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The Method of Integral Characteristics in X-Ray Diffraction Studies of the Structure of the Surface Layers of Single Crystals

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A further development is presented of the integral-characteristics method which is suggested in an earlier work for investigating the damage localized in surface layers of single crystals by X-ray diffraction technique. In the case of ion implantation with a small irradiation dose a generalization of the model for a disturbed layer is suggested which assumes the flux density of incident particles to be insufficient for damaging all the crystal surface. Recommendations for the practical application of the method are also given. The method is used to study a disturbed layer structure of silicon single crystals irradiated with ions of argon, phosphorus, and boron.

Die Integral-Charakteristik-Methode, die in einer früheren Arbeit zur Untersuchung des in der Oberflächenschicht eines Einkristalls lokalisierten Damage mittels Röntgenbeugungstechnik vorgeschlagen wurde, wird weiter entwickelt. Für den Fall von Ionenimplantation mit geringer Bestrahlungsdosis wird eine Verallgemeinerung des Modells für eine gestörte Schicht vorgeschlagen, die annimmt, daß die Flußdichte der eindringenden Teilchen nicht für eine Schädigung der gesamten Kristalloberfläche ausreicht. Empfehlungen für die praktische Anwendung der Methode werden ebenfalls gegeben. Die Methode wird zur Untersuchung der gestörten Schichtstruktur von Siliziumkristallen benutzt, die mit Argon-, Phosphor- und Borionen bestrahlt wurden.

1. Introduction

X-ray diffraction is one of the most perspective methods for studying a structure of surface layers of single crystals, disturbed as a result of ion implantation. The method is attractive due to its rapidity, simplicity and high sensitivity to slight damage. The defects that arise during the ion implantation result in a change of the interplanar spacing which visually appears in the form of rocking curves of X-ray reflection [1 to 5].

It is, however, a rather difficult problem to analyse these curves, i.e. to determine the actual parameters of distortions due to the interference both between the waves scattered from various parts of the disturbed layer and between the waves reflected from the disturbed layer and the perfect part of the crystal. Therefore, it is necessary to develop the so-called "direct" analysis techniques which enable to obtain specific quantitative information on the disturbed layer structure directly from experimental reflection curves.

The present work is devoted to the further development of the integral characteristics method that has been introduced in [6]. The generalization of the model for a disturbed layer is suggested in Section 2 for the case of small irradiation doses when

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the flux density of incident particles is insufficient for damaging all the irradiated surface of the crystal. Recommendations for the practical application of the method are given in Section 3.

Section 4 presents the results of analysing the experimental curves of X-ray reflection for silicon crystals. The results illustrate brightly the possibilities of the integral characteristics method for an investigation of various stages of the accumulation of radiation defects.

2. The Model of a Disturbed Layer and the Integral Characteristics

As a result of ion implantation, a "cluster of radiation defects" [7] is produced along the ion track in the form of a cylindrical region extending from the surface deep into the irradiated crystal. The cluster is a function of the initial energy and mass of the incident ion as well as of masses of target atoms and its temperature. The internal (central) part of the cluster is damaged most of all. The peripheral region becomes considerably deformed due to interstitial atoms accumulated there, which are distributed irregularly along the depth of the crystal. It is the reason for a non-uniform variation of the interplanar distance in the surface region of a crystal.

The lattice defects in the region of a cluster will be described by two parameters: the average displacement $\boldsymbol{u}(z)$ of the atomic planes from their positions in a perfect crystal, and by the amorphization parameter $W(z)$ which characterizes a random displacement of atoms from the plane. The coordinate z is directed from the surface deep into the crystal.

Because cluster sizes and distances between them are much smaller than the extinction length L_{ex}, the X-ray elastic scattering from the disturbed layer can be conveniently described by the polarizability $\chi(\boldsymbol{r})$ which weakly depends on the coordinates, and is averaged over to crystal region with linear dimensions much smaller than L_{ex}, though containing a rather great number of clusters [8]. The h-th Fourier component of the polarizability can be represented by the following expression:

$$\chi_h(z) = \chi_h^{(id)}[a + b \exp\left(-i\varphi(z) - W(z)\right)] , \tag{2.1}$$

where $\varphi(z) = \boldsymbol{hu}(z)$, $\boldsymbol{h}$ is a reciprocal lattice vector on which the diffraction scattering occurs; $b = S_k/S$, where S_k is the crystal surface area occupied by clusters on the surface area S, $a = 1 - b$. The average over the volume polarizability χ_0 has the same value as in the perfect crystal.

