

Double-Crystal Rocking Curve of the Forbidden Si 222 Reflection

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Abstract

The double-crystal rocking curve of the Si 222 reflection was obtained by a high-resolution technique. The angular half-width of the rocking curve was measured using Mo $K\alpha$ radiation on a floating-zone-grown silicon single crystal and found equal to $0.07''$, this value being close to that calculated from the known structure factor of the Si 222 reflection. A refined value for the structure factor was $1.47(2)$. For a Czochralski-grown Si single crystal with oxygen concentration $\sim 10^{18}$ atoms cm^{-3} , the angular half-width is higher by a factor of 2.5. The rocking-curve broadening is explained by the presence of oxygen in the silicon lattice.

Introduction

Since the early experiments by Bragg (1921) the structure factors of the 222 forbidden reflection for diamond-type structures have been measured in many studies. The existence of this reflection is mainly due to asymmetry in the bonding charge and, to a lesser degree, to anharmonic thermal vibrations. The data reported for the Si 222 reflection were obtained predominantly by measuring the integrated intensity of diffracted X-rays (Göttlicher & Wölfel, 1959; Renninger, 1960; DeMarco & Weiss, 1965*a*; Colella & Merlini, 1966; Hewat, Prager, Stephenson & Wagenfeld, 1969; Jennings, 1969; Roberto & Batterman, 1970; Rozenberg & Kleschinski, 1976) and γ -rays (Alkire, Yelon & Schneider, 1982). The *Pendellösung* technique has also been used (Fujimoto, 1974; Fehlmann & Fujimoto, 1975). There are some discrepancies between the data obtained by different techniques.

The structure factor $F(222)$ is smaller by two orders of magnitude than those of 'normal' reflections. The small value of the structure factor results in a large extinction distance, and, in accordance with the uncertainty relation, in a small intrinsic angular width of reflection. The depth of wave generation may be reduced by strong absorption or small crystal thickness. In such cases the angular width of the reflection must increase even for a perfect crystal.

Deutsch, Hart & Cummings (1987) obtained a double-crystal rocking curve of the Si 222 reflection. The angular width of the rocking curve was very small, but did not correspond to the 222 Si structure factor. The broadening was associated with both crys-

tal imperfections and the fact that the crystalline wafers used as specimens were rather thin ($T < A$, where T is the thickness and A is the extinction length). Therefore, the rocking-curve technique used by Deutsch, Hart & Cummings provided a measure of mosaicity in nearly perfect crystals, but could not be used for measuring structure factors.

In this work we measured 222 rocking curves for two dislocation-free silicon crystals grown by the floating-zone (FZ) and Czochralski (Cz) techniques. The experiments were carried out in the Bragg geometry on thick Si wafers considered to be semi-infinite crystals. The rocking width of the FZ-Si crystal was close to the calculated value. This fact led us to a new technique for measuring the structure factor of the forbidden reflection. Considerable broadening of the rocking curve for Cz-Si is explained by impurity oxygen atoms in the Si lattice.

Experimental and results

Measuring very narrow rocking curves (half-width $\Delta\theta$ of about $0.1''$) gives rise to complicated experimental problems and requires a suitable technique. In the present work, use was made of the method of Entin & Assur (1981; Assur & Entin, 1982), analogous to the method developed by Cusatis, Hart & Siddons (1983) (see Fig. 1). The X-ray beam from a fine-focus tube is transmitted through two 0.1 mm wide vertical slits (1 and 2) placed 200 mm apart and a 1 mm wide horizontal slit (3) providing a vertical divergence of 0.25° . The beam is reflected from two 15 mm thick plates of a monolithic silicon single crystal. The plates are joined by a relatively thin link. Attraction or repulsion of a permanent magnet (4) and a DC air-cored solenoid (5) results in misorientation of the plates. This misorientation angle is proportional to a

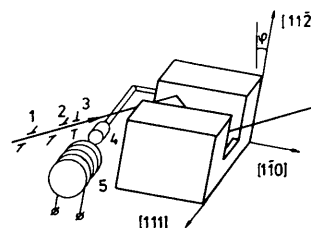


Fig. 1. Experimental set up.

bending moment which is proportional, in turn, to the current I in the solenoid, under the condition that the coercive force of the magnet is sufficiently strong.

