

# STRUCTURAL PERFECTION OF CZOCHRALSKI GROWN SILICON CRYSTALS ANNEALED ABOVE 1500 K UNDER HYDROSTATIC PRESSURE

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The structural perfection of Czochralski grown silicon crystals annealed at 1580–1620 K under hydrostatic pressure up to  $10^9$  Pa was investigated by X-ray diffractometry and topography supplemented by the method of absorption of infrared rays. Such treatment suppresses dissolution of oxygen-related defects. From the static Debye–Waller factor dependence on the reflection order it was concluded that large clusters or dislocation loops are the dominant type of defects for most of the samples.

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## 1. Introduction

Czochralski grown silicon crystals (Cz-Si) with oxygen-related defects subjected to high temperature annealing (HT) above 1500 K under hydrostatic pressure (HP) change their defect structure. This effect takes place due to dissolution of oxygen precipitates in the undersaturated Si–O solid solution. The mentioned phenomenon may be caused by the action of hydrostatic pressure at the oxygen precipitate/matrix boundary [1, 2]. HP may also activate the nucleation centers for oxygen precipitation.

In this paper the effect of HP on the dissolution of oxygen-related defects in Cz-Si crystals at temperature  $\geq 1580$  K was investigated by means of determination of the static Debye–Waller factor,  $e^{-L}$ , as well as by the direct observation of the defect structure by synchrotron diffraction topography. Infrared radiation absorption was measured to follow the concentration of interstitial oxygen in the samples under investigation.

## 2. Theoretical background

The value  $L$  is known to be connected with the integrated reflectivity,  $R_i$ , of a real crystal. It depends considerably on the magnitude of the diffraction vector,  $H$ . The slopes of corresponding graphs, i.e.  $\ln L = f(\ln H)$  or  $\ln L = f(\ln N)$ , where  $N$  is reflection order, are equal to 1.5 or 2 for large precipitates (dislocation loops),  $L = 8nr^{9/2}(\beta H)^{3/2}$ , and for small clusters,  $L = kA^2H^2$ , respectively [3]. Here  $n$  and  $r$  are the mean concentration and the radius of microdefects, respectively;  $\beta$  and  $k$  are the constants depending on the lattice parameter and on the deformation characteristics of the matrix. The parameter  $A$  is the so-called "cluster force" [3], being proportional to the deformation level at the defect/matrix boundary.

Under the condition of weak absorption (hard radiation) the integrated reflectivity for a real crystal  $R_i$  is larger than that of a perfect crystal, due to diffuse scattering on defects. From the difference between  $R_i$  for a crystal with defects and that for a perfect sample,  $\Delta R_i$ , one can determine  $L$ , similarly as was done in [2]:

$$L = \Delta R_i / 2Q(t / \cos \Theta) \exp(-\mu t / \cos \Theta), \quad (1)$$

where  $Q$ ,  $t$ ,  $\mu$ , and  $\Theta$  stand for the reflectivity of an ideal-mosaic crystal, the crystal thickness, the linear photoelectric absorption coefficient and the Bragg angle for the chosen reflection  $H$  with the Miller indices  $hkl$ . Therefore one can determine the type of predominant microdefects by the investigation of the dependence:  $\ln L = f(\ln H)$  when measuring  $R_i$  for different reflection orders. From the above mentioned dependence one can also determine the value of  $nr^{9/2}$ , which is a kind of quantitative characteristics for the integral lattice distortions of a crystal.

## 3. Experimental

Cz-Si samples with the initial interstitial oxygen concentration,  $c_0$ , up to  $1.1 \times 10^{18} \text{ cm}^{-3}$ , as determined by Fourier transform infrared spectroscopy, were pre-annealed successively at 1000 K and 1325 K for 20 hours to create oxygen-related microdefects: oxygen precipitates with a density of about  $2 \times 10^4 \text{ cm}^{-2}$  and stacking faults with a density of  $3 \times 10^6 \text{ cm}^{-2}$ .

Afterwards the samples with such kind of defects were annealed at 1580 K-HP for 5 min or at 1620 K-HP for 30 min. The diffractometrical determination of  $R_i$  was performed as in [2] by the observation of the Laue diffraction of Mo  $K_{\alpha_1}$  radiation for different reflection orders: 220, 440, 660 and 880 from the  $\{110\}$  planes perpendicular to the (100) sample surface. Synchrotron X-ray diffraction topography (done at the D5 Optics beam line at the ESRF Grenoble) was used for the visualization of the defect structure of the samples (Fig. 1).

## 4. Results and discussion

The condition of the HT-HP sample treatment, the values of  $L_{660}$  and  $nr^{9/2}$  as well as the oxygen atoms concentration  $c_0$  are presented in Table.

One can note that the crystal perfection was much higher for all the samples annealed at 1580–1620 K, as compared to the initial state (sample no. 1) because

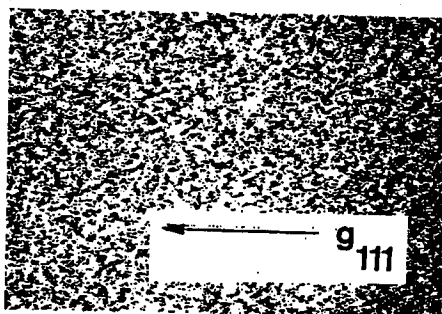


Fig. 1. X-ray topograph of sample no. 6,  $\lambda = 0.4 \text{ \AA}$ , 111 reflection, magnification  $\times 120$ .

