

A New Method for Surface Analysis of Crystals using X-ray Diffraction under the Specular Reflection Conditions

BY P. A. ALEKSANDROV AND A. M. AFANAS'EV

I. V. Kurchatov Institute of Atomic Energy, 123182, Moscow, USSR

AND A. L. GOLOVIN, R. M. IMAMOV, D. V. NOVIKOV AND S. A. STEPANOV

Institute of Crystallography, USSR Academy of Sciences, 59, Leninskii Prospekt, 117333, Moscow, USSR

(Received 25 October 1983; accepted 17 September 1984)

Abstract

A new method is suggested for simultaneous determination of small misorientations of the surface from the chosen crystallographic plane and the thickness of the surface amorphous layer. The method is based on X-ray diffraction experiments under specular reflection conditions. The determination of misorientation consists of the comparison of diffraction curve intensities for hkl and $\bar{h}\bar{k}\bar{l}$ reflections obtained from the plane normal to the crystallographic plane along which the crystal surface is cut. The accuracy of the determination exceeds the accuracy known for other methods. The amorphous layer is considered to be either an oxide film or any other disordered layer having no crystal structure. The layer thickness is determined from the consideration of the diffraction curve shapes using comparison with theoretical calculations. The method provides detection of layers ~ 5 Å in thickness, which seems to be unique for X-ray diffraction methods. The method may find wide application in the surface analysis of perfect crystalline specimens, in particular, of materials used in semiconductor microelectronics.

1. Introduction

The progress achieved recently in the investigations of the crystal structure of solids by X-ray diffraction has given rise to a new method of studying very thin surface layers.

The diffraction arrangement for the realization of the method was first suggested by Marra, Eisenberger & Cho (1979) and combines the conditions providing symmetric Laue-case diffraction with glancing incidence of the beam (Fig. 1). The small value of the glancing angle provides intense specular reflection of the incident and the diffracted waves from the crystal surface, which, in principle, gives the possibility of studying the crystal structure of surface layers as thin as several tens of ångströms.

Later, the dynamical theory of diffraction under the

conditions of specular reflection was developed for perfect crystals (Afanas'ev & Melkonyan, 1983). In particular, it has been shown that the value of the departure angle Φ_h of the specularly reflected diffracted wave (Fig. 1) strongly depends on how strictly the Bragg condition is fulfilled. Thus, the angular deviation of the incident beam from the exact Bragg condition by $\sim 0.1''$ results in the $\sim 1'$ change of the departure angle.

This theory was used (Golovin & Imamov, 1983a; Golovin, Imamov & Stepanov, 1984) to realize a new scheme for experimental measurements where the incident beam is collimated only in the plane of incidence, whereas the diffracted waves, having different deviations from the Bragg angle, are separated depending on the angle at which they leave the specimen (angle of departure). The simplicity of the experimental arrangement has stimulated fast development of the theory in close relation with the experiment and provided practical applications of the method.

On the basis of the dynamical theory several diffraction problems have been solved under the conditions of specular reflection with due account of diffracting plane misorientations from the surface normal and the possible presence on the crystal surface of an amor-

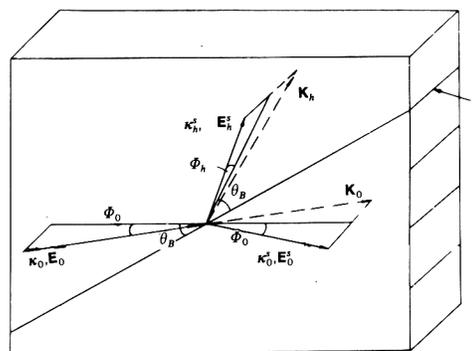


Fig. 1. The optical scheme of diffraction under specular reflection conditions. (1) Diffracting planes.

phous layer (Aleksandrov, Afanas'ev & Stepanov, 1984; Aleksandrov, Afanas'ev, Melkonyan & Stepanov, 1984). It has been predicted that the method has high sensitivity to small misorientations ($\sim 0.5^\circ$). It has also been suggested that there are very thin ($\sim 10 \text{ \AA}$) amorphous films on the specimen surface. On the basis of this theory (Aleksandrov, Afanas'ev, Melkonyan & Stepanov, 1984) the thicknesses of amorphous layers on the surface of silicon crystals have been determined experimentally (Golovin & Imamov, 1983b). The measurements were taken in the integral angular mode and the data obtained were confirmed by ellipsometry data.

