Substrate-mediated multiwave resonance grazing incidence x-ray diffraction in thin films: A method for direct phase determination

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Direct phase determination of surface in-plane reflection is realized for thin films on substrates by using substrate reflections as an intermediary to enhance the coherent interaction in resonant multiwave grazing incidence diffraction in thin films. The coupling of the in-plane diffracted waves at the interface between the thin film and the substrate is essential. The intensity variation due to this enhanced interaction/coupling becomes clearly visible, thus leading to unambiguous phase determination. This opens a different way for direct phase determination of surface reflections in thin films.

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I. INTRODUCTION

The intensity measurement of a single Bragg reflection from two- or three-dimensional atomic structures usually provides no phase information about the related structure factor. This fact constitutes the well-known important x-ray phase problem in diffraction physics, x-ray optics, and crystallography,1 mainly because the phases and the amplitudes of structure factors are necessary information needed for structure determination. Although there have been several methods,1,2 including multiple diffraction,3–12 which provide solutions to this problem for three-dimensional periodic atomic structures, direct determination of the phase of surface in-plane reflection for a two-dimensional or quasi-two-dimensional (2D) system is yet lacking. So far, phases of reflections from 2D systems, such as surfaces and interfaces, have been determined mainly by structure modeling through intensity matching or by Patterson methods on a trial and error basis.13 Although the interference of the diffracted x-ray wave from a 2D crystal and the backward reflected x-ray wave from a gold mirror layer grown on the back side of the crystal has demonstrated the possibility for phase determination in a 2D crystal,14 the applicability of that technique to common thin-film/overlayer systems is not clear, because of the special sample treatment required. Recently, the three-wave resonance grazing incidence x-ray diffraction (GIXD) has been developed to determine the phases of surface in-plane reflections of a single-crystal bulk.15 However, direct phase determination for thin films/overlayers on a crystal substrate has not been demonstrated and yet a model-free operational method for direct phase determination in 2D systems is most desired. Very recently, preliminary results in phase determination for thin film using this three-wave GIXD (Ref. 16) and an attempt to determine the reflection phase from a reconstructed surface layer17 have been reported. The latter involves the coupling between the surface reflections and of the substrate. In this paper, we report the detailed development of the method for phase determination in thin films, utilizing the x-ray grazing incidence diffraction near three-wave resonance diffraction condition and the coupling effect between the substrate and thin-film reflections. The strong in-plane reflection of the substrate used in this method acts as an intermediary to enhance the three-wave interaction in the thin film and thus leads to direct phase determination of x-ray reflections for the thin film.

