Application of the Borrmann effect to x-ray monochromatization and to the overlayer versus substrate signal-ratio enhancement

S. Lagomarsino
Istituto di Elettronica dello Stato Solido, Via Cineto Romano, 42 00156 Roma, Italy

G. Stefani
Dipartimento Matematica e Fisica, Università degli Studi di Camerino, I-62032 Camerino, Italy

P. Castrucci
Istituto di Elettronica dello Stato Solido, Via Cineto Romano, 42 00156 Roma, Italy

P. Letardi
Istituto per le Metodologie Avanzate Inorganiche, Area della ricerca di Roma, Casella Postale 10 00016, Monterotondo, Italy

F. Scarinci, G. Savelli, and A. Tebano
Istituto di Elettronica dello Stato Solido, Via Cineto Romano, 42 00156 Roma, Italy
(Received 14 June 1991)

In x-ray-excited surface spectroscopies one of the most relevant figures of merit is the overlayer versus substrate signal ratio. In this work we propose to utilize the Borrmann (or anomalous-transmission) effect, which takes place in perfect crystals, in order to have a weaker interaction of the incident beam with the substrate. In this way the overlayer versus substrate signal ratio can be enhanced, roughly by a factor varying between 3 and 20, depending on the kind of spectroscopy utilized. To demonstrate the feasibility of this method, the fluorescence signal intensity of a Ge overlayer (200 Å thick) is compared with the Si substrate scattering both in transmission and in reflection geometry. The synchrotron radiation from a wiggler insertion device was used as an x-ray source. An improvement of a factor about 3 is observed in the present experiment, in agreement with the expected value for this particular case. The monochromatization properties of such an arrangement are also presented.

When a plane wave is diffracted by a perfect crystal, the interference between the incident and the diffracted waves gives rise to standing-wave patterns inside the crystal having the periodicity of the diffracting planes.[1] In the reflection (or Bragg) case, the standing-wave pattern is one for each polarization state, and moves inward by half a lattice spacing when the crystal is rotated through the Bragg diffraction. In the transmission (or Laue) case, *two* standing-wave patterns for each polarization state are created inside the crystal. Their positions remain fixed as a function of the rocking angle, and only their intensities change. The synchrotron radiation being linearly polarized, we will consider in the following only the polarization perpendicular to the scattering plane (σ polarization). The first standing-wave (SW) pattern has its origin on the α branch of the dispersion surface and has nodes on the diffracting planes. In the case of a reflection order where all atoms scatter in phase (full reflections), such as the (220) for the diamond structure, the diffracting planes coincide with the atomic rows, and therefore the interaction of this standing-wave pattern with the atoms is very low. The second SW pattern, which originates from the β branch of the dispersion surface, has antinodes on the atoms and therefore a stronger interaction. The effective absorption coefficients for the two branches $\mu_{\alpha,\beta}$ is given, in the case of symmetric Laue case, by[1]

$$\mu_{\alpha,\beta}=\mu_0\{1\mp\epsilon/[1+(\eta')^2]^{1/2}\}\ , \tag{1}$$

where μ_0 is the normal photoelectric absorption coefficient for the given incident radiation and the given material, and the minus and plus signs refer to the α and β branches, respectively. η' is an adimensional angular unit proportional to the deviation from the Bragg angle. ϵ, for full reflections, is the ratio between the imaginary part of the structure factor for scattering angle 2θ (F_H'') and the corresponding term for forward scattering (F_0''). The value of ϵ depends on the distribution of absorbing power in the atom and on lattice vibration. For low-order reflection it is close to unity, and therefore μ_α can be much lower than μ_0, while μ_β can be as large as twice μ_0. μ_α has a minimum corresponding to $\eta'=0$ that is for the exact Bragg angle, and it increases with increasing of $|\eta'|$, reaching the μ_0 value only for $|\eta'|\gg 1$. In the case of a thick crystal ($\mu_0 T\cong 10$, where T is the crystal thickness), only a very collimated bundle of the σ polarization from the α branch has a weak enough interaction with the crystal matrix to allow some power to reach the opposite face where two wave fields are present: one diffracted at 2θ, and the other diffracted in the forward direction. This is the well-known Borrmann or anomalous-transmission effect.[2] The exit beam is strongly polarized because the polarization in the plane of

scattering (π polarization) suffers a higher absorption than the σ one. This effect allowed the use of thick crystals in Laue-diffraction geometry as polarizers.[3,4] The two wave fields suffer strong interaction with matter whenever a break in the substrate periodicity occurs. This effect has been used, for example, to investigate the perfection of Si crystals treated at high temperatures.[5] The break in the substrate periodicity can also be obtained by depositing an overlayer on the exit face of the substrate. It is interesting to evaluate the overlayer versus substrate signal for two possible geometries: (i) the overlayer is deposited on the entrance face (reflection geometry); (ii) the overlayer is deposited on the exit face of a thick single crystal set in the Laue-diffraction condition (anomalous-transmission geometry).

