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# Cellular dislocations patterns in monolike silicon: Influence of stress, time under stress and impurity doping

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ABSTRACT

Besides the well-known local sub-grain boundaries (SGBs) defects, monolike Si ingots grown by Directional Solidification present distributed background cellular dislocation structures. In the present work, the influence of stress level, time under stress, and doping by O and Ge, on the formation of dislocation cells in monolike silicon, is analysed. This is achieved by performing a comparative study of the dislocation structures respectively obtained during crystallisation of pilot scale monolike ingots on Czochralski (CZ) and monolike seeds, during annealing of Float Zone (FZ), CZ, and $1 \times 10^{20}$ at/cm$^3$ Ge-doped CZ (GCZ) samples, and during 4-point bending of FZ and GCZ samples at 1300 °C under resolved stresses of 0.3, 0.7 and 1.9 MPa during 1–20 h. Synchrotron X-ray White-beam Topography and Rocking Curve Imaging (RCI) are applied to visualize the dislocation arrangements and to quantify the spatial distribution of the associated lattice distortions. Annealed samples and samples bent under 0.3 MPa present dislocation structures corresponding to transient creep stages where dislocations generated from surface defects are propagating and multiplying in the bulk. The addition of the hardening element Ge is found to block the propagation of dislocations from these surface sources during the annealing test, and to retard dislocation multiplication during bending under 0.3 MPa. On the opposite, cellular structures corresponding to the final stationary creep stage are obtained both in the non-molten seeds and grown part of monolike ingots and in samples bent under 0.7 and 1.9 MPa. A comparative discussion is made of the dynamics of formation of these final dislocation structures during deformation at high temperature and monolike growth.



## 1. Introduction

The Czochralski (CZ) pulling method allows to grow dislocation-free silicon crystals. However, the more productive and less expensive method of directional solidification appeared more adapted to the processing of photovoltaic silicon. Recently, the so-called monolike growth process has been developed with the aim to combine the effectiveness of directional solidification with a high structural quality of the processed Si material. In this process, directional solidification is performed on a pavement of monocrystalline seeds laid on the bottom of the crucible. In the beginning of the monolike technology, the performance of the ingots was limited by the development of sub-grain boundaries (SGBs) which propagate and multiply as the crystallisation front advances [1]. The mechanisms of formation of these defects have been investigated, thus opening ways to reduce them [1]. However, even when these SGBs are suppressed, there remains, contrarily to the case of CZ and FZ grown Si crystals, a background of distributed dislocations generally adopting a cellular structure [2–3].

These self-organized structures, which are observed during the growth of crystals of various materials, result from a dissipative structuring by a process of point-defect assisted interaction of dislocations driven by the thermo-mechanical stresses imposed during growth, in a similar way to what occurs during deformation at high temperature [4–5]. The formation of these structures has been extensively studied in the case of GaAs grown by the different methods LEC, VCZ and VGF [6–7]. In semiconductors, where the resistance to dislocation motion is higher than in metals, the transient of formation of these structures is longer, which gives rise to successive transient creep stages during deformation at high temperature, as discussed for instance by Myshlyaev et al. [8] for the case of silicon. Impurities may be able to affect the kinetics of this process as was shown in the case of In doped GaAs LEC crystals,

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where the formation of dislocation cells was prevented [9]. In silicon, Ge doping was shown to block dislocation propagation during growth of CZ crystals without necking [10], and a reduction of dislocation densities was observed during directional solidification of mc-Si [11], while only a weak effect of Ge was found during annealing at 800 °C [12].

Concerning monolike silicon, the influence of thermal stresses during growth and cooling on dislocation densities was discussed in [13,14] on the basis of a comparison between ingots and annealed crystals. Cellular patterns observed in the non-molten part of seeds in monolike growth in [2] were explained by the mutual pressure between seeds during growth. Cellular dislocations structures in non-molten seeds have been examined near their junction with the grown part in [3]: regions with smaller cells and associated aligned dislocations domains were qualitatively attributed to seed bending. Thus, there is still a lack of data on the dynamics of formation of the cellular dislocation structure during growth of monolike silicon. The objective of the present work is to investigate the influence of stress, time under stress, and impurity doping by comparing the dislocations structures obtained during crystallisation experiments at a pilot scale with those observed in single crystals after annealing in conditions similar to crystal growth, or after 4-point bending at high temperature.

## 2. Experimental procedure

Reference dislocation structures of monolike silicon are obtained by processing in a pilot scale furnace in conditions representative of the industrial process. The influence of the different parameters (stress level, time under stress, and use of the strengthening elements O and Ge) is studied with the help of additional experiments: (i) simultaneous annealing test of Float Zone (FZ), CZ and Ge-doped CZ (GCZ) samples at high temperature, and (ii) 4-points bending experiments on FZ and GCZ samples at 1300 °C.