Although these results can be considered only as preliminary, they still prove that the method suggested is very promising for practical needs.

The present work solves the diffraction problem under the conditions of specular reflection with simultaneous study of the possible presence of an amorphous film on the specimen surface and small misorientations of diffracting planes in the crystal from the surface normal. On this basis we have developed a new method to check how perfect the single-crystal surface is, which, in particular, can be used to check the initial quality of semiconductor wafers in microelectronics. In other words, we are suggesting a method to measure small misorientations of the specimen surface from the given crystallographic plane with the accuracy $\pm 0.5'$ and simultaneously to determine the amorphous layer depth (e.g. an oxide film or any other disordered amorphous layer on the specimen surface) with the accuracy 5–200 \AA depending on the film thickness. The method is illustrated by intensity measurements both in the integral and differential modes.

2. Theory

The solution of the problem is based on the considerations made by the authors in previous papers (Aleksandrov, Afanas'ev & Stepanov, 1984; Aleksandrov, Afanas'ev, Melkonyan & Stepanov, 1984). In our case (Fig. 2), for each polarization mode there are three wave fields in vacuum (incident, specularly reflected and specularly reflected diffracted waves, respectively), four fields in the amorphous film, and four fields in the crystalline substrate. These eleven fields are joined with the aid of eight boundary conditions for the fields and their derivatives at the vacuum–film and film–substrate interfaces. These conditions are similar to those suggested by Aleksandrov, Afanas'ev & Stepanov (1984) but with due account of misorientation (Aleksandrov, Afanas'ev & Stepanov, 1984). In addition, the wave fields in the crystalline substrate are related by two other conditions following from the basic equations of the dynamical theory (Aleksandrov, Afanas'ev &

Stepanov, 1984). As a result, we have ten conditions that permit us to express the amplitudes of all the waves *via* the amplitude of the incident wave, *i.e.* to solve the problem posed. Then, the final expression for the amplitude of the reflected diffracted wave is

$$E_h^s = \frac{2\Phi_0 W_1 W_2 (U_2 - U_1) E_0}{C \chi_h (W_2 b_0^1 b_h^2 - W_1 b_0^2 b_h^1)}, \quad (1)$$

where

$$b_0^j = (\Phi_0 + U_j) \left[\cos(sp_0) - i\Phi_0 \frac{\sin(sp_0)}{p_0} \right] - i\chi_0^{am} \frac{\sin(sp_0)}{p_0},$$

$$b_h^j = (\Phi_h + \psi + U_j) \left[\cos(sp_h) - i\Phi_h \frac{\sin(sp_h)}{p_h} \right] - i\chi_0^{am} \frac{\sin(sp_h)}{p_h},$$

$$p_{0,h} = (\Phi_{0,h}^2 + \chi_0^{am})^{1/2}, \quad j = 1, 2.$$

Φ_0 = angle of incidence, Φ_h = departure angle of the specularly reflected diffracted wave, $\psi = 2\varphi \sin \theta_B$, θ_B = Bragg angle, φ = misorientation angle of diffracting planes with respect to the surface normal (the values $\varphi > 0$ correspond to the misorientation of the diffracting planes towards the specularly reflected beam), $s = 2\pi t/\lambda$, λ = wavelength of the incident radiation, t = thickness of the amorphous film, $W_j = U_j^2 - \Phi_0^2 - \chi_0$; $U_{1,2}$ = roots of the dispersion equation in the form (Aleksandrov, Afanas'ev & Stepanov, 1984):

$$(U^2 - \Phi_0^2 - \chi_0)[(U + \psi)^2 - \Phi_h^2 - \chi_0] - C^2 \chi_h \chi_{\bar{h}} = 0.$$

The dispersion equation is solved numerically; of four roots we should choose two for which $\text{Im } U_j > 0$; C is the polarization factor ($C = 1$ for σ polarization and $C = \cos 2\theta_B$ for π polarization); $\chi_0, \chi_h, \chi_{\bar{h}}, \chi_0^{am}$ are the Fourier components of the crystal polarizability. The reflection coefficient is determined by the ex-

