impact on solar cell performance. Grain or sub-grain boundaries are known to be major sources for the development of dislocation cascades and clusters [5]. Indeed, emissions of dislocations from specific kinked regions of a sub-grain boundary have been observed by TEM [6]. It has been shown that the distribution of shear stresses along slip planes and the resulting generation of dislocations depend on the crystallography of the grain boundary [7,8]. A possible cause of stress generation is the volume expansion of a solidifying trapped liquid: indeed, Kutsukake et al. [9] reported that, during solidification, liquid Si trapped at triple points of grain boundaries, favours the formation of a new twin boundary and this is a key condition for the generation of dislocations. Another more general cause of stress generation is the build-up of thermomechanical stresses in the cooling solid. Lastly, another known mechanism for dislocation nucleation is the punching mechanism where there are inclusions in the crystal. Ryningen et al. [10] noted the generation of dislocations in directionally solidified multicrystalline Si around impurities such as Si_3N_4 and SiC due to the differences in the thermal expansion coefficients during cooling. During cooling, stresses are produced around the inclusion due to the differential contraction of the crystal and the inclusion. When these stresses reach a critical value of about $\mu/30$ (where μ is the shear modulus), dislocations are nucleated [11]. These are dependent on the size of the inclusion, since more dislocations are punched out to release the increased misfit strain associated with larger precipitates.

In the present work, the generation of structural defects developed at the junction between the seeds in mono-like silicon processed by directional solidification on a pavement of seeds is investigated. In particular, we apply synchrotron X-ray diffraction rocking curve imaging (RCI) and RCI section topography to analyse the generation mechanism of dislocation clusters in the early stages of mono-like Si solidification. We focus on the region where the liquid Si penetrates between two seeds and we follow the evolution of the dislocations along the growth direction. Besides

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X-ray diffraction imaging (X-ray topography), Field-Emission Gun Scanning Electron Microscopy (FEG-SEM) and micro-Fourier Transform Infrared Spectroscopy (μ-FTIR) mapping are applied and the correlation between segregation-precipitation, along and near the sub-grain boundary, and the generation of dislocation cascades is discussed.

2. Experimental methods and procedure

2.1. Samples processing and preparation

A mono-like ingot was grown by directional solidification using a furnace with top and bottom heaters. Nine (001)-oriented seeds 110 mm × 110 mm × 20 mm were cut from a Czochralski-grown single crystal. The seeds were placed at the bottom of a Si_3N_4-coated silica crucible (380 mm × 380 mm base dimension) (Fig. 1) which was then filled with B-doped electronic grade silicon as feedstock. The feedstock and the top of the seeds were melted and the ingot was grown from the bottom towards the top by controlled lowering of the top and bottom temperatures. A dipping device was used in order to ensure that the seeds were partially and not fully melted. Due to the concavity of the isotherms (∼4° angle) the melting is stabilized at around 6 mm

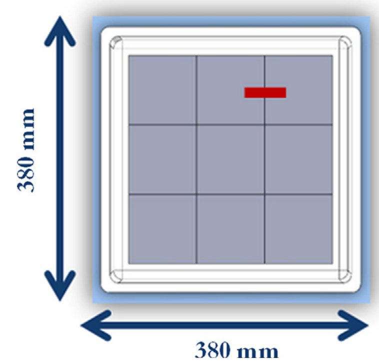

Fig. 1. A schematic view of the seed pavement, the position of extraction of the sample being illustrated by the red line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

from the bottom of the seed in the middle of the ingot. The process was carried out in an argon flow.

The solidified ingot was sliced parallel to the growth direction for evaluation. From the slice positioned 270 mm away from the front face of the ingot, a 20 mm × 10 mm slice was cut in the zone between two seeds. Fig. 1 shows a schematic view of the seeds pavement, the position from where the sample was extracted being illustrated by a red line.

The sample was mechanically polished on both sides down to a thickness of 800 μm. Finally, it was chemically etched on one side with standard Wright solution for observation of etch pits by optical microscopy and FEG-SEM.