The double-crystal unit with the necessary configuration was cut entirely from the crystal under investigation. After lapping, at least $100\ \mu\text{m}$ was removed from each surface by chemical etching. The etchant was a solution of HF and HNO_3 (1:8 in volume). One of the plates was glued to a goniometer axis by a slowly polymerizing adhesive. The magnet holder was glued to another plate. The whole unit could be rotated about the diffraction vector (angle φ in Fig. 1).

To eliminate harmonics from the continuous spectrum of the X-ray tube, the beam intensity was recorded by a solid-state detector. The spectrum of the diffracted radiation shows, in addition to the 222 reflection of Mo $K\alpha$ radiation, also the 111 and 333 reflections with wavelengths 2λ and $2\lambda/3$ respectively (Fig. 2).

Another factor to be considered is the multiple-beam scattering. It is known (e.g. Fujimoto, 1974) that the multiple reflection intensities decrease considerably in comparison with the true 222 reflection

with decreasing wavelength, and, on the other hand, the choice of angular ranges free of multiple-beam effects becomes a problem. For this reason, in most of the experiments described in the literature the measurements were performed with Cu $K\alpha$ or Co $K\alpha$ radiation.

We used the relatively hard Mo $K\alpha$ radiation to decrease absorption. The contrast of the multiple diffraction peaks above the 222 intensity is enhanced by double diffraction, because the intensity is proportional to the square of the reflectivity in this experiment. Fig. 3 shows the intensity of the doubly reflected beam *versus* the angle of rotation about the diffraction vector (if $\varphi = 0$, the $[11\bar{2}]$ direction is normal to the scattering plane). The multiple-beam peaks are 50% greater than the two-beam background.

The peaks were indexed using a program for calculating peak positions. In addition to the indices of secondary reflections, the indices of coupling reflections are also given for every peak, which makes evident the symmetry of the pattern with respect to $\varphi = 0$. The calculated and measured peak positions are in agreement within $5'$. The arrows in Fig. 3 indicate the angles used in the experiments.

The 222 and 333 rocking curves for the FZ silicon crystal are shown in Fig. 4. The left intensity scale refers to the 222, the right one to the 333 curve. The calibration of current *vs* angle was obtained by comparing the experimental 333 profile with that calculated using $F(333) = 33.17$ (Saka & Kato, 1986). Dispersion corrections and absorption were taken into account. The linear absorption coefficient μ was taken to be $14.64\ \text{cm}^{-1}$ and a value for the ratio of the imaginary parts of the polarizabilities $\chi_i(333)/\chi_i(0) \approx 0.6$ was used (Hildebrandt, Stephenson & Wagenfeld, 1973). Initially, the intrinsic reflection curve was calculated and then the convolution of two identical curves was performed. Comparing the measured and calculated half-widths, we obtained the following correspondence: $0.1'' - 36\ \text{mA}$. A similar correspondence, $0.1'' - 35.5\ \text{mA}$, was also obtained by comparing the rocking-curve tails. The angular half-width of the 222 rocking curve is 10.5 times smaller than that of the 333 and is equal to $0.07''$.

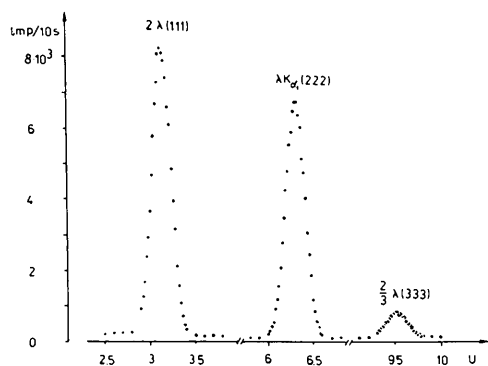


Fig. 2. Radiation spectrum of the 222 singly diffracted beam. U is the detector pulse height in volts.

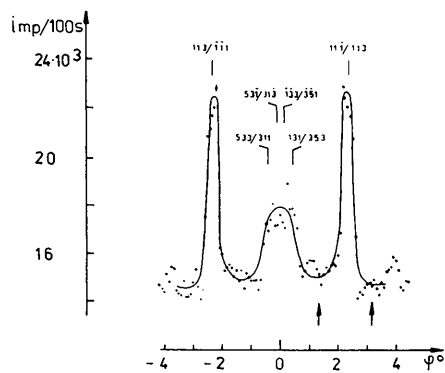


Fig. 3. Intensity of the 222 doubly diffracted beam *versus* the azimuthal angle φ .

