Methods for the Quantitative Structural Analysis of Amorphous Ge Thin Film by X-rays

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The atomic scale structure of the 0.9 \( \mu \text{m} \) thick amorphous Ge film on the Si single crystal substrate was determined by Mo K\( \alpha \) radiation with the Seemann-Bohlin arrangement with a small angle of incidence. Some difficulties of the quantitative analysis of the thin film were pointed out and our solutions were presented. At the same time, a new method has been proposed, by applying the anomalous dispersion effect of the constituent element of the film. The effective difference of the intensity profiles in this method estimated by the calculation was actually observed in the experiment at Photon Factory, National Laboratory for High Energy Physics, Tsukuba.

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I. Introduction

Both physical and chemical properties of thin films are applied to many new materials. For example, magnetic or optical memory devices, heat- or wear-resist coating, and as a very recent application, a high temperature superconductor, etc. Thus, the investigation of atomic scale structures of these thin films has become a significant and interesting topic from both engineering and scientific points of view.

X-ray and electron diffractions have been widely used to determine the atomic scale structures of these thin films. In principle electron diffraction is much superior to X-ray diffraction since scattering intensities by electrons are several orders of magnitude higher than those by X-rays. However, in electron diffraction strongly-scattered inelastic scattering must be eliminated experimentally to obtain elastic scattering which contains the information on atomic scale structures. Graczyk(1)(2) and Chaudhari(3)(4) determined the atomic scale structures of very thin films of a few hundred angstrom thickness by using an electron microscope with an attachment consisting of scanning, filtering and detection of intensities of the diffracted electrons. On the other hand, in the case of an X-ray experiment, the inelastic (or Compton) scattering is usually much smaller and can be numerically eliminated. Thus, if the diffraction geometry is devised, an ordinary diffraction apparatus can be used for measurements of thin films. The scattering profiles can be obtained in transmission or in reflection geometry. If a film is formed on a substrate which is relatively thin or consists of materials with low atomic numbers, of if the film can be removed from the substrate that might have been used during their preparation, the transmission method can be applied. Lukens and Wagner(5) determined the atomic structures of Ag–Cu and Cu–Mg films of a few hundred nanometers thickness deposited on about 25 \( \mu \text{m} \) thick beryllium in the transmission method. But practically a substrate is always neither made of light elements nor removable from a film. In many cases, films are retained on substrates. In this case, the reflection method with the Seemann-Bohlin arrangement with a small angle of incidence(6) is used. Its diffraction geometry is schematically described in Fig. 1. Since a sample is irradiated with a small angle of incidence \( \alpha \), the penetration depth of the beam becomes small and scattering from the surface is amplified relative to scattering from the bulk. This method is widely employed in the structural analysis of a
crystalline thin film, but very few applications have been actually done for a non-crystalline film.

Keeping these facts in mind, we examined the quantitative analysis of a thin film by X-rays, through an attempt of the measurement of scattering intensity from an amorphous germanium film on a Si single crystal substrate. In the present study, we will reveal some significant points of this type of measurements and describe our methods to solve them, including a new method using the anomalous dispersion effect.

II. Experimental

Amorphous Ge film was grown 0.9 μm thick on a Si 111 wafer about 0.5 mm thick, by plasma deposition of GeH₄ gas diluted by hydrogen gas. The substrate was heated at about 500 K during deposition. The details of the sample preparation have been described in ref. (7). Size of the wafer is about 30 mm by 20 mm and the amorphous layer covers only the upper half of it, that is, the size of the area covered is about 30 mm by 10 mm. The wafer mounted on the sample holder is shown in Fig. 2. The reason why the half-deposited sample was used will be explained below.

The intensity was measured with the reflection method explained above. Monochromatic and parallel beam was obtained by a Ge 111 flat single crystal monochromator in the incident beam. In this way, the angle of incidence is accurately set and the beam size on the sample surface is easily determined simply by adjusting the size of the slits built at the exit of the monochromator housing. The size of the beam on the sample surface was kept smaller than the opening of the soller slits placed in front of the detector, so that all diffracted beam from the sample is collected by the counter at all scattering angles. The soller slits are placed to limit the horizontal divergence of the diffracted beam. This divergence was 0.57°. High intense X-ray beams were obtained by the Rigaku RU-200 rotating anode X-ray generator with a Mo target of 47.5 kV and 190 mA. The angle of incidence was 1°. The scintillation counter was used with the pulse height analyzer to eliminate the Ge fluorescence from the sample. Data collection was controlled by an NEC 9801E personal computer. The intensity profile was observed from 3° to 60°, which corresponds to a wavevector \( Q = 4\pi \sin \theta / \lambda \) from 9 to 153 nm\(^{-1}\) where \( \lambda \) is the wavelength and \( 2\theta \) is the angle between the incident and diffracted beams.