2.2. Sample characterisation

In order to investigate the segregation and precipitation phenomena in the area between the two seeds, the sample was studied using a Field-Emission Gun Scanning Electron Microscope (FEG-SEM) equipped with an Energy-Dispersive X-ray Spectrometer (EDX) that provides qualitative and semi-quantitative analysis of elemental composition, and a Transmission Infrared Microscope (IRM). The concentrations of dissolved oxygen and carbon in the sample were determined by micro-Fourier Transform Infrared Spectroscopy (μ-FTIR). In the case of oxygen, the measurement was performed in imaging mode, with a spot size of 6.25 μm × 6.25 μm, a spectral resolution of 12 cm^{-1} and a spectral range from 2500 cm^{-1} to 650 cm^{-1}, while in the case of carbon, the measurement was carried out in point-by-point mode with a spot size of 20 μm × 20 μm, a step size of 12 μm × 12 μm and a spectral range from 2500 cm^{-1} to 500 cm^{-1}. These two modes were used because interstitial oxygen $[O_i]$ and substitutional carbon $[C_s]$ are associated with optical absorption lines at 1107 cm^{-1} and 605 cm^{-1}, respectively, in silicon, and the imaging mode configuration is not available in the range below 650 cm^{-1}.

The rocking curve imaging (RCI) technique, on both projection [12–14] and section [15–20] modes, in transmission, was used to study the crystalline quality of Si and visualise the defects in the same area of the sample. The principle of these techniques is presented schematically in Fig. 2

The experiments were carried out at beamline BM05 at the European Synchrotron Radiation Facility (ESRF). The synchrotron radiation from a bending magnet was monochromated at 20 keV using a vertically diffracting Si (111) double-crystal monochromator.

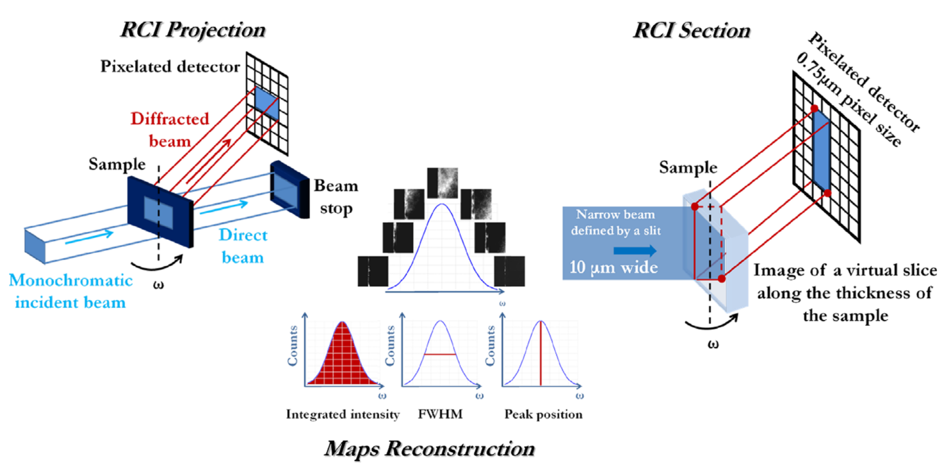

Fig. 2. Rocking curve imaging (RCI) is a quantitative version of monochromatic beam diffraction topography. The crystal is rotated along the diffraction curve for a given set of lattice planes, and the Bragg diffracted beam is recorded on a 2D pixel detector. Each pixel of the detector records its own "local" rocking curve (RC), so maps of the whole diffracted area of the sample can be reconstructed. Maps of integrated intensity provide information about the crystal perfection, maps of the angular position of the diffraction peak give access to the rotations of crystal lattice and maps of the FWHM give information about the level of local distortion in each zone of the crystal. RCI section topography is based on the same concept except that the beam is incident through a narrow slit and thus the diffracted beam corresponds to a virtual slice through the thickness of the sample.