TABLE

Conditions of the HP-HT treatment, the values of  $c_0$ ,  $L_{660}$  and  $nr^{9/2}$  for investigated  $C_2$ -Si samples.

Sample no.	HT-HP treatment	$c_0 \times 10^{17}$ [ $\text{cm}^{-3}$ ]	$L_{660}$ $\times 10^3$	$nr^{9/2} \times 10^{13}$ [ $\text{cm}^{3/2}$ ]
1	—	6.1	168	2.42
2	1580– $10^5$ Pa 5 min	8.6	26	0.40
3	1620– $10^5$ Pa 5 min	8.9	3	0.04
4	1580– $10^7$ Pa 5 min	7.7	58	0.91
5	1620– $10^7$ Pa 30 min	9.2	7	0.11
6	1580– $10^9$ Pa 5 min	7.9	33	0.52
7	1620– $10^9$ Pa 30 min	6.9	112	1.79

of the dissolution of oxygen precipitates in the silicon matrix (see the corresponding values of the  $L$  parameter). This was confirmed by the increase in the  $c_0$  values (Table). However, the structural perfection of the crystals (samples no. 4–7) annealed under HP ( $10^7$ – $10^9$  Pa) as compared to those (samples no. 2 and 3) heated at the same temperatures but at atmospheric pressure ( $10^5$  Pa) was in general worse.

Large precipitates or dislocation loops were found to be the dominant type of microdefects in most of the (1580–1620 K)–HP treated samples. This was shown by the analysis of the  $\ln L$  vs.  $\ln H$  plots (Fig. 2). These graphs were straight lines with slopes of about 1.5, except for the sample no. 5. Similar conclusion may be

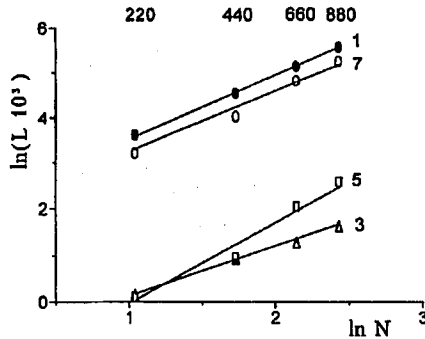


Fig. 2. Dependencies of the factor  $L$  on the reflection order  $N$  ( $N = (h^2 + k^2 + l^2)^{1/2}$ ) for the samples no. 3, 5, 7 and that for the non-treated sample no. 1.

drawn from the X-ray topography (Fig. 1). As is known, such dislocation loops may be generated near large oxygen precipitates by a prismatic dislocation punching mechanism. Therefore it follows that the defect spectrum of the investigated samples was probably of complex character.

The structural parameter  $nr^{9/2}$  was equal to  $0.40 \times 10^{-13} \text{ cm}^{3/2}$  and  $0.04 \times 10^{-13} \text{ cm}^{3/2}$  for the samples annealed at 1580 K (5 min) and 1620 (30 min) at  $10^5 \text{ Pa}$ , respectively. The HT-HP treatment at HHP =  $10^9 \text{ Pa}$ , for 5 or 30 min at the same temperatures resulted in higher levels of these parameters which were equal to  $0.52 \times 10^{-13} \text{ cm}^{3/2}$  and  $1.79 \times 10^{-13} \text{ cm}^{3/2}$ , respectively. Note that this value was much higher ( $2.42 \times 10^{-13} \text{ cm}^{3/2}$ ) in the case of the nontreated sample no. 1 (Fig. 3).

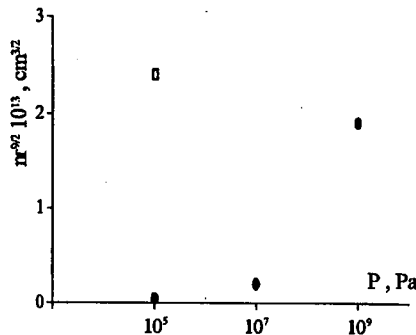


Fig. 3. Lattice distortion parameter  $nr^{9/2}$  versus pressure  $P$  for the samples annealed for 30 min.

It is important to note that the rise of pressure during annealing of the investigated samples at temperatures above 1500 K suppresses the dissolution of oxygen-related microdefects in the silicon matrix, as compared to the case of annealing at  $10^5 \text{ Pa}$ . This effect may be related to the lower diffusivity of oxygen atoms under HP conditions. According to [4], HP suppresses the out-diffusion of

oxygen from the oxygen-containing precipitates and probably of silicon interstitial from dislocation loops surrounding them. Another possible mechanism of the worsening crystal structure perfection can be related to the enhancement of the oxygen precipitation during the sample cooling, though such effect seems to be much less probable. For example, samples no. 2 and 3 annealed at temperature above 1580 K at atmospheric pressure and cooled at the same conditions as the other crystals had different defect structure.

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