II. THREE-WAVE GIXD EXPERIMENTS

Three-wave resonance GIXD occurs when a grazing incident x-ray wave, denoted as O wave, is diffracted simultaneously by two sets of atomic planes, G and L, perpendicular to the crystal surface for a specific photon energy $E_M$. The interaction of the incident O wave with the diffracted G and L waves inside the crystal gives rise to intensity variation on the diffracted waves, as well as their surface-specularly reflected components. This intensity variation thus depends on the phase $\delta_3$ and the amplitude of the structure-factor triplet, $F_{-G}F_{G-L}$, where $G-L$ is the coupling between the G and L reflection, and $\delta_3 = \delta_3 + \delta_L + \delta_{G-L}$. Figure 1(a) shows a schematic of the three-wave ($O, G, L$) resonance diffraction in reciprocal space, where $O, G$, and $L$ stand for (000), (440), and (404) for germanium and the photon energy $E_M = 7.1571$ keV. In this paper, a 90-Å-thick Ge$_{0.7}$Si$_{0.1}$ thin film grown on the ($\bar{1}$11) surface of a 1-mm-thick Ge substrate by organometallic chemical vapor deposition (MOCVD) is investigated. The mosaic spread in the in-plane direction of the film is about 0.066°, much larger than that of the substrate. The reciprocal-lattice points of the same reflections for GeSi as for Ge are also shown in Fig. 1(a) with larger open circles, relating to the larger mosaic spread. The experiments near the three-wave resonance condition were carried out at the wiggler beamline BL-17B of the Synchrotron Radiation Research Center (SRRC). The storage ring is operating at 1.5 GeV and 200 mA. The incident radiation is focused and monochromatized by a focusing mirror and a sagittal double-crystal monochromator (DCM). The beam divergences are 0.008° horizontal and 0.005° vertical. The energy resolution of the DCM is 2 eV. Figure 1(b) shows the experimental setup. The GeSi/Ge sample is mounted on an eight-circle diffractometer with the [$\bar{1}$11]
tively, the Bragg angles of the substrate are nearly the same, i.e., 5.6541 and 5.6578 Å, respectively. Since the lattice constants of the GeSi film and the Ge substrate are different for the two materials, for example, 0.065° for the GeSi film and the Ge substrate. The small kinks, B and D, are due to the multiwave interactions involving (404) and (440) reflections of GeSi and the influence of (404) and (440) of Ge, respectively [see Fig. 3(a)]. The positions of the peaks and kinks change as the energy $E$ varies. For (440), the peak position shown in Fig. 2 shifts towards high $\omega$ angles for lower energies, while the kink position shifts in the opposite direction, following the position of the (404) peak [see Fig. 3(a)]. According to the $\omega$ rotation of the crystal, the reciprocal-lattice point of (440) moves towards the surface of the Ewald sphere, which corresponds to the incoming (IN) situation. The reverse outgoing (OUT) situation takes place for the (404). In Fig. 3(a), near $\omega=59.933°$ and 60.067°, the peaks and kinks are the combined four-wave diffraction cases: (A) (000) (404) (440) S (440) F; (B) (000) (404) F.
FIG. 4. The measured intensity profiles (ω scans): (a) the four-wave, (000),(440)F, (404)S, (404)F, case (solid lines: calculated profiles for different values of the triplet phase δ3 in the vicinity of ω position of the (404) reflection of the substrate), and (b) (000),(440)F, (440)S, (404)F, case. The energy scan of the five-wave case: (000),(440)S, (440)F, (440)S, (004)F. The letter O abbreviates for (000). The dashed lines of zero intensities of (a) and (c) in linear scales, resulting from the subtraction of the intensities of respective (440)F and (404)S reflections from the measured profiles, represent the intensity levels of the corresponding (440)F and (440)S primary reflections. The dashed line in (b) shown in a log scale represents the unity intensity level of the (440)F primary reflection.

![Graph](image)

(404)S, (404)F; (C) (000), (440)F, (440)S, (404)F; and (D) (000), (440)S, (440)F, (440)F, The labels S and F denote substrate and film, respectively. After subtracting the intensity distribution of thin film (440) from the measured one, the detailed profiles of cases B and C are shown in Figs. 4(a) and 4(b), where the IN directions of the crystal rotations are indicated. The dashed lines in Figs. 4(a) and 4(b) represent the intensities of the two-wave (440)F reflection at the corresponding ω angles, respectively. The intensity increasing and decreasing on the (440)F intensity background are readily seen.

The mosaic spread of the sample is measured at E = 8 keV. The full widths at half maximum (FWHM) of the sharp substrate peaks and the broad thin-film profiles in θ = 2θ scans are about 0.018° and 0.101°, respectively. The latter is mainly due to the particle-size broadening, about 0.080° of the thin film, whose crystallite size is about 452 Å. The measured FWHM’s in ω scans of the Ge and GeSi are 0.018° and 0.106°. The estimated mosaic spread Δω of the thin film from the particle size and ω scans is 0.066°. Clearly, the particle-size broadening in ω scans [Fig. 3(a)] facilitates the detection of the intensity variation due to multiwave interaction.