### 2.1. FZ, CZ and GCZ monocrystalline Si materials

A 8″ diameter [0 0 1] Ge-doped CZ crystal has been grown in-house in a Kayex puller at a rate V = 2.3 cm/h. The temperature gradient in the solid under the front was G = 17 °C/cm as determined by numerical simulation. GCZ samples are extracted from the same central region where the Ge concentration measured by GDMS was $\sim 1 \times 10^{20}$ at/cm$^3$. CZ samples are extracted from an undoped 9″ [0 0 1] CZ crystal of PILLAR with an oxygen concentration $\sim 8 \times 10^{17}$ at/cm$^3$, and FZ samples from an undoped 8″ [0 0 1] SILTRONIC crystal.

For the GCZ crystal the V/G ratio is a factor 1.7 higher than the transition value for nearly zero native point defects given by Voronkov (cited in [15]), so that frozen-in vacancies are dominating in the initial state. The same conclusion applies for the CZ crystal grown at a higher conventional rate (of the order of 5 cm/h). As for the FZ crystal, its large diameter should favour a vacancy-rich core according to the simulation predictions of [16].

The FZ, CZ and GCZ crystals were examined by White Beam Topography before the experiments to confirm that they were dislocation free.

### 2.2. Crystal growth

Monolike ingots of size G2 ($380 \times 380$ mm$^2$ base, height 180 mm) are processed in a pilot scale furnace where heating and heat extraction are designed to get a slightly convex shape of the isotherms. The seeds are four $156 \times 156 \times 20$ mm$^3$ [0 0 1] CZ plates, which are arranged at the bottom of a standard silica crucible with silicon nitride internal releasing coating, and covered with 50 kg of electronic grade silicon feedstock with B dopant ($9.75 \times 10^{15}$ at/cm$^3$). Directional melting onto the seeds is followed by solidification at a rate of 1 cm/h. A roughly constant vertical temperature gradient G = 10 °C/cm is maintained in solidifying Si, as determined from the one dimensional description of the thermal field proposed by Kvande et al. [17], using the temperature $T_{top}$ and $T_{bottom}$ measured with the thermocouples located respectively above and below the crucible. The radial temperature differences $\Delta T$ in the solid below the growth front at different times is simply estimated as $\Delta T = G\ H$, where H is the bow of the front at the corresponding height revealed by the shapes of the iso-resistivity curves on a resistivity map. $\Delta T$ varies between 9 °C at the bottom and 25 °C at the top.

In a particular experiment, an ingot was cast with a seed pavement made of one half of the bottom of a prior monolike ingot (thus recycling two CZ seeds), and another half extracted from the monolike grown part of the same ingot at an intermediate height (i.e. at ~32% fraction solidified).

### 2.3. Annealing

FZ, CZ and GCZ slices of the same dimensions as the seeds were simultaneously annealed with the intention to better understand the influence of O only (CZ), O and Ge combined (GCZ) and the absence of both elements (FZ), on the formation of dislocations. In order to be able to visualize the dislocation structures in an early stage of their development, the test conditions were voluntarily chosen to reduce both mechanical and thermo-mechanical stresses comparatively to those experienced by the seeds in standard crystal growth conditions. The FZ, CZ and GCZ seeds were placed directly on the graphite support plate thus avoiding contact with the rough nitride powder coated crucible bottom, and silicon bricks were laid upon them to simulate the silicon feedstock while avoiding the risk of indentation that might result from a granular feedstock [18]. Then an annealing was applied below the melting point with $T_{top} - T_{bottom} = 1350 - 1310$ °C = 40 °C, instead of $T_{top} - T_{bottom} = 1480 - 1290$ °C = 190 °C used at the start of monolike ingot crystallisation.

### 2.4. 4-points bending

The samples used for bending (half-length l = 37.5 mm, width w = 15 mm, thickness h = 2–3 mm) were extracted from the same CZ, FZ and GCZ crystals as above. Two Si wafers of standard thickness of 200 μm were placed above and below the specimens in order to avoid furnace contamination and direct contact with the bending rods. These wafers have a negligible effect on the stress imposed on the specimens due to their low moment of inertia. In order to promote multiple slip planes activation, all the specimens were cut in such a way that all surfaces are {1 0 0}. In this configuration, if the direction of the uniaxial stress is named [0 1 0], the 8 slip systems among 12 which exclude the Burgers vectors ±½[1 0 1] and ±½[ −1 0 1] perpendicular to the direction of stress are equivalently activated with a Schmid factor F = 0.408 (see Fig. 7 (c) (c′) in [19]).

The 4-point bending device consisted of $2 \times 2$ alumina rods with a diameter of 6 mm glued on a upper and a lower alumina plate (half-distances between rods resp. $x_1$ = 12.5 cm and $x_2$ = 32.5 cm) with a free weight (P = 1–10 N) placed on top. The assembly was implemented inside a laboratory scale DSS furnace. Heating and cooling times were 4 and 6 h respectively, and the time spent at the upper temperature (1300 °C) varied from 1 to 20 h.

Sample deformation is measured *post mortem* at discrete points with a height gauge. Since there is no localization of the deformation as shown by detailed profile measurements, the radius of curvature $r_0$ is uniform in the region between the two inner rods, and