

phys. stat. sol. (a) **64**, 359 (1981)

Subject classification: 1.6 and 17; 22.1.2

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On the Theory of External Photoeffect Accompanying X-Ray Diffraction in an Ideal Crystal with Disturbed Surface Layer

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A theory is developed to explain the angular dependence of X-ray photoelectrons quantum yield under X-ray diffraction in an ideal crystal with the surface layer disturbed due to diffusion or ion implantation. A procedure is suggested for the computation of photoemission curves for the most general relation between parameters characterizing both, the experimental conditions and the disturbed layer itself. A particular example of Bragg diffraction of non-polarized CuK_α -radiation on a silicon crystal with a model disturbed layer of about $3\ \mu\text{m}$ is considered. The distortions correspond to a gradual lattice compression when approaching the surface. "Proper" X-ray and photoemission curves (without convolution) are shown to be more informative than those obtained by a double-crystal spectrometer.

Es wird eine Theorie entwickelt, um die Winkelabhängigkeit der Röntgenphotoelektronenquantenausbeute bei Röntgenbeugung in einem idealen Kristall mit einer durch Diffusion oder Ionenimplantation gestörten Oberflächenschicht zu erklären. Ein Verfahren wird vorgeschlagen für die Berechnung der Photoemissionskurven für die allgemeinste Beziehung zwischen den Parametern, die sowohl die experimentellen Bedingungen als auch die gestörte Schicht selbst charakterisieren. Ein spezielles Beispiel einer Braggbeugung von nichtpolarisierter CuK_α -Strahlung an einem Siliziumkristall mit einer gestörten Modellschicht von etwa $3\ \mu\text{m}$ wird betrachtet. Die Störungen entsprechen einer graduellen Gitterkompression bis zur Oberfläche. Es wird gezeigt, daß korrekte Röntgen- und Photoemissionskurven mehr Informationen liefern, als die mit einem Doppelkristallspektrometer erhaltenen.

1. Introduction

In recent years there has been an increasing interest in studying the structure of surface layers of single crystals exposed to different effects, diffusion and ion irradiation in particular. One of the most perspective methods of investigation of the disturbed surface layer structure is X-ray diffraction with simultaneous registration of the angular dependence of the secondary emission.

Foundations of this approach were laid already in [1] (fluorescence), [2 to 4] (external and internal photoemission), [5] (Compton scattering) [5, 6] (thermal diffused scattering), [7] (X-ray-voltaic effect). Recently, experimental works have been done clearly demonstrating the high sensitivity of photoemission to weak disturbances of the crystal lattice in near-surface layers [8, 9].

The general theory of secondary processes, photoemission in particular, in an ideal crystal with disturbed surface layer was developed in [10]. In this paper attention was

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also paid to the reconstruction of the disturbed layer characteristics directly from experimental data. This problem was found to be solved relatively simply only in the case $L_{el} \ll L_d \ll L_{ex}$, where L_{ex} is the extinction length, L_{el} the depth of photoelectron detachment, and L_d the disturbed layer depth.

However, some other situations are frequently encountered. For instance, the condition $L_d \geq L_{ex}$ takes place when the disturbed layer results from impurity diffusion and X-rays are reflected from low-index planes. On the contrary, in the case of implanted layers formed by hard radiation a situation may occur where $L_{el} \approx L_d$.

Theoretical calculation of the angular dependence of X-ray reflection and external photoeffect for all these cases is a rather complicated problem and may be solved only numerically. In this respect it is necessary to develop the theory further for describing adequately the most general experimental situation. This paper is devoted to the solution of this problem.

General formulae describing the angular dependence of the external photoeffect are presented in Section 2, while the derivation of calculation formulae and the computation method are presented in Section 3. Section 4 presents computation results for a specific model of the disturbed layer.

2. Formulation of the Problem

Since the interaction between X-rays and crystal atoms is weak it is convenient to characterize the disturbed layer by averaged parameters such as the mean displacement of atomic planes from their positions in an ideal crystal, $u(z)$, and also by the static Debye-Waller factor, $W(z)$, accounting for random atom displacements from their positions in the plane [11]. We shall consider only the situations where disturbances are uniform in the sample surface, that is they depend only on the single coordinate z measured along the inner normal to the surface.