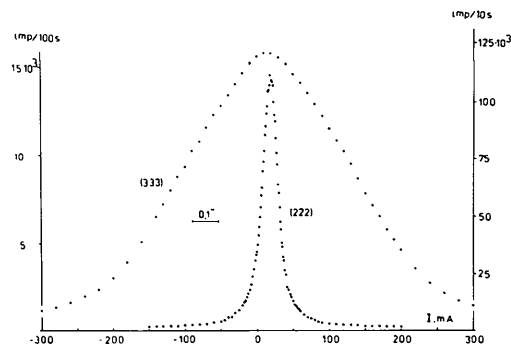


Fig. 4. The 222 and 333 rocking curves for the FZ silicon crystal.

Using the same procedure, the 222 rocking curve for the Cz silicon crystal was also measured (see Fig. 5; R is the reflection coefficient for a singly reflected beam incident on the second block). The angular scale was calibrated as for Fig. 4. The 222 rocking curve of Fig. 4 and the calculated curve for $F(222) = 1.47$ are given in Fig. 5 for comparison. The half-width for Cz silicon is greater by a factor of 2.5 than that for FZ silicon and has a value of $0.17''$. The peak values of the reflection coefficient differ by a factor of 2.1.

Fig. 5 shows that the reflection coefficient is not larger than 0.3 under the present conditions. This is associated with absorption, which is of great significance for extremely weak forbidden reflections (if absorption was neglected, we should get $R_{\max} \approx 0.75$).

The rocking curves obtained for FZ silicon crystals were used to determine $F(222)$. The most reproducible data were obtained by fitting the calculated to the observed values of the ratio

$$q(333)/q(222),$$

where q is the area under the rocking curve. From experiment

$$q(\mathbf{H}) = \int_{I_{\min}}^{I_{\max}} \mathcal{I}(I) dI,$$

$\mathcal{I}(I)$ is the intensity of the doubly diffracted beam for a certain value of current I . The theoretical value is

$$q(\mathbf{H}) = \sum_{c=\sigma, \pi} \int_{-\infty}^{\infty} d\theta \int_{-\infty}^{\infty} R_c(\alpha) R_c(\alpha - \theta) d\alpha = \rho_{\sigma}^2 + \rho_{\pi}^2,$$

where $R_{\sigma(\pi)}(\alpha)$ is the reflection coefficient, and $\rho_{\sigma(\pi)}$ is the integrated reflectivity for σ or π polarization. In this way, the error in the calibration of the angular scale is avoided, and the statistical error becomes small. Thus, the value $F(222) = 1.47$ (2) is obtained.

The accuracy is limited by two factors. One is related to incomplete removal of multiple scattering. An analysis of the rocking-curve profile, with no slowly decreasing background, yields an upper limit

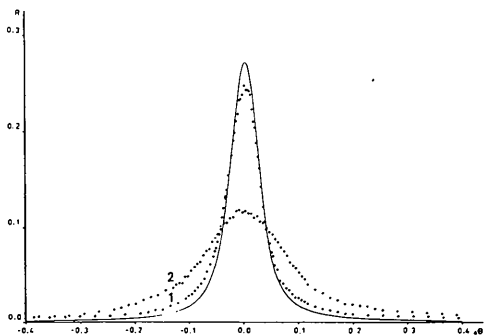


Fig. 5. Observed (points) and calculated (continuous line) 222 rocking curves. (1) FZ silicon crystal; (2) Cz silicon crystal.

of 1% for such an error. The second factor is associated with microdefects and macrostrains in the crystal, which result in broadening the rocking curve. As is seen from Fig. 5, the experimental half-width for a FZ crystal exceeds by 5–10% the calculated value, whereas the reflection-coefficient peak is 5–10% lower than its calculated value. This indicates that the FZ crystal under study was not quite perfect. But this analysis shows that such a small broadening cannot cause any increase in the q value (within 1%). Either factor may only lead to an overestimate of $F(222)$. It should be stressed that an estimate of the principal sources of errors in experimental determinations of structure factors for forbidden reflections is only possible through the shape of the rocking curve.

It may be seen that q is much more sensitive to variations in F than the integrated intensity ρ , since $q = \rho^2$, the difference between the two polarizations being neglected.

