$(1\bar{1}1, 1\bar{1}\bar{1}/002)$ Enhanced Borrmann Effect in Heat Treated Czochralski Grown Silicon Crystals

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The "enhanced" Borrmann effect present in the case of simultaneous reflection on $(1\bar{1}1)$ and $(1\bar{1}\bar{1})$ (three beam case $(1\bar{1}1, 1\bar{1}\bar{1}/002)$) is for the first time applied to the investigation of defects in crystals, i.e. oxygen clusters in heat treated Czochralski grown Silicon. From a comparison of the three beam intensities with those of the two beam case on (220) with CuKα radiation in crystals annealed at 1000 °C it is concluded that at the beginning of the heat treatment a relaxation of the strains due to unstable positioning of the interstitial oxygen atoms and an increase of local strains due to the growth of precipitates proceeded simultaneously.

Since Borrmann and Hartwig [1] reported that (in Germanium) the well known minimum X-ray absorption coefficient for two-beam diffraction on $\{111\}$, $\mu^{(2)}_{\min 111}$, decreased again when simultaneous diffraction on $(1\bar{1}1)$ and $(1\bar{1}\bar{1})$ occurred, which in the three beam case is symbolized by $(1\bar{1}1, 1\bar{1}\bar{1}/002)$, such many beam effects have been studied by many authors [2].

In two beam cases parameters such as $\mu_{\min}$, amplitudes of diffracted waves etc. are easily calculable for any given values of a deviation parameter W. In many beam cases, however, analytical solutions of the fundamental equations are obtainable only at the exact Bragg position, i. e. $W=0$. $\mu^{(3)}_{\min} = 19\ \mathrm{cm}^{-1}$ resulted from such calculations for Ge, CuKα, $(1\bar{1}1, 1\bar{1}\bar{1}/002)$ [3], which is much smaller than $\mu^{(2)}_{\min 111} = 105\ \mathrm{cm}^{-1}$. A direct measurement of $\mu_{\min}$ is impossible, because the related wave field can be isolated only by an infinitely thick crystal. Computer simulations, however, for $\mu^{(3)}_{\mathrm{eff}}$ in crystals with definite thickness were in good agreement with measurements [4].

Enhanced anomalous transmission arises in three beam cases because the wave field with $\mu^{(3)}_{\min}$ is more concentrated to the potential dips of the unit cell as is $\mu^{(2)}_{\min}$ in the related two beam cases [3]; also the polarization plays a more important role [5]. Consequently, many beam cases are considered to be more sensitive against lattice distortions and thus to be useful for the investigation of lattice defects in nearly perfect crystals [6]. However the effect is pronounced only in thick crystals which, while delivering weak intensities, are difficult to adjust. The use of white X-rays from synchrotron radiation will relax this problem: the adjustment is then simpler, the intensities are much higher, and the wavelengths are variable.

Two beam anomalous transmission has already been used for the characterization of nearly perfect crystals containing small defects [7]. J. R. Patel reported on the effect of oxygen clusters to the (220) anomalous transmission of CuKα_1 in heat treated Czochralski grown silicon crystals showing its usefulness to the study of oxygen precipitation [8]. We tried similar experiments using the three beam enhanced anomalous transmission in the $(1\bar{1}1, 1\bar{1}\bar{1}/002)$ case and compared it with the two beam case on $(2\bar{2}0)$. Among a lot of many beam cases just this one was used, because it is theoretically well analyzed and easy to adjust.