III. PHASE DETERMINATION

Referring to the diffraction geometry shown in Fig. 1(a), the (404)S diffracted wave in case B interacts with the (440)F wave at ω = 59.933°, because the two diffracted waves have the possibility of propagating in the same direction with the same tangential components of the wave vectors at the interfacial boundary. This is due to the fact that the difference in Bragg angle between the two is comparable with the mosaic spread of the film, i.e., Δθ = Δω. Namely, the phase matching of the two (404) waves propagating in the same direction at the interface is met, that ensures the coupling to occur. Thus the (404)F wave is modified by this coupling. Since the intensity and the directionality of (404)S is much stronger and better than those of (404)F, the coupling between the two waves is enhanced in a small angular range, about 0.06° in ω, which is consistent with the condition for phase matching. This modified (404)F wave inside the film, in turn, interacts with the (440)F wave via the coupling reflection, i.e., (440)F → (404)F = (004)F, just as in the usual three-wave diffraction for a bulk crystal. Hence this combined four-wave case is actually a three-wave thin-film diffraction coupled with the substrate (440)F reflection. Because the coupling of (404)S is indirect to the measured (440) reflected wave which is monitored by the detector, the intensity variation on the (440)F along the IN direction, first decreasing then increasing, is not very strong but visible [see Figs. 3(a) and 4(a)]. This variation is useful for phase determination. According to Ref. 15, the sign of cos δ3 depends on the signs of the polarization phase δp, the geometry phase δg, and the sign S_L defined by the asymmetry of the intensity variation, i.e., S(cos δg) = S(cos δp)S(cos δg)S_L. The beam-polarization phase δp = 0° for a σ polarized incident wave. The geometry phase δg = 0° for the IN situation and g = 1 ∈k^2 > 0, where g and k are the reciprocal-lattice vectors of the G and L reflections. S_L is positive for the intensity first decreasing then increasing, and negative for the reverse asymmetry. With the asymmetry of the profile shown in Fig. 4(a), the triplet phase is therefore determined as δ3 = δ2(440F) + δ2(440F) + δ(440F) = 0°, because S_L > 0, S(cos δp) > 0, and S(cos δg) > 0. However, without the presence of the substrate, the intensity asymmetry due to the three-wave diffraction in the thin film would be difficult to detect, owing to the large mosaic spread.

The combined four-wave case C, (000), (440)F, (440)S, (404)F, can also be considered as a thin-film three-wave case coupled with the substrate (440)S, except that the coupling is direct to the measured (440) reflection. The intensity variation on the (440)F is therefore much stronger.
than that in case B. The intensity asymmetry shown in Fig. 4(b) leads to \( \delta_1 = \delta(440F) + \delta(04F) + \delta(044F) = 0^\circ \), because \( S_L > 0, S(\cos \rho_L) > 0 \), and \( S(\cos \rho_1) > 0 \). If the photon energy \( E \) is far from the resonance energy \( E_M \), i.e., the two broad profiles do not overlap, the intensity asymmetry does not appear. This has been experimentally confirmed at \( E = 8 \) keV.

The triplet phases of cases A and D can also be determined as: \( \delta_1 = \delta(440F) + \delta(04F) + \delta(044F) = 0^\circ \), and \( \delta_2 = \delta(404F) + \delta(440F) + \delta(044F) = 0^\circ \), respectively. Because the symmetry of the in-plane lattice of the thin film Ge_{0.9}Si_{0.1}, verified experimentally by surface in-plane diffractions, is similar to that of Ge, the phase relations, \( \delta(440) \), of the in-plane reflections in the family \{440\} of Ge_{0.9}Si_{0.1} follow the space group \( Fd\bar{3}m \) of Ge. That is, the phases \( \{440\} \) are equal. With the triplet phases determined and the phase relations imposed by the space group, the phase values can be deduced as: \( \delta(440F) = \delta(04F) = \delta(044F) = \delta(404F) = \delta(440F) = \delta(044F) = 0^\circ \).

We have also measured the maximum intensities of the \{440\} peaks of Fig. 2 for various \( E \) and plotted the intensity versus \( E \) at the IN situation in Fig. 4(c). Clearly, the intensity asymmetry is observed, which reveals the phase effect on the diffracted intensities in the three-wave, \( (000)(440) \), resonance GIXD for Ge at the photon energies near \( E_M = 7.1571 \) keV. Similarly, the phases of individual \{440\} reflections for Ge are determined experimentally to be \( 0^\circ \), according to Ref. 15. Actually, this three-wave diffraction is really a combined five-wave case, because, in reality, in addition to the three-wave case of Ge, there is the same three-wave case of GeSi coexistent. These two three-wave cases share the same direct reflection \( O \) (000). Owing to that the diffracted intensities from GeSi are so weak, the three-wave case of Ge becomes dominant and visible.