The electric field amplitude of an X-ray wave in the region of angles corresponding to the Bragg diffraction represents a superposition of two plane waves with the wave vectors $\boldsymbol{k}_0$ and $\boldsymbol{k}_h = \boldsymbol{k}_0 + \boldsymbol{h}$. Wave amplitudes, in their turn, weakly depend on z.

They satisfy the set of differential equations, first proposed by Takagi ([9], see also [10]). In the Bragg reflection case, the ratio $R(z)$ of the amplitudes of the reflected wave to the incident wave is of interest. The quantity $R(z)$ is a solution of the Taupin non-linear differential equation [11] with the boundary conditions $R(z) = R_0$ at $z = L$ where L is the disturbed layer thickness and R_0 is the amplitude of reflection by the perfect part of the crystal. In the general case this differential equation can be solved only numerically.

However, in the case of ion implantation the condition $L \ll L_{ex}$ holds well. It permits to obtain an approximation with respect to the parameter L/L_{ex}, the amplitude of reflection by the whole crystal has the following form:

$$R(y) = R_0(y)\,(a + b\,e^{-iqL}) + R_1(y) + R_0^2(y)\,R_2(y) , \tag{2.2}$$

where

$$R_{1,2}(y) = -i \frac{C}{L_{ex}} b \int_0^L dz \exp\left(-iqz \mp i\varphi(z) - W(z)\right). \tag{2.3}$$

Here C is the polarization factor,

$$y = -\left(\frac{\sin\theta_0}{\sin\theta_h}\right)^{1/2} \frac{\sin 2\theta_B}{|\chi_h^{(id)}|} (\theta - \theta_m), \tag{2.4}$$

where $\theta_{0,h}$ are the angles between the wave vectors $k_{0,h}$ and the crystal surface; θ_B is a Bragg angle; $(\theta - \theta_m)$ is the variable angle counted from the reflection maximum for the perfect part of a crystal; $q = 2y/L_{ex}$; R_0 can be found from the equation

$$R_0 = -\frac{C}{2y}(1 + R_0^2). \tag{2.5}$$

The X-ray reflection coefficient is

$$P_R(y) = \left|\frac{\chi_h}{\chi_{\bar{h}}}\right| |R(y)|^2 = \left|\frac{\chi_h}{\chi_{\bar{h}}}\right| \{|R_1|^2 + |R_0|^2 \left(1 - ab \sin^2(qL/2)\right) + 2|R_0|^2 \operatorname{Re}[(a + b\,e^{-iqL}) R_1/R_0] + 2 \operatorname{Re}[R_1 R_2^* R_0^{*2}] + |R_0^4 R_2^2| + 2|R_0^4| \operatorname{Re}[(a + b\,e^{-iqL}) R_2/R_0]\}. \tag{2.6}$$

According to (2.6) in the experimentally measured reflection coefficient we can select six terms, each, in general, contributing to different parts on the angular dependence of X-ray reflection. The reflection amplitude for the case of an ideal crystal $|R_0|$ is known to have a value near to unity in a narrow region of angles corresponding to the condition $|y| < 1$ and outside this region it decreases sharply and becomes equal to $C/2\,|y|$ (see formula (2.5)). On the contrary, the amplitude $R_{1,2}$ of reflection by the disturbed region has a maximum on the "tails" of the reflection curve. If the lattice is compressed, then $R_1(y)$ has a maximum where y is negative, and $R_2(y)$, on the contrary, has a maximum where $y > 0$.

If the effective interplanar distance in the region of clusters greatly differs from that in an ideal crystal, then the reflection curve can be divided into two parts: the central part and "tails". In the central part, the main contribution to the reflection coefficient is made by the second term in the curly brackets of (2.6), and among the others, by the third and sixth terms. On the "tails" of the curve, the main contributor is the first term, and among the other terms — the third, though its contribution is much less than that of the first term.