Crystal plates of $18 \times 25 \times 4\ \mathrm{mm}^3$ with [110] orientation were cut from a [115] Czochralski grown silicon ingot. The content of interstitial oxygen atoms was $1.1 \cdot 10^{18}$ atoms/cm^3, that of carbon was undetectable by infrared absorption. The plates were mechanically and chemically polished to a thickness of nearly 3 mm, then annealed at 1000 °C in Ar atmosphere for 2, 4, 6, and 10 hours, resp., cooled in a furnace and finally chemically etched down to a

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thickness of 1.5 mm ($\mu_0 t = 21.6$ for CuKα). For each specimen the integrated intensities of the two reflections in the symmetrical two beam case on (2$\bar{2}$0) and of the three reflections in the three beam case (1$\bar{1}$1, 1$\bar{1}\bar{1}$/002) were measured. CuKα_1 radiation from a Johannson type quartz monochromator was used (the fine focus tube was operated at 15 kV to avoid second order reflection). The specimen crystal was set on a precision goniometer which allowed an adjustment of the crystal, by rotating it around the θ-axis and also in a plane parallel to its surface, to a position where both reflections R_L and R_M had equal intensities and were arranged symmetrically within the vertical plane (R_L and R_M: reflections on (1$\bar{1}$1) and (1$\bar{1}\bar{1}$)). With this setting the (2$\bar{2}$0) reflection was also obtained in the horizontal plane by rotating the crystal around the θ-axis, i. e. around [001]. The X-rays irradiated, around the center of the specimens, areas of 4.5 mm^2 for (2$\bar{2}$0) and of 1.2 mm^2 for (1$\bar{1}$1,1$\bar{1}\bar{1}$/002) (in the three beam case the bundle fulfilling the Bragg condition is restricted also vertically). In both cases the maximum intensities of the rocking curves of the transmitted and diffracted beams were simultaneously measured with two scintillation counters.

The dependence of the integrated intensities on the annealing times in (2$\bar{2}$0) and (1$\bar{1}$1,1$\bar{1}\bar{1}$/002) diffraction is shown in Figures 1 and 2. The intensities are normalized by the transmitted intensity of the as-grown crystal.

a) Two beam case on (2$\bar{2}$0): We found the maximum of intensity for the specimen annealed for 2 hours, while in Patel's experiment [8] the anomalous transmission intensities decreased monotonously. This difference might be due to the different thermal histories of the specimen crystals, to the contents of dissolved carbon atoms and also to the different specimen preparations. The concentration of interstitial oxygen atoms, measured from the absorption of infrared light ($\lambda = 9\,\mu$m) at the same area, showed the maximum also for the specimen annealed for two hours and varied almost proportionally to the intensity of (2$\bar{2}$0) anomalous transmission. This could be understood, if the amount of oxygen atoms contained in the crystal, interstitial and/or precipitated, was the same for all specimens; in the present experiment, however, the concentration of the oxygen atoms was not uniform.

b) Three beam case (1$\bar{1}$1,1$\bar{1}\bar{1}$/002): The intensities decreased almost linearly with annealing time.

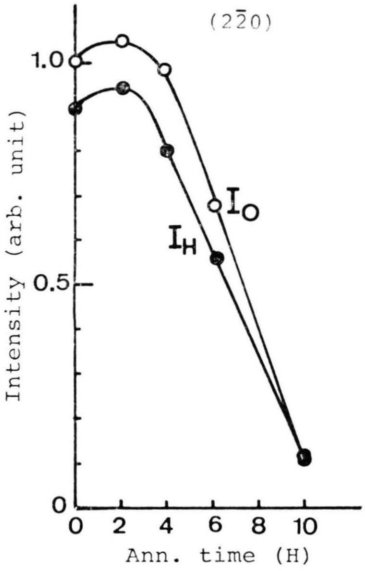

Fig. 1. Integrated intensities of the reflections R_0 and R_H in the symmetrical two beam case on (2$\bar{2}$0) vs. annealing times H (in hours) of the Czochralski grown silicon crystal plates. I_0 and I_H mean the transmitted and reflected intensities, respectively.