The electrical field vector of X-rays in the angular region corresponding to the Bragg diffraction is known to be a superposition of two plane waves with the wave vectors k_0 and $k_h = k_0 + h$ where h is a reciprocal-lattice vector of the ideal crystal. In the disturbed layer the amplitudes E_0 and E_h of these waves become weakly depending on z and satisfy the Takagi differential equations.

The external photoeffect experiments give us the total number of electrons knocked out from the crystal atoms in a vacuum through the sample surface as a result of X-ray absorption. This process proceeds in two stages: at first the electrons are knocked out in the crystal volume and then several of them come out of the crystal.

The number of primary X-ray electrons $dN^{(s)}$ knocked out from the layer with a thickness of dz at a depth of z per unit area and per unit time is equal to the number of absorbed X-ray quanta in a polarization state s , which in turn is equal to the ratio of the absorbed electromagnetic energy ΔW to the quantum energy $\hbar\omega$. The quantity ΔW is equal to the difference between incident and leaving fluxes for the layer dz and may be calculated directly from the Takagi equations. A corresponding formula was obtained in [10]. This formula is convenient because it enables the electrons to be divided in a natural way into groups detached from different atomic shells and having different kinetic energy. Let the probability of m -group electrons to reach the surface of a crystal be $P_m(z)$. Then integrating over z we obtain the following expression:

$$N^{(s)}(\theta) = \sum_m \int_0^\infty dz P_m(z) \frac{dN_m^{(s)}(z, \theta)}{dz}, \quad (2.1)$$

where

$$\frac{dN_m^{(s)}(z, \theta)}{dz} = \frac{c}{8\pi} \frac{\mu_{0m}}{\hbar\omega} \left\{ |E_{0s}(z, \theta)|^2 + |E_{hs}(z, \theta)|^2 + 2 \operatorname{Re} \left[E_{0s}^*(z, \theta) E_{hs}(z, \theta) \frac{\chi_{ih}^{(s)}(m)}{\chi_{i0}(m)} \exp(i\varphi(z) - W(z)) \right] \right\}. \quad (2.2)$$

Here θ is the variable angle between the incident wave direction \mathbf{k}_0 and reflection plane, $\varphi(z) = \mathbf{h}\mathbf{u}(z)$, c is the light velocity. The quantities χ_{i0} and $\chi_{ih}^{(s)}(m)$ are the contributions to the imaginary part of Fourier components of crystal polarizability from the processes in which the absorption of the X-ray quanta in a polarization state s is accompanied by the detachment of m -group photoelectrons. $\mu_{0m} = (2\pi/\lambda) \chi_{i0}(m)$ is the contribution of these processes to the total X-ray absorption coefficient. In the case of non-polarized radiation (2.1) should be summed over the polarization states.

In experiment, secondary electrons arising from the transition of atoms from an excited to the ground state are also detected. These secondary electrons are Auger electrons and electrons detached due to the absorption of fluorescent radiation [12]. The number of electrons arising from the excitation of the m -th shell is proportional to $dN_m^{(s)}$. Thus, they may also be accounted for in (2.1) by using an appropriate definition of the function $P_m(z)$.

It should, however, be noted that at present the problem is at a stage when the theoretical account of such "fine" effects as the influence of Auger effect and contribution of all the excited atomic shells, except for the very first one, on the angular dependence of photoelectron yield is obviously exceeding the experimental accuracy, since the information on the disturbed layer structure, that is on the quantities $\varphi(z)$ and $W(z)$, is practically absent, and it is the main problem to determine, though qualitatively, these quantities from experimental data.

That is why in the sum over m in (2.1) we shall take into account only the first term corresponding to the excitation either of the K or L shell depending on the incident quanta energy. In this case $P(z)$ is equal to $(1 - z/L_{el})/2$ at $z \leq L_{el}$ and zero at $z > L_{el}$ where L_{el} is the depth of electron detachment to the crystal surface [12].