Let us now consider a part of the total reflection coefficient $P_R^{(1)}(y)$ which is related to the first term in formula (2.6) and calculate the integral over y. Taking into account (2.3) we may write

$$\left|\frac{\chi_{\bar{h}}}{\chi_h}\right| \int_{-\infty}^{\infty} dy\, P_R^{(1)}(y) = \left(\frac{Cb}{L_{ex}}\right)^2 \int_0^L dz \int_0^L dz' \exp[-W(z) - W(z') - i\varphi(z) + i\varphi(z')] \int_{-\infty}^{\infty} dy \exp\left(iq(z' - z)\right). \tag{2.7}$$

The last integral is equal to $\pi L_{\text{ex}}\,\delta(z' - z)$. As a result, summing over the polarization states we obtain the effective parameter

$$L_{\text{eff}} = b^2 \int_0^L \mathrm{d}z\, \mathrm{e}^{-2W(z)} = \frac{L_{\text{ex}}}{\pi \sum\limits_{i=1,2} C_i^2} \left|\frac{\chi_{\bar h}}{\chi_h}\right| \int_{-\infty}^{\infty} \mathrm{d}y\, P_{\text{R}}^{(1)}(y)\,. \tag{2.8}$$

The left-hand side of the formula defines the physical sense of the parameter, and the right-hand side may be used for its practical calculation using experimental data. In fact, we know from the experiment only the total reflection coefficient $P_{\text{R}}(y)$ and not $P_{\text{R}}^{(1)}$. Since in tail parts the curve $P_{\text{R}}(y)$ practically coincides with $P_{\text{R}}^{(1)}(y)$ and the contribution of the central part of the curve to the total integral (3.2) is small, L_{eff} can actually be calculated using the experimentally obtained value of P_{R} and subtracting the central part of the curve.

As follows from (3.2) the parameter L_{eff} is determined primarily by the average depth of clusters. Secondly, it depends on the degree of lattice amorphization in the disturbed part of the crystal, and thirdly, it depends on the area of the disturbed surface in the case of small irradiation doses. Varying gradually the irradiation dose, for example, or the energy of incident ions, we may observe the trends for defect accumulation in the crystal.

Together with the quantity (2.8) we can use a characteristic connected with the first moment of the curve $P_{\text{R}}^{(1)}(y)$, namely,

$$\left|\frac{\chi_{\bar h}}{\chi_h}\right| \int_{-y_1}^{y_2} \mathrm{d}y\, P_{\text{R}}^{(1)}(y)\, y \approx \lim_{x\to 0} \left|\frac{\chi_{\bar h}}{\chi_h}\right| \frac{\partial}{i\,\partial x} \int_{-\infty}^{\infty} \mathrm{d}y\, P_{\text{R}}^{(1)}(y)\, \mathrm{e}^{ixy}\,. \tag{2.9}$$

Here y_1, y_2 are the limits over the angles from left and right, respectively, within which the experimental curve has been obtained. When calculating the integral (2.9) we may neglect the derivative $(\mathrm{d}W/\mathrm{d}z)$ as compared with $(\mathrm{d}\varphi/\mathrm{d}z)$. It should be taken into account that the derivative $(\mathrm{d}\varphi/\mathrm{d}z)$ is directly related to variations in the interplanar spacing in the disturbed part of the crystal $\mathrm{d}\varphi/\mathrm{d}z = -|h_z|\,\Delta d(z)/d_0$. As a result we obtain a new parameter,

$$\overline{\left(\frac{\Delta d}{d}\right)} L_{\text{eff}} = b^2 \int_0^L \mathrm{d}z\, \mathrm{e}^{-2W(z)}\, \frac{\Delta d(z)}{d} = \frac{2\,|\chi_{\bar h}/\chi_h| \int_{-y_1}^{y_2} \mathrm{d}y\, P_{\text{R}}^{(1)}(y)\, y}{\pi\,|h_z| \sum\limits_{i=1,2} C_i^2}\,. \tag{2.10}$$

We note that (2.10) gives a simpler recipe for finding the parameter $(\overline{\Delta d/d})$ than that presented in [6] because it does not demand to calculate the Fourier component of $P_{\text{R}}^{(1)}$.

3. Practical Recommendations

To determine the integral parameters L_{eff} and $(\overline{\Delta d/d})$ from formulae (2.8), (2.10) we need to find the area under the experimental reflection curve $P_{\text{R}}(y)$ and its first moment without the central part $|y| < y_0$. The characteristics can, now, be found by selecting boundaries of the region to be subtracted from the central part of the curve, since calculation of the area and the first moment of the remaining part present no difficulties and may be performed by using known numerical methods.

The condition $P_{\text{R}}(y) \approx P_{\text{R}}^{(1)}(y)$ is the major criterion for selecting the boundaries of the region to be excluded from consideration. As follows from (2.6) the condition

holds well in the region of angles, where the amplitude of reflection from the ideal part of the crystal $R_0(y)$ becomes smaller than the amplitude of reflection from the disturbed part of the crystal, $R_1(y)$. Thus, to select the point y_0 we have the following condition: $R_0(y) = R_1(y)$ or squaring it $P_R^{(id)}(y) = P_R^{(1)}(y)$.