The scattering intensity from the sample consists of the intensities from the thin film and the substrate holding the film. Thus, in order...
to obtain the scattering intensity from the film, \( I \), alone, the contribution from the substrate should be eliminated in the following procedures. Namely, the intensity from the substrate itself, \( I_s \), is measured and corrected for absorption by the film and then subtracted from the intensity of the sample, \( I_t \). This procedure is expressed by the following equation:

\[
I = I_t - \exp \left[ -2\mu t \frac{\sin \theta \cos (\theta - \alpha)}{\sin \alpha \sin (2\theta - \alpha)} \right] I_s,
\]

where \( \mu \) and \( t \) are the linear absorption coefficient and thickness of the film, respectively. The value of \( I \) is used for the further analysis.

The polarization correction for an ideally perfect monochromator was applied, and the Compton scattering was corrected using the values reported by Cromer and Mann and the so-called Breit-Dirac recoil factors. In order to convert the observed intensities into electron units, the generalized Krogh-Moe-Norman method was used with atomic scattering factors tabulated in ref. (10) including the anomalous dispersion corrections. In this study, the observed intensity data at \( Q \) values \(<10 \text{ nm}^{-1}\) have been smoothly extrapolated to \( Q=0 \). The effect of the extrapolation and the truncation up to \( Q=153 \text{ nm}^{-1}\) is known to give no critical contribution in the calculation of the radial distribution function (RDF) by the Fourier transformation. The RDF of \( 4\pi r^2 \rho(r) \) is evaluated from the total structure factor \( S(Q) \) for an amorphous material.

\[
S(Q) = \frac{I_{\text{coh}}(Q) - \langle f^2 \rangle + \langle f \rangle^2}{\langle f \rangle^2}. \quad (2)
\]

\[
4\pi r^2 \rho(r) = 4\pi r^2 \rho_o + \frac{2r}{\pi} \int_0^\infty Q[S(Q) - 1] \times \sin(Qr) \, dQ \quad (3)
\]

where \( I_{\text{coh}}(Q) \) is the coherent X-ray scattering intensity in electron units per atom, which is directly determined from the scattering experiments; \( \langle f \rangle \) and \( \langle f^2 \rangle \) are the mean and mean-square scattering factors; the term \( \langle f^2 \rangle - \langle f \rangle^2 \) is called the Laue monotonically scattering; \( r \) is the radial density function and \( \rho_o \) is the average number density of atoms.

### III. Results and Discussion

For the measurements of thin film, a longer wavelength is preferred as an incident beam to reduce the contribution from the substrate as much as possible. This is not always an advantage for the measurement of non-crystalline materials because truncation of data sometimes causes a serious error in a resultant RDF. Thus, we dared to use the short wavelength Mo K\( \alpha \) radiation instead of a target of longer wavelength, Cu, Cr, Co, etc. As a substrate, a Si single crystal was chosen instead of amorphous or poly-crystalline material. In polycrystal or amorphous material, any tilting of the sample still satisfies the diffraction condition. On the other hand, the intensity from the single crystal is drastically reduced by arranging it in an appropriate direction. This is why the Si single crystal was chosen as a substrate. The sample was mounted on a goniometer head to tilt it in any orientation (see Fig. 2).

The relation between the diffraction vectors and a section of the reciprocal lattice of the Si 111 substrate is schematically drawn in Fig. 3. Since only the counter is scanned in the present measurement, the trace of the reflection vector \( S \) becomes an arc. In this example, the counter detects tails of some Bragg peaks, 422, 822, 1111, etc. Thus, the intensity profile is very sensitive to the orientation of the sample placed on the sample holder. As explained in eq. (1), the two measurements are required. Because of this directional sensitivity of the scattering intensity, the orientation relationship in both measurements must be exactly identical in order to carry out a successful structural analysis. If the sample is detached from the sample holder in each measurement, it is extremely difficult to get the same orientation of the substrate in these two measurements. In the present measurement, height adjustment mechanism was combined with the goniometer head and the half-coated sample was prepared (Fig. 2). By simply changing the height of the sample, both measurements were carried out in exactly the same orientation relationship. These careful measurements enabled us to eliminate the substrate intensity from the
intensity of the sample even at high $Q$ region where the intensity observed from the substrate alone was almost the same or sometimes larger than the intensity of the sample.