For the same reason we neglect the dispersion corrections in the real part of the polarizability χ_r , and the quadrupole contribution to χ_i . In this approximation $\chi_h^{(s)} = \chi_h C$ where C is the ordinary polarization factor.

3. Calculation Formulae and Computation Method

Let us consider the case where the reflected wave leaves the crystal through the "entering" surface (diffraction in Bragg geometry). In this case in the region of total reflection the field is known to penetrate a thick ideal crystal only to a depth of the order of the extinction length

$$L_{\text{ex}} = \frac{\lambda \sqrt{\gamma_0 |\gamma_h|}}{\pi |\chi_{rh}|}, \quad (3.1)$$

where λ is the wavelength of radiation, γ_0 and γ_h are the cosines of the angles between the vectors \mathbf{k}_0 and \mathbf{k}_h and the inner normal to the crystal surface.

On the other hand, to obtain the reflection with the ratio of reflected and incident intensities of the order of unity, a layer with fixed parameters and the thickness of the order of L_{ex} must exist in the crystal. Therefore, it is clear that the angular dependence of the photoelectron yield depends significantly on the relation between such parameters as L_{el} , L_{ex} , and L_d (the depth of the disturbed layer).

In this paper we shall consider the general case where the relation between the parameters L_{ei} , L_d , and L_{ex} may be arbitrary. In this case a specific calculation of the angular dependence of the photoelectron yield may be performed only numerically (by using a computer) for a certain model of the disturbed layer.

It is known that the Takagi equations should be solved, for Bragg geometry under the boundary conditions of a given E_0 at $z = 0$ and zero E_h at $z = t$ where t is the plate thickness. Since the boundary conditions are rather complicated it is convenient to use a new quantity

$$R(z) = \frac{E_h(z)}{E_0(z)} \left(\frac{\chi_{\bar{h}} |\gamma_h|}{\chi_h \gamma_0} \right)^{1/2} e^{i\varphi(z)} \quad (3.2)$$

and a new coordinate $z' = L_d - z$. The equation for $R(z')$ will be written in the form

$$iL_{ex} \frac{dR}{dz'} = 2[y - iy_0 - Y(z')] R(z') + \tilde{C} e^{-W(z')} [1 + R^2(z')]. \quad (3.3)$$

Here we use the following notations:

$$y = -\sqrt{\beta} \frac{\sin 2\theta_B}{|\chi_{rh}|} (\theta - \theta_0), \quad \beta = \frac{\gamma_0}{|\gamma_h|}, \quad (3.4)$$

$$y_0 = \frac{\chi_{i0}}{|\chi_{rh}|} \frac{(1 + \beta)}{2\sqrt{\beta}}, \quad \tilde{C} = C \frac{(\chi_h \chi_{\bar{h}})^{1/2}}{|\chi_{rh}|}, \quad (3.5)$$

$$Y(z') = \frac{1}{2} L_{ex} \frac{d\varphi}{dz'} = \frac{1}{2} L_{ex} |h_z| \frac{\Delta d(z')}{d}, \quad (3.6)$$

where θ_B is the Bragg angle, θ_0 corresponds to the reflection maximum, d is the distance between the reflecting planes.

Equation (3.3) is convenient since its boundary condition may be given in the point $z' = 0$, because in the region $z' < 0$ the crystal is ideal. For a thick ideal crystal ($t \gg L_{ex}$) the reflection coefficient is known to be independent of the thickness. Therefore, the boundary condition for $R(z')$ may be found in a very simple way from (3.3) if we assume $(dR/dz') = Y = W = 0$.

As a result we obtain

$$R(0) = -\frac{1}{\tilde{C}} \left[y - iy_0 + \sqrt{(y - iy_0)^2 - \tilde{C}^2} \right]. \quad (3.7)$$

Here the branch with the positive imaginary part should be used for the square root.