As for $P_R^{(id)}$, the angles outside the region of total reflection, with the account of (2.5), would be $P_R^{(id)} = C^2/4y^2$. To find the order of $P_R^{(1)}(y)$ let us assume that it weakly depends on y in the region of angles considered. It can be estimated, then, directly from formula (3.2) to give

$$y_0 = \left(\frac{L_{ex}}{8\pi} \frac{\Delta y}{L_{eff}}\right)^{1/2}, \tag{3.1}$$

where $\Delta y = y_1 + y_2$ is the angular length of the diffraction region on the experimental curve.

As follows from (3.1), to determine y_0 we need to know the value of L_{eff} which, in turn, is determined from the experimental curve and depends on y_0. Therefore, we have a self-consistent problem which can be solved iteratively.

The experience shows that the main advantage of the integral characteristics is that they permit to reveal the trends of the radiation damage formation in the crystal when the energy of incident ions or the irradiation dose gradually changes. Naturally, a small change in the irradiation dose will result in a slight variation of L_{eff}. The procedure of choosing the point y_0 described above is needed only for making an analysis of the first experimental curve. When studying the next curves for determining y_0 use can be made of the value L_{eff} calculated at a previous stage.

Let us note that elimination of the central part of the reflection curve $|y| < y_0$ actually corresponds to neglecting the part of the disturbed layer exhibiting a weak change in the lattice parameter.

In the above analysis, it was assumed that the experimental curves represent "intrinsic" reflection curves. In other words, the incident X-ray beam has a very small angular divergence (for example, compared to that of a three-crystal spectrometer). There are many cases, however, where X-ray diffraction experiments are carried out using a two-crystal spectrometer with symmetrical reflection in both crystals. Here the experimental curve represents a convolution of the reflection curves of the first and second crystals. Note, that using "two-crystal" reflection curves one can also determine the parameter L_{eff}. As for the parameter $(\overline{\Delta d/d})$, its estimation from "two-crystal" curves is a much harder procedure. Since the "two-crystal" curves are significantly distorted in the central part, an additional difficulty arises when choosing the value of y_0.

4. Experimental Technique and Results

We have investigated a series of silicon crystals irradiated by ions of various elements, such as argon (Ar), phosphorus (P), and boron (B). The energy of irradiating ions was constant: for argon and phosphorus, 100 keV; for boron, 25 keV. Meanwhile, the dose (D) varied within a wide range from 6×10^{12} to 6×10^{15} atoms/cm^2. Irradiation was carried out at room temperature using a conventional set-up for ion implantation under conditions which eliminated channelling.

Diffraction-reflection curves were measured by a three-crystal X-ray spectrometer [12, 13] using the technique described in [14]. The first crystal was located in the position of the symmetrical Bragg diffraction for (333) reflection (Bragg angle $\theta_B \approx 45°$). The second crystal took the position of the asymmetric (111) reflection and formed a beam with a small angular divergence. The intrinsic (111) reflection curves were

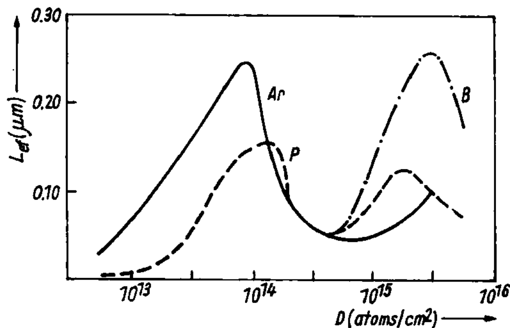

Fig. 1. Integral parameter L_{eff} as a function of the irradiation dose D. Ar: irradiation with argon; P: phosphorus irradiation; B: boron irradiation

measured using polarized and parallel CuK_α radiation by rotating the third crystal within a small angular range ($\theta_B \mp \Delta\theta$). These curves have a major principle difference from those corresponding to reflection from the perfect (non-irradiated) crystal in that the angular region of the diffraction increases and additional intensity oscillations appear together with the basic maximum.

