The Evaluation of Crystal Perfection by Means of the Asymmetric Bragg Reflections

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Abstract

A new X-ray method for the evaluation of single-crystal perfection is presented. The method is based on the analysis of the dependence of integrated intensity on the asymmetry parameter of the asymmetric Bragg reflections in the case of plate-shaped crystals. As a result, the parameters describing the level of crystal perfection can be determined. The application of the presented method enriches considerably the capabilities of the Bond method applied in precise lattice-parameter determination of thin near-surface single-crystal layers. An example of the investigation of a boron-doped epitaxial layer on silicon is described.

List of symbols

- $\varphi$: angle of rotation around diffraction vector
- $\alpha_0$: angle between crystal surface and reflecting planes
- $\alpha$: arc $\tan\left(\tan\alpha_0 \sin \varphi\right)$
- $\gamma_0$: $-\cos \theta_B \sin \alpha_0 \sin \varphi - \sin \theta_B \cos \alpha_0$
- $\gamma_H$: $-\cos \theta_B \sin \alpha_0 \sin \varphi + \sin \theta_B \cos \alpha_0$
- $b$: $\gamma_0/\gamma_H$; asymmetry parameter
- $Q$: kinematical integrated intensity per unit length
- $\mu$: linear absorption coefficient
- $\rho_{M}, \rho_{P}$: integrated intensities for ideally mosaic and perfect crystal, respectively
- $\rho_{IN}$: integrated intensity for a crystal plate of infinite thickness
- $\rho^{N}$: normalized integrated intensity
- $f_1, f_2$: deformation functions connected with finite plate thickness and crystal perfection, respectively
- $r^-, r^+$: shape coefficients of conchoids
- $W(A)$: mosaic blocks misorientation function
- $b$: Burgers vector
- $g, t$: real structure parameters
- $a$: lattice parameter
- $D$: layer thickness
- $t_{ext}$: extinction length
- $d$: X-ray penetration depth

Introduction

In our previous paper (Wołczyrz, Pietraszko & Łukaszewicz, 1980) the application of asymmetric Bragg reflections in the Bond method of precise lattice-parameter measurements was described. In the present work, attention is paid to the utilization of the properties of asymmetric reflections for the evaluation of single-crystal perfection. The dependence of the integrated intensity on the reflection asymmetry and on the crystal perfection has been used for this purpose. The application of the procedure described below enriches considerably the capabilities of the Bond method allowing us to discuss the supplementary features of the investigated crystal. As a result, one can obtain the parameters describing the degree of crystal perfection, the knowledge of which makes it easier to interpret the experimental results, obtained by means of the procedure discussed in the previous paper.

The method of crystal-perfection investigation based on integrated intensity measurements was suggested many years ago (Evans, Hirsch & Kellar, 1948). It was developed mainly on the basis of the Zachariasen (1967) theory and for symmetric reflections (Brown & Fatemi, 1974; Werner, 1974; Olekhnovitch, Rubtsov & Schmidt, 1975). The possibility of applying the asymmetry to the evaluation of crystal perfection was first shown by Mathieson. His two experimental works (Mathieson, 1975, 1977) were supplemented by general considerations (Mathieson, 1979). At the same time Stephan (1978) proposed a simple theoretical model of the real crystal structure, describing sufficiently Mathieson's experimental data. Papers published recently by Kato (1980a, b) allow one to replace the Stephan model by the more general one, based on the statistical dynamical diffraction theory.

The works mentioned above used two slightly different effects resulting from extinction. The first is the variation of reflection intensity with the changes of the degree of crystal perfection. This phenomenon may be relatively easily observed and is simple to interpret although it is not very useful from the
The experimental point of view, because of the necessity of measuring intensities on the absolute scale. The second phenomenon is a characteristic dependence of the integrated intensity on the reflection asymmetry, represented by the angular position $\varphi$ of the crystal rotated around the diffraction vector $S$. The shape of the conchoid shown in Fig. 1 is the result of the variation of the so-called 'level of interaction' (Mathieson, 1979) qualifying the character of the diffraction process. The utilization of this phenomenon in the evaluation of the crystal perfection is especially convenient, because it is enough to know the shape of a conchoid, disregarding its absolute dimensions. It constitutes the basis of the method described below.