The X-ray reflection coefficient P_R is related to $R(z')$ by a simple formula

$$P_R(y, z') = \left| \frac{\chi_h}{\chi_{\bar{h}}} \right| |R(y, z')|^2. \quad (3.8)$$

Let us note that the calculation procedure considered enables one to evaluate in a relatively simple way the reflection coefficient when accounting both for the total disturbed layer ($z' = L_d$) and for its part ($0 \lesssim z' \lesssim L_d$). Thus, there is a possibility of simultaneously obtaining (in a single computation) a family of curves corresponding to the experimental situation that the disturbed layer is gradually removed by etching.

The angular dependence of the photoelectron yield is usually characterized by a dimensionless quantity $\kappa(y) = N(y)/N(\infty)$. Allowing for the above approximations and quantities introduced above let us rewrite (2.1), (2.2) in the following form:

$$\begin{aligned} \kappa(y) = \frac{1}{L} \int_{L_d - L_{el}}^{L_d} dz' \tilde{P}(z') |E_0(z', y)|^2 \left\{ 1 + \beta P_R(z', y) + \right. \\ \left. + 2C \exp(-W(z')) \sqrt{\beta} \operatorname{Re} \left[\left(\frac{\chi_h}{\chi_{i0}} \right)^{1/2} \frac{\chi_{ih}}{\chi_{i0}} R(z', y) \right] \right\}, \end{aligned} \tag{3.9}$$

where

$$L = \int_0^{L_{el}} dz P(z) e^{-\mu_0 z/\gamma_0}, \quad \tilde{P}(z') = \frac{z' - (L_d - L_{el})}{2L_{el}}. \tag{3.10}$$

The dependence of $E_0(z', y)$ on $R(z')$ has the following form:

$$|E_0(z', y)|^2 = e^{-\Phi(L_d)} e^{\Phi(z')}, \tag{3.11}$$

where

$$\Phi(z') = \frac{\mu_0 z'}{\gamma_0} - \frac{2}{L_{ex}} \operatorname{Im} \left(\tilde{C} \int_{z_0}^{z'} dx e^{-W(x)} R(x, y) \right). \tag{3.12}$$

The coordinate z_0 has an arbitrary value of the interval $0 \leq z_0 \leq L_d - L_{el}$.

It follows from (3.9), (3.12) that to calculate the curve $\kappa(y)$ one should perform a double integration together with the solution of differential equation (3.3); the calculation procedure may be as follows. Let us divide the whole disturbed layer into thin layers of thickness h and number the layer boundaries by the index k . Then, assuming that within two thin layers the right-hand side, $F(z')$, of (3.3) depends linearly on z' we obtain a recurrence formula

$$R_{k+1} = R_{k-1} + \frac{2h}{iL_{ex}} F_k + 0(h^3). \tag{3.13}$$

Along with determining the R value in the chosen points we calculate the exponent $\Phi(z')$ in the same points using the trapezoidal rule for integration over the layer thickness h . In (3.9) integration is performed by the same technique. The value of $\Phi(L_d)$ is determined only after "passing" the total disturbed layer, so the corresponding exponential should be taken out of the integral sign and used at the end of the calculation. We note that the procedure suggested may be easily modified for the simultaneous calculation of $\kappa(y)$ curves both for the total disturbed layer and for its part, as well as for simultaneous calculations at several L_{el} values.

At present, experiments measuring photoemission curves have been performed by a double-crystal technique using the so-called non-dispersive geometry where the two crystals are identical and their reflecting planes are parallel. In this case for the comparison with the experimental curves one has to calculate the convolution of the theoretical curve for the reference crystal with the angular distribution curve of the intensity for X-rays diffracted by the first crystal. We present here the formula in the most general case where asymmetrical reflection is used in both crystals,

$$\overline{\kappa(2, y)} = \frac{\sum_s \int_{-\infty}^{\infty} dy_1 P_R^{(s)}(1, y_1) \kappa^{(s)}(2, y + y_1 \sqrt{\beta_1 \beta_2})}{\sum_s \int_{-\infty}^{\infty} dy_1 P_R^{(s)}(1, y_1)}. \tag{3.14}$$