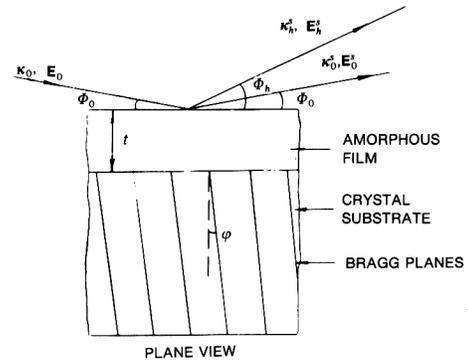


Fig. 2. The arrangement for X-ray diffraction from the model crystal; t is the thickness of the amorphous film, φ is the misorientation angle.

pression (Afanas'ev & Melkonyan, 1983)

$$p_h^s = \frac{|E_h^s|^2}{|E_0|^2} \frac{\Phi_h}{\Phi_0}. \quad (2)$$

Angles Φ_0 and Φ_h are related by the following expression:

$$\alpha = (\Phi_0 + \psi)^2 - \Phi_h^2, \quad (3)$$

where $\alpha = -2 \sin 2\theta_B(\theta - \theta_B)$ is the conventional parameter describing the deviation from the Bragg condition in the dynamical theory. Thus, if the rays incident on the crystal have various deviations from the Bragg conditions, we can record the intensities of the diffracted radiation as a function of the departure angle Φ_h and obtain the diffraction curve.

The above relationships permit us to calculate the intensity of reflected diffracted waves from crystals covered with thin amorphous films and at the same time to take into account the misorientation of diffracting planes.

The parameters sought are t , φ and χ_0^{am} . At $t=0$ the expression derived coincides with the corresponding expression of Aleksandrov, Afanas'ev & Stepanov (1984) and at $\varphi=0$ with the expression for the intensity of the diffracted wave Aleksandrov, Afanas'ev, Melkonyan & Stepanov, 1984).

Amorphous layers on the surface of semiconductor wafers are either oxide films or disordered layers caused by the surface treatment. In both cases $\chi_0^{am} = \chi_0$.

To be able to compare the calculated data with experimental measurements taken in the differential mode, the expressions derived should be averaged over departure angles Φ_h within the limits determined by the slit of the detector and then summed up taking into account relative contributions from different polarizations:

$$\begin{aligned} I^{\text{diff}}(\Phi_0, \Phi_h) &\sim \frac{\cos 2\theta_B}{1 + \cos 2\theta_B} \\ &\times \int_{\text{slit}} T(\Phi_0, \varphi_h - \Phi_h) 2\varphi_h p_h^{s(\sigma)}(\Phi_0, \varphi_h) d\varphi_h \\ &+ \frac{1}{1 + \cos 2\theta_B} \\ &\times \int_{\text{slit}} T(\Phi_0, \varphi_h - \Phi_h) 2\varphi_h p_h^{s(\pi)}(\Phi_0, \varphi_h) d\varphi_h. \end{aligned}$$

Here integration is a convolution with the transmission function T of the detector slit; the integrand $2\Phi_h$ is due to the renormalization of reflection coefficient connected with integration over the departure angle.

To compare the theoretical results with the experimental measurements taken in the integral mode the

expressions derived should be integrated over all departure angles Φ_h .

$$\begin{aligned} I^{\text{int}}(\Phi_0) &\sim \frac{\cos 2\theta_B}{1 + \cos 2\theta_B} \int_0^\infty 2\Phi_h p_h^{s(\sigma)}(\Phi_0, \Phi_h) d\Phi_h \\ &+ \frac{1}{1 + \cos 2\theta_B} \int_0^\infty 2\Phi_h p_h^{s(\pi)}(\Phi_0, \Phi_h) d\Phi_h. \end{aligned}$$

These operations are performed numerically by computer.

3. Measurement procedure

The method here suggested is based on the fact that the misorientations and amorphous films on the surface influence diffraction curves in different ways. An amorphous layer on the crystal surface changes the curve shape, whereas small misorientations, affecting the shape of the curves only slightly, drastically change their total intensities (Aleksandrov, Afanas'ev, Melkonyan & Stepanov, 1984; Aleksandrov, Afanas'ev & Stepanov, 1984).