**Theory**

Let us consider a plate-shaped flat single crystal with outer surface greater than the beam cross section. Diffraction geometry in this case and the basic notation were explained in our previous paper (Wolczyk et al., 1980).

The main reason for the conchoid-like dependence of the intensity on the angle $\varphi$ is absorption. In the frame of the kinematical diffraction theory, for the infinitely thick crystal, we have

$$\rho_M = \frac{Q}{2\mu} (1 - \beta_0 \sin \varphi),$$

where

$$\beta_0 = \tan \alpha_0 \cot \theta_B.$$  

For a plate of thickness $T$, the ideal conchoid (1) suffers a deformation and can be described by

$$\rho_M = \rho_M f_1(\varphi),$$

where

$$f_1(\varphi) = 1 - \exp(-\mu \zeta T)$$

is the deformation function connected with the finite plate thickness, and

$$\zeta = \frac{\cos \alpha}{\cos \alpha_0} [\csc(\theta_B + \alpha) + \csc(\theta_B - \alpha)].$$  

The second reason for the deformation of the curve (1) is the extinction. The theory of Hirsch & Ramachandran (1950) allows one to obtain the deformation function $f_2(\varphi)$, which transforms the kinematical curve $\rho_M^*(\varphi)$ into a dynamical one $\rho_M^*(\varphi)$, according to the formula

$$\rho_M^*(\varphi) = \rho_M^*(\varphi) f_2^\star(\varphi).$$

Function $f_2^\star(\varphi)$ is given by

$$f_2^\star(\varphi) = \left\{ \frac{1}{|g|} \exp\left[-(1 + k^2)(|g| + C) + 1\right] \right\}^{-1},$$

where

$$g = \frac{m c^2}{e^2 \lambda N} \mu (1 + k^2)^{1/2} (1 - \beta_0^2 \sin^2 \varphi)^{-1/2},$$

$$C = \ln \frac{32}{3\pi}.$$  

In the general case, the curve of intensity as a function of $\varphi$ takes the form

$$\rho(\varphi) = \rho_M^*(\varphi) f_1(\varphi) f_2(\varphi).$$

The function $f_1(\varphi)$ depends on the plate thickness, and for silicon crystals of more than several tens of $\mu$m thick for Cu $K\alpha_1$ radiation it takes to a good approximation the value 1. The function $f_2(\varphi)$ for the crystals of intermediate perfection is strongly dependent on the perfection degree.

Since the intensity conchoids $\rho(\varphi)$ for crystals of intermediate perfection are obtained from the kinematical curve by its multiplication by the functions $f_1(\varphi)$, they essentially differ in shape. It is useful to compare them by reducing the conchoids to the normalized form:

$$\rho^N(\varphi) = \rho(\varphi) / \rho(0).$$

The normalized conchoids (10) have the common point $\rho^N(0) = 1$, whereas their values for the extreme asymmetries $\rho^N(-90^\circ)$ and $\rho^N(90^\circ)$ can be treated as curve-shape coefficients $r^-$ and $r^+$. Therefore

$$r^- = \rho^N(-90^\circ);$$

$$r^+ = \rho^N(90^\circ).$$

The shape coefficients are connected with the asymmetry parameter introduced in the previous paper:

$$\frac{r^-}{r^+} = |b^+|.$$  

Fig. 2 shows the normalized conchoids $\rho^N(\varphi)$ for the kinematical and dynamical limits in the case of the 533 and 444 reflections for the silicon wafer with the surface (111).
It happens very seldom that a crystal plate is cut with a sufficiently great accuracy in relation to the surface assumed. It influences the values of the asymmetry parameter $b$, the experimentally determined values $b_{\text{exp}}$ and the experimental shape coefficients.