In this formula the first argument is the crystal number. The value of y is determined in this case by the angle ψ between the reflecting planes of the first and second crystals

$$y = -\sqrt{\beta_2} \frac{\sin 2\theta_B}{|\chi_{rh}|} (\psi + \psi_0); \quad \psi_0 = \frac{|\chi_{ro}|}{\sin 2\theta_B} \left(\frac{1 + \beta_1}{2} - \frac{1 + \beta_2}{2\beta_2} \right). \quad (3.15)$$

The formula for $\overline{P_R(2, y)}$ is obtained from (3.14) by substituting $P_R^{(s)}$ for $\kappa^{(s)}$. According to (3.15), the smaller the parameters β_1 and β_2 are, the closer are the averaged values to the proper curves, since the width of the total reflection region depends weakly on β (in the y scale).

4. Specific Example

The calculation procedure considered in the previous section was used as a basis for a computation program in "FORTRAN".

As an example, we shall consider the most characteristic experimental situation: Bragg diffraction of non-polarized CuK_α radiation ($\lambda = 1.54 \text{ \AA}$) on a silicon crystal for (111) reflection. In this case $L_{\text{ex}} = 1.54 \text{ \mu m}$. The calculation was performed for the disturbance distribution profile shown in Fig. 1. The profile corresponds to the gradual decrease of the inter-plane distance in the layer, i.e. to lattice compression. This case arises as a result of diffusion of impurity atoms with small size. For simplicity, the parameter $W(z)$ is assumed to be zero.

Fig. 2 shows the curves $P_R(y)$ and $\kappa(y)$ under the condition of a plane monochromatic wave incident on the crystal studied. Fig. 3 shows the curves $\overline{P_R(y)}$ and $\overline{\kappa(y)}$ calculated with account of the angular divergence of the incident beam. The calculation corresponds to a non-dispersive double-crystal spectrometer with symmetric Bragg reflection for both crystals ($\beta_1 = \beta_2 = 1$).

A method based on measuring X-ray diffraction curves at gradual etching of the disturbed layer [8, 9] (for instance, by anodic oxidation [13]) is commonly used to obtain a more detailed information on the structure of the layer. Such a situation is shown in Fig. 2 and 3.

The first curve in each figure corresponds to an ideal crystal. Let us note that the maximum of the reflection curve $P_R^{(\text{id})}$ (Fig. 3a) is 71%, and the maximum and minimum of the photoemission curve $\overline{\kappa}^{(\text{id})}$ 1.70 and 0.78, respectively. These data coincide, within the given accuracy, with the results of [14]. As the disturbed layer thickness increases (z' grows) the curve $\overline{P_R(y)}$ at the initial stage changes slightly its shape and only broadens a little. When the disturbed layer thickness reaches its maximum the reflection curve exhibits an additional, rather intensive maximum located near the angles corresponding to a compressed lattice.

At the same time, the photoemission curves change their shape more appreciably.

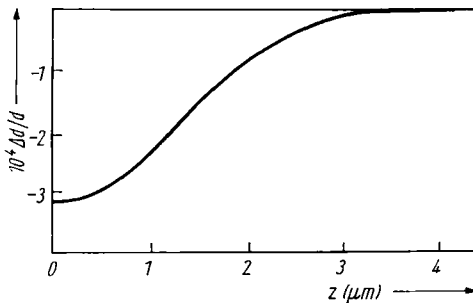


Fig. 1. Disturbance profile $\Delta d/d$ along the layer depth z

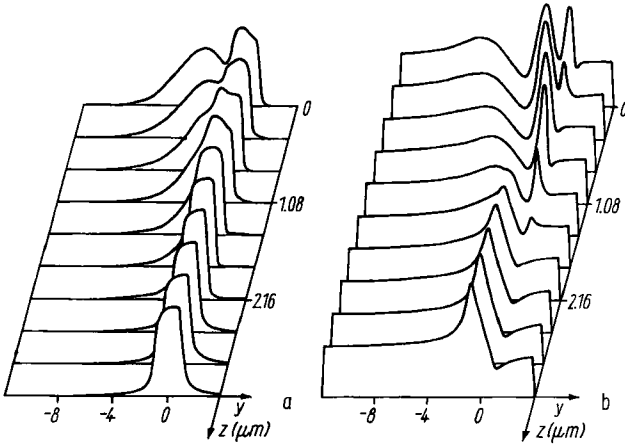


Fig. 2. a) X-ray reflection $P_R(y)$ and b) photoemission $\kappa(y)$ curves calculated for silicon crystal ((III) reflection) and CuK_α radiation under the condition of a plane monochromatic wave incident on the crystal