IV. THEORETICAL CONSIDERATION

The intensity distributions of multiply diffracted waves can be calculated based on the dynamical theory of x-ray diffraction. For a qualitative interpretation of the measured intensity distributions, Born approximation\(^{19-21} \) can be used. For a given three-wave \( (O, G, L) \) diffraction, according to the Born approximation, the wave field \( \mathbf{D}_{G(3)} \) of the three-wave diffraction is considered as the sum \( \mathbf{D}_{G(3)} = \mathbf{D}_{G(2)} + \mathbf{D}_{G(3\text{det})} \) of the wave field \( \mathbf{D}_{G(2)} \) of the two-wave diffraction and the wave field \( \mathbf{D}_{G(3\text{det})} \) of the detoured diffraction. The latter involves the successive secondary \( L \) and the coupling \( G-L \) reflections. The wave field \( \mathbf{D}_{G(3)} \) is given as

\[
\mathbf{D}_{G(3)} = A_G \mathbf{X}_G \mathbf{S}_G \times \mathbf{s}_G \times [\mathbf{D}_O - A_L (|\chi_G - L||\chi_L||\chi_G|)] \\
\times \exp(i \delta_2 \mathbf{s}_2 \times (\mathbf{s}_2 \times \mathbf{D}_O)),
\]

where \( \mathbf{D}_O \) is the incident wave field with the magnitude \( D_O, A_H = K_H^2 / [k^2 - K_H^2 (1 - \chi_H)] \) (for \( H = G, L \)) is the resonance term, \( \mathbf{s}_G \) is the unit vector of the \( H \) diffracted wave, and \( \chi_H \) (for \( H = O, G, L, G-L \)) is the Fourier component of the crystal polarizability proportional to the structure factors of the \( H \) reflection. Here, \( k = 1/\lambda \) and \( K_H \) are the magnitudes of the wave vectors in vacuum and inside the crystal, respectively.

The \( \omega \) scanning of the crystal accompanies with the movement of the reciprocal-lattice points \( G \) and \( L \) through the surface of the Ewald sphere. According to Ref. 19 the resonance terms \( A_G \) and \( A_L \) in this case can be approximately described as

\[
A_H = 1/[(\omega - \omega_H) + i(\eta_H/2)]
\]

(for \( H = G, L \), where \( \omega_H \) and \( \eta_H \) are the \( \omega \) position and the Darwin width of \( H \) reflection, respectively, and \( |A_H|^2 \) is a Lorentzian. The resonance term \( A_H \) describes the \( 180^\circ \) phase shift of \( H \) reflection when the reciprocal-lattice point \( H \) crosses the surface of the Ewald sphere.

The theoretical approach described above is valid for the single-crystal plate, in particular, for crystalline thin film without substrate. In the case of thin film when the reflection from a substrate is present and the condition \( \Delta \theta = \Delta \omega \) is satisfied, the resonance term \( A_H \) is modified as \( A_H' = A_H + \Delta A_H' \), where \( \Delta A_H' \) is the deviation from \( A_H \) for the thin film due to the presence of the reflection from the substrate. According to the continuity of the tangential components of the wave fields at the boundary between the film and the substrate, the strong substrate reflection with resonance term

\[
1/[(\omega - \omega_H') + i(\eta_H'/2)]
\]

produces the same deviation \( \Delta A_H' \) for the film. The terms \( \omega_H \) and \( \eta_H \) are the \( \omega \) position and the Darwin width of \( H \) reflection for the substrate, respectively. Therefore \( \Delta A_H' \) can be also given, in view of Eq. (2), as

\[
\Delta A_H' = \Delta \epsilon_H' \frac{1}{[(\omega - \omega_H') + i(\eta_H'/2)]}
\]

where the coefficient \( \Delta \epsilon_H' \) (\( |\Delta \epsilon_H'| < 1 \)) depends on the degree of coupling between the film and the substrate.

The resulting diffracted intensity \( I_G \) from the film is given as

\[
I_G(\omega) = \int |\mathbf{D}_{G(3)}(\omega')|^2 I_M(\omega - \omega') I_L(a_r - a) \\
\times I_B(E - E', \omega - \omega') d\omega' d\omega dE dE',
\]

where the intensity \( |\mathbf{D}_{G(3)}|^2 \) is convoluted with the crystal mosaic spread \( I_M \), the lattice mismatch distribution \( I_L \) of the film, and the instrumental function \( I_B \) of the incident beam. All the distributions and functions can be approximately estimated as pseudo-Voigt functions \( f_{ab} = \alpha f_G + (1 - \alpha)f_L \), a linear combination of a Gaussian \( f_G \) and a Lorentzian \( f_L \). The coefficients \( \alpha \) of these combinations depend on the experimental conditions. Here, \( a_r \) is the average lattice parameter of the film and the \( \omega ' s \) of \( \mathbf{D}_{G(3)} \) in Eqs. (2) and (3) are given as