Expression (13) allows one to calculate the $b$ parameter for different asymmetries as a function of the outer surface misorientation:

$$b = \frac{1 + \tan(\varepsilon_1 + \varepsilon_2) \cot \theta_B \sin(\varphi - \varepsilon_1)}{1 - \tan(\varepsilon_1 + \varepsilon_2) \cot \theta_B \sin(\varphi - \varepsilon_1)}.$$  \hspace{1cm} (13)

This misorientation is defined by angles $\varepsilon_1$ and $\varepsilon_2$ representing tilting of the vector $n$ from the ideal position in the two perpendicular directions as is shown on the stereographic projection in Fig. 3. In practice, (13) allows calculation of the real value of angle $\varepsilon_1$, when $b_{\text{exp}}$ is known. In the next step, the substitution of $\varepsilon_1$ into the equation $r^+ = r^+(\varepsilon_1)$ leads to the calculation of the proper value of the shape coefficient.

Relation (13) is a purely geometrical one, whereas the function $r^+ = r^-(\varepsilon_2)$ possesses the degree of structure perfection as a parameter, and for the crystals of intermediate perfection it can be evaluated on the basis of a concrete model of the real crystal.

Following Stephan (1978), we take into account the layer model of mosaic blocks of thickness $t$ and angular misorientation described by the Lorentz function:

$$W(\Delta) = \frac{2g}{1 + (2\pi g)^2 \Delta^2}.$$  \hspace{1cm} (14)

The two parameters characterizing the real crystal, $t$ and $g$, are connected by the relation

$$g = \frac{1}{\pi} \frac{2}{3\sqrt{\pi |b|}}.$$  \hspace{1cm} (15)

where $b$ is the Burgers vector of the dislocations forming the grain boundaries. For silicon, $|b| = a/\sqrt{2}$ and

$$g, t \approx 5 \times 10^8 \text{ m}^{-1}.$$  

Expression (15), resulting from a simple model of mosaic block formation induced by the dislocation clustering on the small-angle grain boundaries, was discussed by Larson & Corey (1969) and Kuznetsov (1973).

Stephan (1978) gives the relation between the integrated intensity and asymmetry for certain real structure parameters $g$ and $t$, connected by (15). This formula is the basis of calculations carried out in the present work.

Fig. 4 presents the dependence of the integrated intensity of the 533 reflection from silicon (111) and Cu Kα$_1$ radiation on the perfection degree, represented by the parameter $t$. Fig. 5 shows the plot of the shape coefficient $r^-$ defined by (11) versus $t$, for 533 and 444 reflections. There exists a region of ambiguity in which the two values of $t$ correspond to one $r^-$ value. This ambiguity, connected with the application of one parameter $r^-$ describing the curve $\rho(\varphi)$, may be eliminated by the analysis of the function $f_2(\varphi)$ in the full range of the angle $\varphi$ values.

Fig. 6 presents the results obtained for the low-dislocation silicon crystal. The appropriate deformation function is shown against the background of the curve family $f_2^x(\varphi)$, where

$$f_2^x(\varphi) = f_2(\varphi)/f_2(0)$$  \hspace{1cm} (16)

$$\rho \times 10^4$$

$\varphi = -90^\circ$

$\varphi = 0^\circ$

$\varphi = 90^\circ$

Fig. 4. The dependence of the integrated intensity for the 533 reflection of silicon (111) on the perfection degree represented by parameter $t$.
are the curves $f_2(\phi)$ normalized to unity at the point $\phi = 0$. The experimental curve represents quite well the ideal perfect curve.

A further characteristic resulting from the Stephan model is the dependence of the X-ray penetration depth on the perfection degree, which can be calculated from the relation

$$d = \left[ \left( \mu + \frac{1}{t_{\text{ext}}} \right) \left( \frac{1}{\gamma_0} + \frac{1}{\gamma_2} \right) \cos \frac{\pi}{2} \cos \alpha \right]^{-1},$$

(17)

where

$$t_{\text{ext}} = 1/\bar{g}Q$$

(18)

is the extinction length, depending on the quantities $\bar{g}$ and $Q$, included in the paper by Stephan (1978) in (6). The penetration depths depending on $t$ according to (17) are shown in Fig. 7 for the most typical Cu K$_\alpha_1$ reflections of silicon (111).

**Experimental**

In order to present the procedure, the investigations were performed on the perfection and lattice parameters of the epitaxial layer with known parameters. As a test sample, the 2.5 µm thick silicon epitaxial layer with boron concentration equal to $10^{26}$ m$^{-3}$ was used. The layer was deposited on the silicon plate, 200 µm thick, doped with arsenic ($10^{26}$ m$^{-3}$).