As the disturbed layer thickness increases the curve $\overline{\kappa(y)}$ is gradually smoothed, and then it exhibits two maxima.

Comparing Fig. 2 and 3 one can easily see that these curves are significantly distorted due to the angular divergence (convolution) of the incident beam. (The curves in Fig. 2 and 3 are plotted in the same scale.) However, the reflection curves $\overline{P_R(y)}$ differ from the “proper” curves $P_R(y)$ only quantitatively, contrasting with the curves $\overline{\kappa(y)}$ which differ from the “proper” curves $\kappa(y)$ qualitatively.

As was shown in [10], in the case of $L_d < L_{ex}$ the wave field amplitude changes slightly and the variation of the photoemission curves is mainly determined by an additional phase factor $\exp(i\varphi)$ appearing in the interference term (see (2.2)). Since in our case the phase $\varphi(z) < 0$ (lattice compression) the character of the photoemission curve variation, at small layer thickness $z' < L_{ex}$, is evident. However, as the layer thickness increases, the variation of the incident and reflected X-ray amplitudes becomes appreciable and the shape of the $\kappa(y)$ curve becomes more complicated.

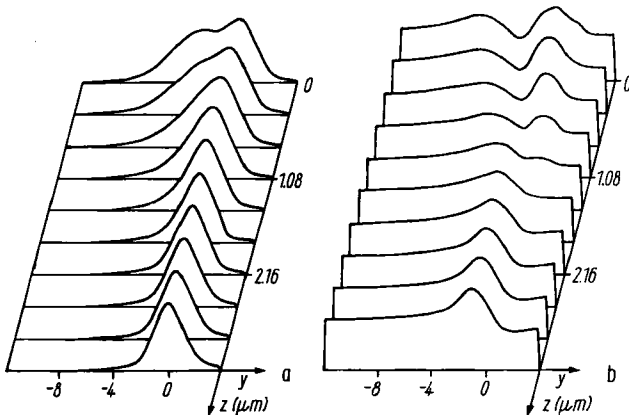


Fig. 3. a) X-ray reflection $\overline{P_R(y)}$ and b) photoemission $\overline{\kappa(y)}$ curves as in Fig. 2 with the account of the incident beam divergence

The results of calculation clearly demonstrate that it is most convenient to measure "proper" photoemission curves either by a double-crystal spectrometer with asymmetrical reflection for the monochromator crystal ($\beta_1 \ll 1$), or, which is better, by a three-crystal spectrometer using polarized and collimated radiation [15, 16].

5. Conclusion

The results presented in the previous section demonstrate the effectiveness of the approach lying in the simultaneous automatic calculation of X-ray and photoemission curves for an arbitrary model of the disturbed layer. If the information on the disturbed layer structure is available from some indirect sources, the direct comparison between the calculated and experimental curves enables the disturbed layer model to be checked and in some cases to improve it.

If the disturbed layer parameters are unknown, then they may be reconstructed directly from the experimental data by comparison of the curves calculated for different disturbed layer models with the experiment. In this respect the use of experimental data both on diffraction and photoemission is very promising and guarantees the reliability of the results obtained.

We may also note that the experimental measurement of "proper" curves is very important for this problem since they contain rather valuable information which is frequently lost in experiments with divergent beam.

Acknowledgements

The author's pleasant duty is to express their gratitude to A. M. Afanasyev and R. M. Imamov for permanent interest in the work and valuable remarks.

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(Received May 7, 1980)