\[
\omega_G = \omega_M + \tan(\theta_G)(\Delta E/E_M + \Delta a/a),
\]

\[
\omega_L = \omega_M + \tan(\theta_L)(\Delta E/E_M + \Delta a/a),
\]

\[
\omega_G' = \omega_M - \tan(\theta_G)\Delta E/E_M,
\]

\[
\omega_L' = \omega_M + \tan(\theta_L)\Delta E/E_M.
\]
where $\Delta a = a - a_s$ and $\Delta E = E - E_M$, and $a_s$ is the lattice parameter of the substrate, $\omega_M$ and $E_M$ are the $\omega$ position of the primary reflection and the resonance energy of the incident beam for which the multiple-wave diffraction for the substrate is realized. Such kind of convolution tends to broaden the diffraction width of the film without much widening the perturbed intensity distribution due to the presence of the reflections $G$ and $L$ of the substrate. The profile broadening of the latter is mainly owing to the experimental conditions of the incident beam. The calculated intensity profiles of the overall $(440)F$ and of case $B$ are superimposed on the measured profiles in Figs. 3(a) and 4(a), respectively. According to the experimental conditions, a Gaussian distribution ($\alpha = 1.0$ for $f_{PS}$) is used for the incident beam $I_B$ and a Lorentzian ($\alpha = 0.1$ for $f_{PS}$) for the convoluted distribution of $I_L$ and $I_M$ of the film. The used calculation model does not take into account the real experimental asymmetry of the lattice mismatch distribution $I_L$ of the film. Therefore some deviation of the calculated curve from the experimental one for higher $\omega$ angles shown in Fig. 3(a) is expected (see the dashed curve). Figures 3(b) and 3(c) show the calculated intensities and phase shifts of the $(404)S$ and $(440)S$ reflection, respectively. In the calculation, the widths $\eta_H$ and $\eta_M$ and also the width of the convoluted distribution of $I_M$ and $I_L$ for the thin film are estimated from the experimental data, while the values of $\Delta c_H^L = 0.09$ of the deviations $\Delta A_G$ and $\Delta A_L$ are estimated from the qualitative fitting of the experimental curves to the calculated ones. The positions $\omega_H$ and $\omega_M$ are calculated from Eqs. (5) for the used photon energy of the incident radiation. Deviations $\Delta A_G$ and $\Delta A_L$ of the primary and secondary reflections of the film, which are treated qualitatively the same for all mosaic blocks, due to the presence of correspondent substrate reflections provide the phase sensitivity needed. As shown in Fig. 4(a), the calculated intensity profiles for $\delta_3 = -90^\circ$, $0^\circ$, $90^\circ$, and $180^\circ$ exhibit phase-sensitive asymmetry. From the asymmetry of the experimental profile shown, the corresponding triplet phase $\delta_3$ is $0^\circ$.

V. CONCLUDING REMARKS

In conclusion, we have demonstrated the direct determination of the phases of surface in-plane reflections from a thin-film/substrate system, using substrate-mediated multiwave resonance GIXD. The success in detecting the interference effects in this thin-film system mainly relies on the phase matching condition, i.e., the constraint on the lattice mismatch between the film and the substrate, compared to the mosaic spread of the thin film, i.e., $\Delta \theta = \Delta \omega$. The visibility of intensity variation on the general background due to the particle-size broadening is also important. Without this phase matching, the strong $(440)$ reflection of Ge cannot act as the intermediary between the substrate and the thin film so that the interference of the three waves in the thin film alone is hard to be observable. This condition for interference has also been verified in other systems, such as the molecular-beam epitaxy Au/GaAs. No effects of multiwave interference are observed, due to the large lattice mismatch between Au and GaAs. Moreover, it is well understood that the coherent dynamical interaction in multiwave diffraction is usually smeared out by large crystal mosaicity. Therefore good quality thin films/overlayers are also required for successful application of this phasing method for thin-film systems.

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1See, for example, H. A. Hauptman, Phys. Today 42(11), 24 (1989).