From the preliminary X-ray goniometric studies it appeared that the plate surface was misoriented by 1–2° from its theoretical position, parallel to the (111) crystallographic planes.

The results of measurements performed by means of the double-crystal attachment to the Bond diffractometer, proposed by Hart & Lloyd (1975), are shown in Fig. 8. A highly boron-doped epitaxial layer has got a distinctly wider diffraction profile than the substrate, which results from the high level of structure mosaicity.

For the sample described above, the measurements of the conchoid $\rho(\phi)$ for 444 reflection (Cu K$_\alpha_1$ radiation) was performed. For this purpose, the intensity profiles were registered for seven asymmetry angles $\phi$ by using the Bond diffractometer, described by Łukaszewicz, Kucharczyk, Malinowski & Pietraszko (1978). The profiles were numerically split into components connected with the substrate and layer. Two
Table 1. Experimental integrated intensity versus asymmetry for layer and substrate component of the 444 reflection

<table>
<thead>
<tr>
<th>$\varphi$ (°)</th>
<th>$\rho_L$ (relative units)</th>
<th>$\rho_S$ (relative units)</th>
<th>$\rho_L/\rho_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-90</td>
<td>46.0</td>
<td>26.5</td>
<td>1.73</td>
</tr>
<tr>
<td>-60</td>
<td>41.1</td>
<td>26.4</td>
<td>1.56</td>
</tr>
<tr>
<td>-30</td>
<td>32.4</td>
<td>23.4</td>
<td>1.38</td>
</tr>
<tr>
<td>0</td>
<td>23.6</td>
<td>18.3</td>
<td>1.29</td>
</tr>
<tr>
<td>30</td>
<td>18.0</td>
<td>13.1</td>
<td>1.37</td>
</tr>
<tr>
<td>60</td>
<td>14.2</td>
<td>9.1</td>
<td>1.56</td>
</tr>
<tr>
<td>90</td>
<td>12.3</td>
<td>7.1</td>
<td>1.73</td>
</tr>
</tbody>
</table>

The numerical results are collected in Table 1.

(a) Determination of the misorientation angle

The following values of the asymmetry parameters for the layer and substrate can be estimated by using $\rho_L$ and $\rho_S$ from Table 1:

$$ b_{exp L} = \rho_L(-90°)/\rho_L(90°) = 3.73, $$

$$ b_{exp S} = \rho_S(-90°)/\rho_S(90°) = 3.74. $$

In this case (13) gives the following value of the misorientation angle:

$$ \varepsilon_2 = +1.5^\circ, $$

which overlaps the previous estimation.

(b) Evaluation of the level of perfection

According to (6), the intensity ratio of the layer and substrate is given by

$$ \frac{\rho_L}{\rho_S} = \frac{f_{1 L} f_{2 S}}{f_{1 S} f_{2 L}}, $$

where the functions $f_{1 L}$ and $f_{1 S}$ have the form

$$ f_{1 L} = 1 + \exp(-D/d_L), $$

$$ f_{1 S} = \exp(-D/d_S). $$

Table 2. Theoretical data for 444 reflection from silicon epitaxial layer of thickness $D$

<table>
<thead>
<tr>
<th>$t$ (μm)</th>
<th>$f_{2 L}$</th>
<th>$f_{2 S}$</th>
<th>$f_{2 L}/f_{2 S}$</th>
<th>$d_1$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.231</td>
<td>0.189</td>
<td>1.24</td>
<td>1.00</td>
</tr>
<tr>
<td>40</td>
<td>0.232</td>
<td>0.240</td>
<td>1.05</td>
<td>1.03</td>
</tr>
<tr>
<td>30</td>
<td>0.234</td>
<td>0.271</td>
<td>1.00</td>
<td>1.40</td>
</tr>
<tr>
<td>20</td>
<td>0.242</td>
<td>0.336</td>
<td>1.05</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table 3. Comparison of the experimental and theoretical normalized conchoids for substrate and layer