Let us assume the overlayer to be a thin film over a thick substrate; as a consequence, the overlayer signal S_{ov} is directly proportional to the photon flux incident on it and to the integrated cross section for the observed process (refl and trans refer, respectively, to the reflection and the transmission geometry): $(S_{ov})_{refl} \propto I_0$; $(S_{ov})_{trans} \propto (I_0/2)[\exp(-\mu_\alpha T)]$. The substrate signal S_s is assumed to be proportional to the x-ray absorption in a slab whose thickness t is related to the mean free path of the particles detected in the experiment: $(S_s)_{refl} \propto I_0[1-\exp(-\mu_0 t)]$, $(S_s)_{trans} \propto (I_0/2)\exp(-\mu_\alpha T)[\exp(\mu_\alpha t)-1]$. From the above equations, $R = S_{ov}/S_s$ has been evaluated for the two geometries:

$$\frac{R_{trans}}{R_{refl}} = \frac{1-\exp(-\mu_0 t)}{\exp(\mu_\alpha t)-1} . \tag{2}$$

Assuming $\epsilon = 0.95$ [silicon (220) reflection at room temperature] the ratio R_{trans}/R_{refl} in Eq. (2) varies from about 3 to 20 according to the value of t. The first limiting case is expected to be met in the case of photon scattering, the second one in the case of electron yield measurement. The t value has been taken as five times the mean free path. Typical values are $\mu_0 = 52$ cm^{-1} at a photon energy of 11.5 keV, $t = 0.1$ cm for photons, and $t = 250$ Å for photoelectrons. It is to be noted that this enhancement in the value of the overlayer versus substrate signal is obtained at the expense of a reduction of the peak intensity of radiation impinging on the overlayer that does not exceed a factor of 3. Furthermore, the substrate itself can act as a monochromator because of the very narrow angular width of the reflection, which is given, in the thick-crystal approximation and for a polarized beam, by

$$W = \frac{2\Gamma F'_H}{\sin 2\theta} \left[\frac{2\ln 2}{\epsilon(\mu_0 T/\gamma_0)} \right]^{1/2} , \tag{3}$$

where $\gamma_0 = \cos\theta$ (θ is the Bragg angle), F'_H is the real part of structure factor for the given reflection, and $\Gamma = (r_e \lambda^2)/(\pi V)$, where r_e is the classical electron radius, λ is the wavelength, and V is the unit-cell volume. For the reflection case, W is given by $W = (2\Gamma F'_H)/\sin 2\theta$.

Concerning the monochromatization properties of the transmission geometry, we start from the consideration that for a collimated beam, the energy resolution is determined by the intrinsic angular width W of the diffraction peak through the simple relation $\Delta E/E = W/\tan\theta$, where W is given for the transmission case in thick crystals by Eq. (3). The resulting intrinsic resolution is therefore $\Delta E/E = 2\times 10^{-5}$ for the (220) reflection in Si at a photon energy of 11.5 keV and a thickness of about 1.7 mm. This value has to be compared with the intrinsic resolution of the same reflection in the Bragg case: $\Delta E/E = 6\times 10^{-5}$. An improvement by a factor of 3 in energy resolution is therefore expected to be obtained in the transmission case.

In order to prove the feasibility of these ideas, we carried out an experiment at the wiggler beam line of the synchrotron radiation facility Adone in Frascati, using the experimental station for x-ray standing waves.[6] The photon beam was monochromatized by a Si(111) channel-cut crystal. We used the symmetric $(2\bar{2}0)$ reflection in (111)-oriented Si platelets of thickness $T = 1.7$ mm with an incoming beam energy $h\nu = 11.5$ keV. At this energy $\mu_0 = 52$ cm^{-1}, so that the thick-crystal condition $\mu_0 T \cong 10$ is fulfilled; $\epsilon = 0.95$, and $W = 1.4''$. The silicon platelets were covered by a layer of Ge nearly 200 Å thick. The geometry of the experiment in the transmission case is shown in Fig. 1. The experiment we carried out is composed of two parts. The first one regards the measurement of the overlayer versus the substrate signal, the second one the monochromatization properties of such an arrangement.