As a rule, semiconductor wafers are cut out of crystals in such a way that their surfaces coincide with certain crystallographic planes. Therefore, it is possible to choose several non-parallel diffracting planes that are normal to the surface. Measuring diffraction curves on both sides of such planes and considering the differences in their intensities, we can determine the plane misorientations. The vector that is the sum of misorientation vectors of these two nonparallel planes determines both the direction and the value of the maximum surface misorientation relative to the given crystallographic plane. On the other hand, analyzing the curve shape, *i.e.* fitting the data calculated with the use of different values of parameter t to the experimental results, we can determine the depth of an amorphous layer.

4. Experimental

The set up used in the experiment was first described by Golovin & Imamov (1983a) and Golovin, Imamov & Stepanov (1984) (Fig. 3). An X-ray beam from a source is collimated in the horizontal plane by a crystal monochromator (silicon, 220 reflection) and a vertical slit and then falls onto the crystal under study, forming a small angle Φ_0 with its surface. At the same time the specimen is oriented in such a way that the Laue-case diffraction conditions are realized for planes normal to the surface. Since the angle of incidence is small, both the transmitted and diffracted waves experience intensive specular reflection in the crystal. As a result, two waves appear – a specularly

reflected wave and a specularly reflected diffracted wave – which are registered by two detectors rotating about the goniometer axis (detectors 2 and 1, respectively). Since there is no collimation with respect to the deviation from the Bragg angle, the waves with all possible deviations from the Bragg angle experience diffraction from the crystal. To separate specularly reflected diffracted waves corresponding to different deviations from the Bragg angle, detector 1 has an adjustable vertical slit, since, in virtue of (3), such waves have different departure angles Φ_h .

Diffraction curves were measured in two different modes. In the first, integral, one (Golovin & Imamov, 1983a), the crystal under study is rotated about the goniometer axis, thus changing the angle of beam incidence, while detector 1 (without a slit) records simultaneously the intensities of specularly reflected diffracted waves having all possible departure angles Φ_h . In the second, differential, mode (Golovin, Imamov & Stepanov, 1984), the specimen is rigidly fixed at a certain angle with respect to the beam, whereas detector 1 with a slit is rotated about the goniometer axis and records the intensities of specularly reflected diffracted waves having certain departure angles Φ_h .

We have used a standard 1.2 kW source with a copper anode. A crystal monochromator (Si 220 reflection) provided an angular divergence in the horizontal plane equal to $\sim 6''$. The divergence in the vertical plane was about 1° and determined by the spectrometer design. The vertical slit behind the crystal monochromator separated $\text{Cu K}\alpha_1$ line of the spectrum and formed a beam $\sim 25\text{--}100\ \mu\text{m}$ wide.

We studied a perfect silicon single crystal, $25 \times 25 \times 1\ \text{mm}$ in size, cut parallel to (100) within $\pm 5'$. The surface was chemically and mechanically polished in the usual way and then rubbed with cotton gauze to

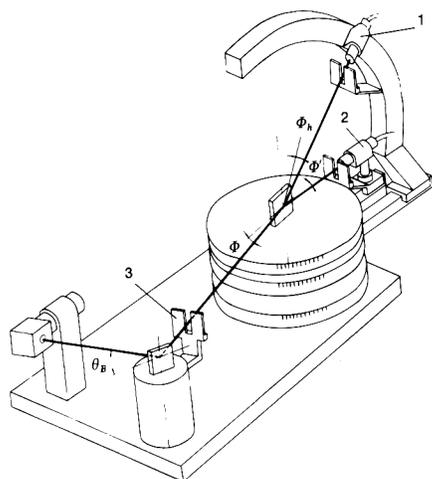


Fig. 3. The schematic drawing of the experimental set up. (1) and (2) X-ray detectors, (3) slit.

create a disturbed layer. After taking measurements, the surface was etched to a depth of $\sim 1\ \mu\text{m}$ and the measurements were taken anew.

Two diffracting planes, (022) and (0 $\bar{2}\bar{2}$), were chosen for the experiment, the diffraction curves being measured on both sides of each plane, *i.e.* for hkl and $\bar{h}\bar{k}\bar{l}$ reflections.