<table>
<thead>
<tr>
<th>$\varphi$ (°)</th>
<th>$\rho_L^e$</th>
<th>$\rho_S^e$</th>
<th>$\rho_L^t$</th>
<th>$\rho_S^t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-90</td>
<td>1.50</td>
<td>2.02</td>
<td>1.50</td>
<td>1.89</td>
</tr>
<tr>
<td>-60</td>
<td>1.45</td>
<td>1.79</td>
<td>1.40</td>
<td>1.71</td>
</tr>
<tr>
<td>-30</td>
<td>1.29</td>
<td>1.37</td>
<td>1.29</td>
<td>1.71</td>
</tr>
<tr>
<td>0</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>30</td>
<td>0.71</td>
<td>0.62</td>
<td>0.47</td>
<td>0.56</td>
</tr>
<tr>
<td>60</td>
<td>0.50</td>
<td>0.54</td>
<td>0.40</td>
<td>0.51</td>
</tr>
</tbody>
</table>

The substrate deformation function $f_{2 S}$ is in fact a deformation function for a perfect crystal. The shape of $f_{2 L}$ is unknown because of the lack of information about the state of the layer. Therefore it is necessary to choose the real structure parameters so as to get good agreement between the experimental and theoretical values of $\rho_L/\rho_S$.

Table 2 contains the theoretical values of $\rho_L/\rho_S$ according to (21) for several values of $t$, the values of the deformation functions for the layer and substrate and the penetration depths. The calculations of $\rho_L/\rho_S$ are performed for three layer thicknesses $D$. Good agreement between experiment and theory is obtained.
for the following layer thickness and real structure parameter:

\[ D = 2.2 \mu m \]
\[ t = 30 \mu m. \]

The functions \( \rho_1(\varphi) \) and \( \rho_5(\varphi) \) corrected for the finite diffraction volume and their normalized values can be calculated by using these data. It is necessary to apply the simplification taking into the calculation the penetration depth resulting from the layer perfection. For thick layers, such an approximation does not cause any errors; for thinner ones it can influence the final results, when the layer distinctly differs from the substrate in its perfection. The experimental results are compared with the calculations in Table 3. The agreement between experimental and theoretical conoids is satisfactory. It is possible to improve it by fitting the \( \rho_1/\rho_5 \) curves along their whole length and not simply in two points: \( \varphi = 0 \) and \( \varphi = -90^\circ \). This requires a numerical algorithm.

(c) Measurement of the lattice parameters

For the sample discussed, lattice-parameter measurements by using the Bond-type diffractometer and Cu \( K\alpha_1 \) radiation were performed. The \( n \)-rotation method (cf. Wolczyr et al., 1980) was applied. The X-ray reflections were chosen so as to separate the layer and substrate components well. The results are presented in Table 4.

The estimation of the internal stresses induced by dopants leads to the conclusion that their value for the substrate is smaller by two orders than for the layer. Thus, the lattice parameter for the substrate does not depart from the pure silicon value. However, it is seen that the substrate lattice parameter slightly changes in the boundary region, towards the value appropriate to the layer. It testifies the existence of the intermediate region layer–substrate which according to Kuroda & Miyamoto (1979) has a thickness of 1–2 \( \mu m \).

Conclusions

This method for the evaluation of single-crystal perfection is based on the asymmetric-reflection method described in our previous paper. The procedure described provides the basis for the evaluation of the X-ray penetration depth and allows the distribution of the lattice parameter in the layer to be obtained.

The method was applied to epitaxial layer investigation. This choice of experimental example was motivated by the complexity of the problem, providing the occasion to consider several aspects of the method. Obviously, the same procedure can be applied in the case of homogeneous single crystals of any type. The additional measurements carried out for a typical mosaic crystal KCl and for silicon deformed during heat treatment showed the usefulness of the method in both cases.

It seems to be advisable to include other X-ray wavelengths, especially those longer than Cu \( K\alpha_1 \) radiation, in the experiment, which should reduce penetration depth and would allow the differential measurement to be performed with two different wavelengths.

Moreover, the procedure described can be applied to the precise determination of the thickness of thin single-crystal layers. The results seem to be more accurate than those obtained by traditional X-ray methods of layer-thickness determination.

### References