We carried out the experiment taking the fluorescence intensity of the Ge $K\alpha$ line as the overlayer signal. The sum of the thermal diffuse scattering (TDS) and of the Compton scattering was the substrate signal. A Si(Li) solid-state detector was used to measure both the fluorescence and the scattering intensities. The energy of the incoming beam was just above the Ge K edge. In order to observe possible changes in the crystal alignment, the beams diffracted in the forward direction, and at 2θ were monitored with NaI detectors. Care was taken to mask the solid-state detector from the photons scattered from the entrance substrate face. The effectiveness of the screening was checked by observing the fact that when the substrate was moved from the diffraction position, both fluorescence and scattering had practically zero intensity. The resolution of the solid-state detector was good enough to distinguish very clearly the fluorescence from the scattering. Only the tail of the Ge $K\beta$ line was superimposed on the scattering peaks. It was possible to separate them and evaluate the relative intensities by a

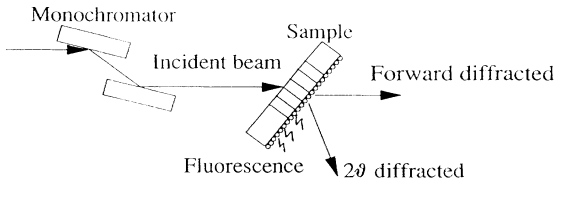

FIG. 1. Schematic layout of the experiment. The incident beam is subjected to the anomalous transmission effect due to the large thickness of the substrate. Only the wave field that has a weak interaction with the substrate can reach the exit face and excite the adsorbate.

least-squares Gaussian fitting. The fitting parameters determined by the MINUIT code were used to evaluate the area of each individual peak. We compared the values of the overlayer and substrate signals obtained in transmission with the corresponding ones obtained in the standard way; that is, with the beam impinging directly on the substrate face covered by Ge (reflection geometry). The incidence angle was nearly 20°, far from any Bragg position. The energy of the incoming beam was obviously the same as in transmission. The scattering intensity in the case of a polarized beam has a strong dependence on the angle between the polarization direction and the scattering direction, being zero in the direction of polarization. We therefore paid attention in positioning the solid-state detector at the same angle for the two geometries (transmission and reflection) with respect to the incident beam in order to have a correct comparison. Figure 2 shows the spectrum for, respectively, the (a) transmission and (b) reflection cases. The measured ratio between the overlayer signal and the substrate signal is 2.8 ± 0.4 times higher for transmission than for reflection. This value is in quite good agreement with the expected value for this kind of experiment [see Eq. (2)]. It is worth noting that a much larger enhancement for the transmission geometry with respect to the reflection one is expected when the electron yield is detected instead of the fluorescence one.

To demonstrate the energy tunability in the transmission geometry, we measured the Ge fluorescence excited by photon energies tuned on the Ge K absorption edge. The sample was the same as in the previously described experiment. To scan the absorption edge in our geometry, we only need to change the sample angular position. The substrate itself acts as a monochromator, letting for each angle a different photon energy to pass through the thick substrate. This arrangement is substantially simpler than standard geometries, and can be useful for fast energy scans. However, a complete white beam cannot be used because higher-energy components could pass easily through the substrate. The best solution would be an incident beam having an energy bandpass of the order of 1%, such as the one produced by an undulator. Unfortunately, we could not produce a beam with such a large bandpass, and therefore we used as a premonochromator the standard Si(111) channel-cut crystal. The geometry was that depicted in Fig. 1, that is, the $(+n,-m)$ following the Allison notation.[7]

Taking into consideration the incident beam divergence (3.3×10^{-5} rad) and the angular widths of monochromator and sample reflections, the total resolution is $\Delta E/E=1.4\times10^{-4}$, as determined with the aid of the Du Mond diagrams.[8] The resolution with the Si(111) monochromator alone was 3.2×10^{-4}. Better resolution could be obtained in the $(+n,+m)$ case. With the same symmetric (111) and $(2\bar{2}0)$ reflections, the resolution would be 6.6×10^{-5}. Obviously, the intensity would be lower.