If the absorption correction term in eq. (1) is considered, it is found that there are three parameters in this equation, i.e. the linear absorption coefficient of the sample, $\mu$, the thickness of the sample, $t$, and the angle of incidence, $\alpha$. To accurately determine these parameters is also very important in order to analyze the data successfully. The monochromatic incident beam by the Ge flat single crystal was parallel. Therefore, by aligning the diffractometer and sample with the 0.05 mm divergent slit, both true zeros of $\omega$ and $2\theta$ were aligned within 0.01°. In this way $\alpha$ was determined with the uncertainty less than ±0.01°. The product of $\mu$ and $t$ was experimentally determined by taking a ratio of the integrated intensities of the Bragg peak of Si 111 at the two regions with and without the film. This product was determined within ±0.1%. Since the thickness of the sample was estimated to be 0.9 $\mu$m on the preparation of the sample, the density was estimated to be 5.3 Mg/m³ which is very close to the value of the crystalline Ge.

The intensities measured at the two parts of the sample are shown in Fig. 4. The intensity from the substrate has been corrected for the absorption by the film already. The difference between them is shown with a broken line. After the correction of polarization and absorption, and normalization process, the quantity of $Q[S(Q)−1]$ was estimated from this difference. This resultant $Q[S(Q)−1]$ and RDF estimated by its Fourier transformation are shown in Figs. 5 and 6, together with the results by other workers. Graczyk and Chaudhari(4) determined the atomic structure of an amorphous Ge film of 9 nm thick by electron diffraction. Kortright(11) also determined the structure of amorphous Ge of a few micrometers thick grown on about 76 $\mu$m thick Kapton tape by X-ray diffraction. Although these results were obtained in the samples of different thickness with different methods, the agreement is, in the present authors’ view, rather surprisingly good in both $Q[S(Q)−1]$. 

![Fig. 3 The schematic diagram for the geometrical relation between the diffraction vectors and a section of the reciprocal lattice of the Si single crystal substrate.](image)

![Fig. 4 X-ray scattering intensities of amorphous Ge sample, $I_t$, absorption-corrected intensity of the substrate, $A_sI_s$, and their difference, $I$.](image)

![Fig. 5 $Q[S(Q)−1]$ obtained in the present measurement with those by Kortright(11) and by Graczyk and Chaudhari(4).](image)
and RDFs. In the RDF of this study, however, there is a small peak at high r side of the first peak. Although it might be caused by some errors during the subtraction, the reason of this peak has not been certainly identified yet.

As shown in the above data processing, some difficulties were realized for structural analysis of thin film by X-ray diffraction. Specially, the two measurements in exactly the same experimental conditions must be carried out in order to estimate the contribution from the substrate. It is the most likely to cause some serious errors during this process. Thus, a new method to avoid such subtraction process is strongly required. With respect to this subject, the use of the anomalous X-ray scattering may bring out a significant breakthrough in the quantitative structural analysis of thin film by X-ray diffraction, by permitting the intensity of thin film without the intensity measurement of the substrate. The principle of this new method is as follows. The scattering factor of Ge near the Ge K absorption edge (11.103 keV) is expressed by

\[ f_{Ge} = f^0_{Ge} + f^{'}_{Ge} + if^{''}_{Ge}, \]  

where \( f^0_{Ge} \) corresponds to the usual atomic scattering factor for radiation at energy sufficiently away from any absorption edge, and \( f^{'}_{Ge} \) and \( f^{''}_{Ge} \) are the real and imaginary parts of the anomalous dispersion terms of Ge. The values of \( f^0_{Ge} \) and \( f^{''}_{Ge} \) near the Ge K absorption edge are shown in Fig. 7. Although \( f^0_{Ge} \) is small and almost constant at lower energy side of the edge, \( f^{'}_{Ge} \) shows the drastic change at this energy. The solid curves in this figure represent the theoretical values computed by Cromer and Lieberman’s method, and the solid circles correspond to the values of \( f^{'}_{Ge} \) experimentally determined from the integrated intensities of the Bragg peaks of Ge powder. The experimental data are known to show a good agreement with the theoretical values at the lower energy side of the edge. Therefore, in the present calculation, the theoretical values were used for the anomalous dispersion terms.