During the experiment in the differential mode with a slit width equal to $\sim 50\ \mu\text{m}$ the angular resolution with respect to angles Φ_h for detector 1 was not worse than $3'$.

The crystal zero position with respect to the angle of incidence was determined with the aid of detector 2, fitted with a $20\ \mu\text{m}$ slit to provide separate registration of the reflected beam and the part of the incident beam that does not go through the crystal. The crystal, being rotated about the goniometer axis, was set at a zero position where the intensity of the beam that passed by the crystal was maximal.

5. Results and discussion

For convenience, we shall denote the two {220} planes normal to the surface for which the diffraction curves were measured as plane I and plane II, respectively.

The integral curves measured on both sides of plane I coincide both in shape and intensity within the limits of experimental resolution. The coincidence of the intensities proves that plane I is normal to the surface with an accuracy not worse than $\pm 0.5'$. At the same time, the shape of the curves (the decrease in intensity for small angles of incidence as compared with the case of perfect crystals) shows that there is an

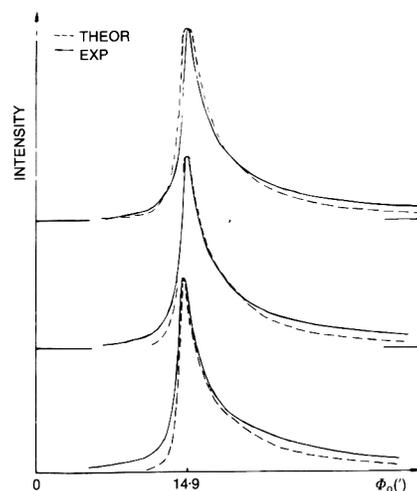


Fig. 4. The determination of the amorphous film thickness by fitting the calculated curves. The solid line denotes the experimental curve (measured in the integral mode). Dashed lines indicate the curves calculated with different values of film thickness. The curves were fitted on the basis of the half-width values and the angular positions of the intensity maxima. Upper curve: $t = 200\ \text{\AA}$; middle curve $t = 250\ \text{\AA}$; lower curve $t = 300\ \text{\AA}$.

amorphous layer on the surface. The fitting of the calculated curves by the use of different parameters t (Fig. 4) indicates this layer to be $250 \pm 25 \text{ \AA}$ thick.

It should be noted that ellipsometry measurements also showed the presence on the surface of a disturbed layer. The results of the measurements did not correspond to the known nomograms. Thus, neither the nature of the disturbed layer nor its thickness could be determined. The disturbed layer may be caused by the scraps on the crystal surface owing to rubbing with the cotton gauze.

The integral curves measured on both sides of plane II are shown in Fig. 5(a) by solid lines. Different intensities of these curves show that plane II is somewhat misoriented with respect to the surface. By fitting the calculated curves, we determined that misorientation in this case was $\sim 3'$ relative to the (100) plane, the direction of maximum misorientation being normal to plane II.

The results obtained are also confirmed by measurements taken in the differential mode for two different angles of incidence:

$$\Phi_0 = 12' \quad \text{and} \quad \Phi_0 = 20'.$$

The differential curves measured on both sides of plane I coincide within the accuracy of the experiment. These curves together with the curves calculated for a 250 \AA thick layer are shown in Fig. 6.

Differential curves measured for plane II have similar shape but different intensities. For incidence angle $\Phi_0 = 12'$ the maximum intensity ratio is 1.33 and for $\Phi_0 = 20'$ it is 1.98. The corresponding calculated values for $\varphi = \pm 3'$ are 1.80 and 1.38.