A drawback in using a crystal premonochromator is the limited energy range ΔE reflected by the premonochromator. In our case, ΔE was 3.9 eV and forced us to measure the near-edge part of the Ge K absorption in successive energy regions. In other words, we set the

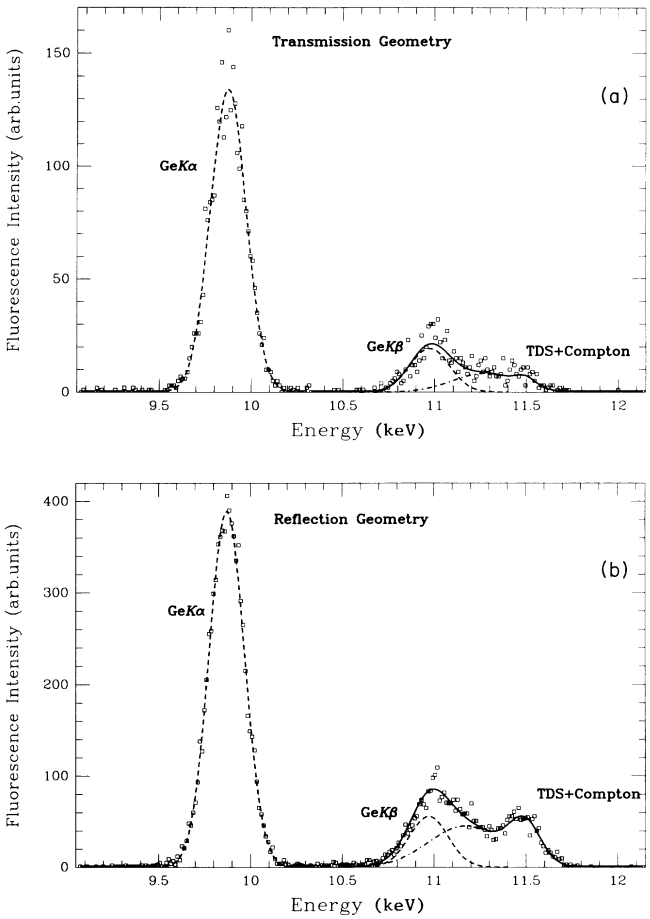

FIG. 2. Spectra obtained in (a) transmission and (b) reflection geometries. The overlayer signal is given by the Ge fluorescence, the substrate signal by the scattering (Compton plus thermal diffuse). The scattering is, however, convoluted with the Ge $K\beta$. Therefore, a least-squares Gaussian fitting has been carried out in order to separate the fluorescence from the scattering. The overlayer vs substrate signal is in this case 2.8 ± 0.4 times higher in the transmission geometry than in the reflection geometry.

monochromator to a certain energy, and we rocked the substrate through the diffracting region, thus describing the ΔE energy range given above. The monochromator was then set at a new position, the difference in energy between the two positions being approximately equal to the ΔE range. Considering the energy resolution discussed above, the energy band that reached the exit face was about 1.5 eV for each fixed position of the substrate.

The fluorescence intensity I_F is proportional to the total intensity I_T that reaches the exit face. In the case of a large bandpass monochromator, I_T would be virtually constant in the limited range of interest. This being not the case, we must normalize the fluorescence intensity to I_T. As the scattered intensity I_S [thermal diffuse scattering (TDS) and Compton scattering] is also proportional to I_T, we normalized I_F to I_S, due to the fact that both were measured with the same detector. We assume that the TDS and Compton cross section for scattering is con-

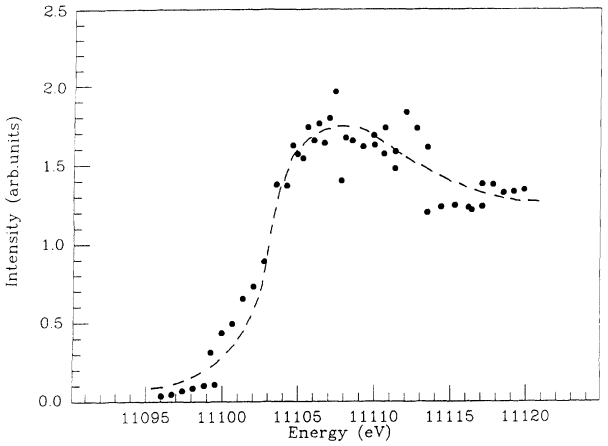

FIG. 3. Normalized Ge fluorescence intensity (closed circles) as a function of the exciting photon energy. The experimental points are the result of several (six) rocking curves taken at different settings of the monochromator. The fluorescence is normalized to the scattering intensity (Compton plus thermal diffuse). The dashed line is the near-edge structure as measured by an x-ray-absorption experiment (Ref. 7).