On the other hand, the atomic scattering factor of Si is almost constant at this energy region because its absorption edge (1.839 keV) is far away. Introduce the intensity \( I(Q, E) = I_{me}(Q) - \langle f^2_{Ge} \rangle \), where \( I_{me}(Q) \) is the measured intensity in electron units per atom and \( \langle f^2_{Ge} \rangle \) is the mean squares of the scattering factor of Ge near the Ge K absorption edge (11.103 keV) is expressed by

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Ge, and consider two energies $E_1$ and $E_2$ at the lower energy side of the Ge K absorption edge. The difference in scattering intensity $\Delta I$ at the energies of $E_1$ and $E_2$ is given by

$$
\Delta I = I(Q, E_1) - I(Q, E_2) = W(Q) \int_{0}^{\infty} 4\pi r^2 (\rho(r) - \rho_o) \frac{\sin (Qr)}{Qr} \, dr,
$$

(5)

where

$$
W(Q) = (f_{\text{Ge}}(E_1) - f_{\text{Ge}}(E_2)) \text{Re} \left[ f_{\text{Ge}}(Q, E_1) + f_{\text{Ge}}(Q, E_2) \right].
$$

(6)

From the above equation, it is readily understood that the difference $\Delta I$ directly relates to the atomic scale structure of the Ge film. The Fourier transform of the above equation becomes

$$
4\pi r^2 \rho(r) = 4\pi r^2 \rho_o + 2r \int_{0}^{\infty} \frac{Q \Delta I}{W(Q)} \sin (Qr) \, dQ.
$$

(7)

Consequently, the RDF of the Ge film is obtained without taking the difference between the two intensities from the sample and from the substrate. However, one problem in this method is how much difference can be obtained in intensities at $E_1$ and $E_2$. Such difference can be estimated by using the Fourier inverse of the RDF in Fig. 6 and the scattering intensity of the substrate in Fig. 4. The energies of 11.0796 and 10.9798 keV were chosen as these two energies, which are $-25$ and $-125$ eV away from the Ge K edge, respectively. The profiles at these two energies are shown in Fig. 8. It clearly suggests that the difference can be obtained even in a very thin sample.

The actual measurement was tried with the synchrotron radiation at Photon Factory in National Laboratory for High-Energy Physics, Tsukuba. The monochromatic and horizontally polarized beam was obtained by the double Si 111 crystal monochromator. By using this monochromator, the incident beam was tuned at any energy from 4 to 20 keV. The portable pure Ge intrinsic solid state detector was used to eliminate the fluorescent radiation from Ge near its K absorption edge. The details of the experimental settings at Photon Factory are explained in ref. (14).

The beam intensity was monitored by the ion chamber placed just before the sample. All measured data was normalized by the direct beam intensity computed from the counts of this ion chamber. Also Ge Kβ fluorescent radiation and escaped peak excited by the tail of incident beam energy were corrected(15). Incidentally, it took for 21.6 ks (6 h) to measure these two intensities, the minimum counts collected at each angle was about 60,000, and the counts at the first peak was about 120,000. The corrected and normalized scattering intensities at these two energies are shown in Fig. 9. From this result, it is found that the difference due to the anomalous dispersion effect theoretically estimated was reproduced in the measurement at Photon Factory. On the other hand, it is noted that the intensity profiles in both the figures are different. The main reason for this differ-

![Fig. 8 Calculated intensity profiles of the amorphous Ge sample at 11.0796 and 10.9798 keV which are $-25$ and $-125$ eV away from the Ge K absorption edge.](image)

![Fig. 9 Intensity profiles of the amorphous Ge sample experimentally determined at 11.0796 and 10.9798 keV which are $-25$ and $-125$ eV away from Ge K-absorption edge.](image)
ence is considered to be as follows. The profile in Fig. 8 was estimated from the intensity pattern measured in the laboratory, using the Mo K\(\alpha\) radiation, and the profile in Fig. 9 was obtained at Photon Factory, using the synchrotron radiation near the Ge K absorption edge. Therefore, the radius of the arc in the reciprocal space defined as the trace of the scattering vector in Fig. 3 is different in each measurement. As a result, the contribution from the Si substrate in both the measurements are completely different. Thus, it is natural that the intensity patterns in both figures should not be identical, and this difference is not essential in the comparison between these two profiles. The complete RDF data is not obtained from the present experimental data by the anomalous X-ray scattering alone, because of the scarcity of beam time. Nevertheless, it is concluded from the results of Figs. 8 and 9 that this new method is one way to reduce the difficulty in the structural analysis of the thin film on the substrate.

IV. Concluding Remarks

The method of the quantitative structural analysis of a thin film on a substrate has been tested, so as to focus on the point, “how to accurately eliminate the contribution of the substrate from measured intensity of the sample.” It is found that as long as the subtraction of the contribution from the substrate is performed correctly, the atomic scale structure of the amorphous film of 0.9 \(\mu\)m thick on the Si substrate can be quantitatively determined by X-rays.

It was also demonstrated that the new method in which the anomalous dispersion effect of a constituent element of the film are utilized can be used to the structural analysis of the film although some further experiments are required before the full potential of this method can be assessed. However, this method is possible to avoid all difficulties in the conventional method by excluding the subtraction process. Thus, it might become a powerful technique for the quantitative structural analysis of the thin film grown on the substrate.

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