Discussion and concluding remarks

The measured value of the 222 structure factor coincides with that obtained by γ -diffractometry, $F = 1.456$ (8) (Alkire, Yelon & Schneider, 1982). The uncertainty in this value was derived only from statistical errors. The errors associated with multiple scattering effects could not be estimated because of the small wavelength used, $\lambda = 0.12 \text{ \AA}$.

There exists a noticeable difference between the value of $F = 1.64$ (3) (Fehlmann & Fujimoto, 1975) and both our results and those of DeMarco & Weiss (1965*b*), Colella & Merlini (1966), Jennings (1969), Roberto & Batterman (1970) and Alkire, Yelon & Schneider (1982). In our opinion, it may be explained as follows. In principle, the *Pendellösung* method is undoubtedly the most precise. However, the oscillation period is rather sensitive to macrostrains inevitably present even in the most perfect crystals. A decrease in the oscillation period due to long-wave sinusoidal deformations was demonstrated by Smirnova & Entin (1988). For weak forbidden reflections, the sensitivity to a strain gradient seems to be much higher.

The broadening of the 222 rocking curve for the Cz crystal could be explained by the presence of oxygen atoms in the silicon lattice. As is known, the oxygen concentration in such crystals may amount to $10^{18} \text{ atoms cm}^{-3}$, the concentration of other impurities being lower by at least an order of magnitude (Richter, 1985). In FZ crystals the oxygen concentration is lower by two orders of magnitude.

The increment in the rocking-curve width, $\delta\theta$, caused by variations in the lattice parameter a is

$$\delta\theta \approx \frac{1}{a} \frac{da}{dc} \delta c \tan \theta_B,$$

where θ_B is the Bragg angle and δc is the variation

in the atomic concentration of oxygen, c . Since oxygen in silicon forms an interstitial solid solution, the coefficient of the concentration dependence of the lattice parameter, $(1/a)(da/dc)$, is of the order of unity. Under the assumption of inhomogeneous distribution of oxygen atoms over the silicon crystal, the quantities δc and c are of the same order of magnitude. Thus, we have $\delta\theta \sim 0.1-1.0''$. This agrees with the experimentally determined broadening value, $\delta\theta \approx 0.1''$. The broadening of higher-order narrow reflections (e.g. 880 for Ag $K\alpha$ radiation) was found to be of the same order of magnitude for other Cz silicon crystals as well.

The assumption that broadening of the rocking curve is caused by concentration variations of the lattice constant is also confirmed by the dependence of this effect on the X-ray wavelength. For Ag $K\alpha$ radiation, $\delta\theta$ was found to decrease by a factor of 1.2-1.3, which agrees with the behaviour of $\tan \theta_B$ in the expression for $\delta\theta$.

Maximum broadening of a rocking curve should be expected when the characteristic length of concentration inhomogeneities is of the order of the extinction length, $\Lambda(222) \approx 1.7$ mm. For smaller characteristic lengths diffraction occurs from an average perfect lattice, without broadening (Smirnova & Entin, 1988). For the other limiting case of very long characteristic lengths we deal, in fact, with a homogeneous solid solution within the irradiated volume of the crystal.

However, it should be noted that similar diffraction phenomena may also be caused by an elastic field of oxygen clusters, with a mean separation distance of the order of Λ . From this condition it follows that these clusters should have the size $D \sim 1-10$ μm .

Although the width ratio for the 222 rocking curves of two silicon crystals is close to 2.5, the integrated reflectivities, ρ , differ by only 20%. This is explained by the fact that the 222 Si reflection is almost kinematical even for the relatively hard Mo $K\alpha$ radiation: $\Gamma \approx 1.43$, where the enhancement factor, Γ , is the ratio of the integrated reflectivities of an ideally imperfect to a perfect crystal (DeMarco & Weiss, 1965b). On the other hand, for strong 'normal' reflections such as 111 or 333, the enhancement factor is much larger ($\Gamma \sim 10^2$). However, this factor indicates

the variation limits of the integrated reflectivity only. A noticeable variation begins when $|\nabla\varepsilon|\Lambda$ ($|\nabla\varepsilon|$ is the effective strain gradient caused by imperfections) reaches a value comparable with the dynamical angular width of the reflection. In our case the integrated reflectivities of the 111, 333 etc. reflections for Cz and FZ silicon crystals are the same. Thus, to make minute lattice disturbances observable one must concentrate on weak reflections, and especially on the shapes of their rocking curves rather than integrated reflectivities.

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