stant in the very limited energy range of the absorption edge explored in our experiment. A least-squares Gaussian fitting of the experimental spectrum, similar to that shown in Fig. 2(a), has been carried out for all the steps to obtain the intensity ratio (I_F/I_S). Figure 3 shows the result of such a "collage" obtained with six successive rocking curves. The horizontal energy scale is determined by $\delta E = E\delta\beta/(\tan\theta_1 - \tan\theta_2)$, where $\delta\beta$ is the angular distance between two points of the rocking curve, and θ_1 and θ_2 are the Bragg angles for Si(111) and Si($2\bar{2}0$), respectively. Within the experimental errors achieved in the present experiment, all the features of the K absorption edge of Ge are clearly measured. The near-edge structure measured by an x-ray-absorption experiment (derived from Fig. 20 in Ref. 9) is also shown in the figure with a dashed line. The agreement between the two experiments is quite good. We are well aware that our spectrum is affected by poor statistics; nevertheless, the feasibility of this technique is clearly demonstrated.

It is clear that for a practical utilization of the technique proposed in this paper, a larger energy range from the premonochromator should be available. For near-edge studies, an energy range value of $\Delta E = 50$ eV should be sufficient. On the other hand, the aim of this work is to present the feasibility of a method that in suitable experimental conditions can allow better energy resolution with respect to standard geometries and a very simple arrangement.

In conclusion, an application of the Borrmann effect has been suggested. The transmission geometry in the thick-crystal case has the unique characteristic of monochromatizing the incident radiation while achieving a better ratio of the overlayer signal versus the substrate signal with respect to the standard reflection geometry. The feasibility of this method has been proven carrying out measurements on a Ge overlayer deposited on a Si single crystal, achieving an enhancement of about a factor of 3. This is in good agreement with the expected value for a fluorescence experiment. A much-larger enhancement is expected when electrons are detected instead of photons. Concerning the monochromatization, it is worthwhile to note that such an arrangement is one of the simplest monochromator conceivable. A better energy resolution with respect to standard geometries can be achieved. Its simplicity could allow very fast acquisition in the case where an energy scan is to be performed, as, for example, in extended x-ray-absorption fine structure (EXAFS) experiments. Further advantages can be obtained by keeping the crystal at low temperature, because the ϵ value becomes closer to one, and as a consequence μ_α becomes smaller. This has the effect of further enhancing the overlayer versus substrate signal with respect to the reflection geometry and enhancing the transmitted intensity with respect to the room-temperature situation.

We gratefully acknowledge all the staff of the Wiggler laboratory, and in particular Professor E. Burattini, for his kind and very helpful assistance. Two of us (G.S. and P.L.) acknowledge partial support from Progetto Finalizzato CNR "Chimica fine." This work has been partially supported by Progetto Finalizzato CNR "Materiali e Dispositivi per l'Elettronica a Stato Solido."

[1]B. W. Battermann and H. Cole, Rev. Mod. Phys. **36**, 681 (1964).

[2]G. Borrmann, Z. Phys. **127**, 297 (1950).

[3]V. O. Kostroun and G. Materlik, Nucl. Instrum. Methods **172**, 215 (1980).

[4]G. Materlik and V. O. Kostroun, Rev. Sci. Instrum. **51**, 86 (1980).

[5]J. R. Patel and B. W. Battermann, J. Appl. Phys. **34**, 2716 (1963).

[6]S. Lagomarsino, F. Scarinci, A. Tebano, S. d'Angelo, and G. Luce, in *Proceedings of the 2nd European Conference on Progress in X-ray Synchrotron Radiation Research, Rome, 1989,* edited by A. Balerna, E. Bernieri, and S. Mobilio (Editrice Compositori, Bologna, Italy, 1990), p. 471.

[7]A. H. Compton and S. K. Allison, *X Rays in Theory and Experiment* (Van Nostrand, New York, 1935).

[8]J. W. M. Du Mond, Phys. Rev. **52**, 872 (1937).

[9]T. M. Hayes and J. B. Boyce, Solid State Phys. **37**, 173 (1982).