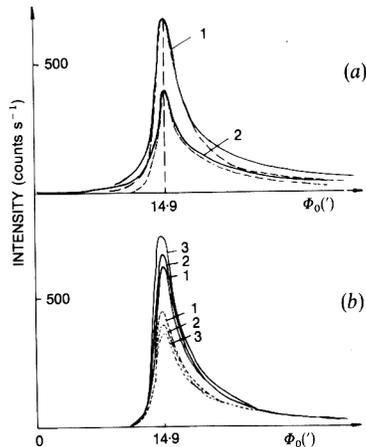


Fig. 5. The determination of the misorientation angle from the intensity ratio for 022 and 022 reflections. (a) Solid lines indicate experimental curves measured in the integral mode for (1) 022 and (2) 022 reflections. Dashed lines indicate the fitted curves for $\varphi = \pm 3'$, $t = 250 \text{ \AA}$. (b) Calculated curves for different misorientation angles. Solid lines correspond to $\varphi < 0$. (1) $\varphi = \pm 2'$, (2) $\varphi = \pm 3'$, (3) $\varphi = \pm 4'$.

It should be emphasized that, in principle, measurements in the differential mode are more informative. Yet, the experimental set up has two main shortcomings: (i) the slit of detector 1 cannot be appropriately adjusted in the vertical plane; and (ii) the zero position of detector 1 cannot be appropriately adjusted either. The former can lead to uncontrolled effective broadening of the slit on detector 1, while the latter results in a somewhat arbitrary matching of experimental and calculated curves with different parameter t (in our experiments the curves were matched using the position of the intensity maximum). Overcoming these difficulties would, no doubt, make the method more reliable, since it would give an opportunity to provide the fitting over a large number of different calculated curves.

Lastly, we should like to note that, after etching off a $1 \mu\text{m}$ thick surface layer in a polishing etchant, the diffraction curves acquired the shape corresponding to that known for the diffraction curves from crystals

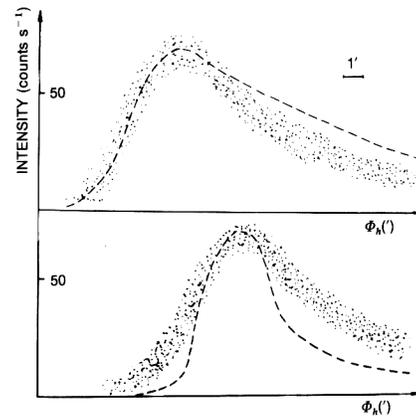


Fig. 6. The experimental data obtained in the differential mode and the corresponding calculated curves for a 250 \AA thick amorphous film. Upper part of figure: $\Phi_0 = 12'$, lower part of figure: $\Phi_0 = 20'$.

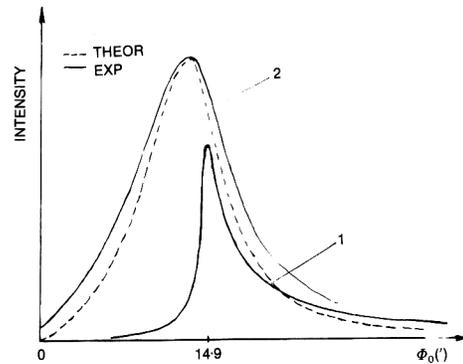


Fig. 7. The restoration of the shape of the diffraction curve measured in the integral mode after etching off the disturbed layer. (1) Before etching, (2) immediately after etching. The dashed line represents the curve calculated for $t = 0 \text{ \AA}$.

with no amorphous films (Fig. 7), the other parameters remaining the same.

The authors express their gratitude to A. Chuzo for technical assistance.

References

- AFANAS'EV, A. M. & MELKONYAN, M. K. (1983). *Acta Cryst.* **A39**, 207–210.
- ALEKSANDROV, P. A., AFANAS'EV, A. M., MELKONYAN, M. K. & STEPANOV, S. A. (1984). *Phys. Status Solidi A*, **81**, 47–53.
- ALEKSANDROV, P. A., AFANAS'EV, A. M. & STEPANOV, S. A. (1984). *Kristallografiya*, **29**, 197–202. (In Russian.)
- GOLOVIN, A. L. & IMAMOV, R. M. (1983a). *Phys. Status Solidi A*, **77**, K91–K94.
- GOLOVIN, A. L. & IMAMOV, R. M. (1983b). *Phys. Status Solidi A*, **80**, K63–K65.
- GOLOVIN, A. L., IMAMOV, R. M. & STEPANOV, S. A. (1984). *Acta Cryst.* **A40**, 225–228.
- MARRA, W. C., EISENBERGER, P. & CHO, A. Y. (1979). *J. Appl. Phys.* **50**, 6927–6933.