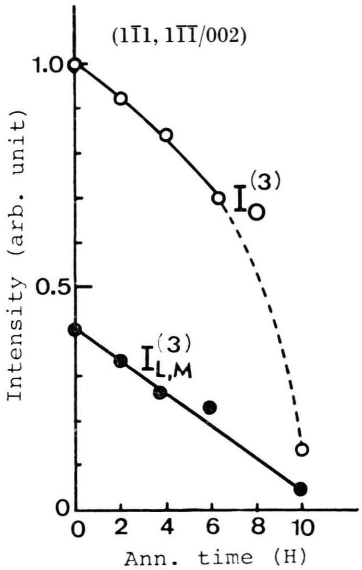

Fig. 2. Integrated intensities $I_o^{(3)}$ and $I_L^{(3)} = I_M^{(3)}$ (measured at the same area of the same crystal plates as in Fig. 1) of the reflections R_0, R_L, and R_M in the three beam case (1$\bar{1}$1, 1$\bar{1}\bar{1}$/002) vs. annealing times H (in hours).

As the measurements were done at the same areas of the crystal plates, the difference of the intensity change in both cases means that the influence of lattice distortions on the two and the three beam anomalous transmission is different.

By assuming a more complicated stage of the oxygen precipitation, we try to give a possible explanation of our observations. Interstitial oxygen atoms usually form Si – O – Si "molecules" where the O atom is situated not exactly in the center of the covalent bonding of two Si atoms, but close to it: the angle of the Si – O – Si bonding is said to be 162° [9]. But due to the comparatively rapid cooling during the crystal growth, Czochralski grown Si crystals contain in the as-grown state many interstitial oxygen atoms located at positions different from the "molecule" positions. These "unstable interstitial oxygen atoms" move in the earlier annealing stage towards nearest "molecule" positions, but at the same time additional oversaturated interstitial atoms (stable and/or unstable) begin to precipitate. The former process relaxes local strains distributed all over the crystal. The latter however introduces new strains around the sites of precipitates, because the oxygen precipitates formed at 1000 °C are of β-crystobalite structure [10], in which the distance of nearest Si atoms is 3.11 Å, instead of 2.25 Å in Si lattice.

These strains decrease the anomalous transmission of our two cases in a different way. In (2$\bar{2}$0) diffraction the mode with the smallest absorption is related to a wave field having its intensity maxima in the middle of adjacent (2$\bar{2}$0) atomic planes, so that its energy does not change in the direction perpendicular to the plane of incidence, that is [001]. In (1$\bar{1}$1,1$\bar{1}\bar{1}$/002) diffraction however the energy concentrates at positions farthest from the atomic rows along [110] [3]. The distances of the energy maxima from the nearest atomic plane or row, resp., are $\frac{1}{2}\,d_{220}$ for (2$\bar{2}$0) diffraction, but d_{220} for (1$\bar{1}$1, 1$\bar{1}\bar{1}$/002) diffraction. Therefore the effect of the strains caused by oxygen precipitates and/or by "unstable interstitial oxygen atoms" is larger in (2$\bar{2}$0) diffraction than in (1$\bar{1}$1,1$\bar{1}\bar{1}$/002) diffraction. In the specimen annealed for two hours the intensity increase of the (2$\bar{2}$0) diffraction due to the ordering of the unstable interstitial oxygen atoms is considered to have exceeded the intensity decrease due to precipitation of oxygen atoms, while in the (1$\bar{1}$1, 1$\bar{1}\bar{1}$/002) diffraction the effect of the local strains due to interstitial atoms is very small. The more rapid decrease of (2$\bar{2}$0) diffraction for longer annealing times, compared to (1$\bar{1}$1,1$\bar{1}\bar{1}$/002) diffraction, can be explained also by the different accomodations of the energy flows to the lattice.

As a conclusion, small defects in nearly perfect crystals influence the intensity of the anomalous transmission of two and three beam diffractions in a different way. The large difference of the intensity change in the present two cases means that the use of different kinds of diffractions, including two beam diffractions, might enable us to obtain informations like amounts, shapes and largeness, and orientations of small defects. Some of the experimental difficulties in many beam diffractions existing in the present experiments would be overcome by using the strong polarized white X-rays from synchrotron radiation sources.

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