Using the experimental curves and the method presented above we calculated the effective thickness of the damaged layer L_{eff}. Fig. 1 shows the dependence of this parameter on the irradiation dose. It is clear from Fig. 1 that when using small doses (up to 5×10^{13} atoms/cm^2) L_{eff} increases with increasing irradiation dose. It is due to the fact that in this case separate non-overlapping clusters are formed in the crystal surface layer. Each cluster corresponds to a disturbed region of the crystalline lattice, formed by a single ion. An increase in L_{eff} points unambiguously to a greater area of the crystal surface that was disturbed by ion bombardment (see formula (2.8)).

We note that an increase in L_{eff} for argon ions begins at lower doses than in the case of phosphorus. This is related to the fact that argon ions cause worse damage in the lattice than phosphorus ions because the former have a greater mass which leads to larger clusters. The increase in L_{eff} for boron starts at much greater radiation doses than in the case of argon and phosphorus because of the small atomic number of boron.

Attention should be drawn to the fact that the obtained value of L_{eff} for boron light ions implanted into the crystal with a small energy of 25 keV, turns out to be the same as in the case of argon heavy ions implanted with an energy of 100 keV. This seeming discrepancy could, probably, be accounted for by the fact that the energy of boron ions is smaller than that of argon ions. Therefore, the former penetrate the crystal to the same depth as do the argon ions due to a smaller effective scattering cross-section.

The maximum value of L_{eff} corresponds to the formation of a completely disturbed layer on the surface of the irradiated crystal. This conclusion agrees with the results of ion irradiation studies by various techniques [15]. It should be noted that already at these doses nucleation of amorphous regions occurs along with the formation of a completely disturbed layer which retains a rather perfect crystalline structure. The integral parameters take into account only those layers which contribute to diffraction scattering. Decreasing the value of L_{eff} with further increase in the number of incident ions is unambiguously related to an overwhelming effect of the amorphization process in the disturbed layer. Here, because of different masses of argon and phosphorus ions, amorphization for the case of argon irradiation begins at smaller doses than with phosphorus irradiation. The most intensive amorphization occurs in the range of doses from 1×10^{14} to 5×10^{14} atoms/cm^2.

A crystalline lattice amorphization in the disturbed layer at the initial stage is accompanied by an increased deformation in the damaged layer. It relates to the increased total number of interstitials (recoil atoms), in particular, in that part of the layer where the crystalline lattice is still retained. Further, with a rise in irradiation dose the heavily disturbed crystalline layers become amorphous.

Consider a particular feature of ion implantation which is unambiguously confirmed by the X-ray diffraction studies. In spite of intensive amorphization caused by crystal irradiation at high ion doses, the disturbed layer does not become completely amorphous but acquires a complex inhomogeneous structure. The presence of crystalline as well as amorphous regions is confirmed by a non-zero value of L_{eff} even in the case of strongest amorphization characterized by a dose equal to about 5×10^{14} atoms/cm^2.

Let us now turn to processes occurring in the disturbed layer at large doses of irradiation. For doses greater than 5×10^{14} atoms/cm^2 we again observe an increase in the value of L_{eff} that evidences the growth of volume of the disturbed crystalline part of the layer. It may be related to both the spread of the disturbed layer deep into the crystal, and a partial crystallization of the amorphous layer as a result of radiation annealing.

The fact that L_{eff} begins to grow also points out that instead of intensive accumulation of radiation defects at low doses, radiation reduction of amorphous regions and interaction of point defects occur in the layer. Here we note that L_{eff} grows much stronger for phosphorus ions than for argon ions (beginning with a dose of $\approx 6 \times 10^{14}$ atoms/cm^2). It can be related to the singular behaviour of phosphorus atoms as reported in [15].

The overall deformation of the lattice in ion irradiation is determined from the excess concentration of silicon interstitial atoms which lead to its expansion. But beginning with a dose of 9×10^{14} atoms/cm^2 for argon and 2×10^{15} atoms/cm^2 for phosphorus the experimental reflection curves exhibit an additional diffraction region which corresponds to X-ray reflection from crystal layers with an opposite sign of deformation. This crystalline region enriched with vacancies and having smaller lattice period as compared to that of an ideal crystal arises after rearrangement of the amorphous layer as the crystal is heated by ion irradiation at large doses.

For layers irradiated with phosphorus ions at large doses the thickness of the damaged layer decreases due to partial radiation annealing of crystal lattice defects. This is not the case for irradiation with argon ions because they create more damage in the lattice during implantation and exhibit a specific behaviour in the crystal.

As for boron ions, all the processes during implantation are displaced to the side of larger doses because of its small atomic number. Therefore in the considered range of irradiation doses we were able to observe the accumulation of radiation defects during irradiation with boron ions including only the initial stage of amorphization.

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