Behavior of Peak Intensity of Rocking Curve for Asymmetric Bragg Reflection Uniquely Determined by Strain Distribution

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Extremely asymmetric x-ray diffraction is a powerful technique for observing minute strains near crystal surfaces. This work focused on the peak intensity of the rocking curve and studied the change in peak intensity with respect to the wavelength of x-rays using dynamical diffraction calculations. From the calculations assuming uniaxial strain along the depth direction of the crystal, it was found that the peak intensity becomes more sensitive to strain as the wavelength decreases below a critical value (critical wavelength λ_c) at which the total reflection of incident x-rays is enhanced. Comparing the profile of peak intensity vs. wavelength for a strained crystal with that for an unstrained crystal, it is clear that the introduction of compressive or tensile strain causes either enhancement or reduction of the intensity. The difference spectra generated by subtraction of the profile of peak intensity vs. wavelength for an unstrained crystal from that for a strained crystal shows a systematic change with respect to the strain parameters, the maximum strain value ε_0 and the thickness of the strained layer H . It is expected that we can evaluate the strain more quickly and easily by fitting the difference spectra than by using the rocking curves when the rocking curves are featureless.

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I. INTRODUCTION

Recently, there has been active development of tools that can observe the strain near a crystal surface because the strain field plays an important role in the growth of films or nanostructures near the surface. In general, techniques to evaluate minute strain introduced to a single crystal can be classified according to probe type. The first group involves the techniques based on transmission electron diffraction like nano beam electron diffraction (NBED) [1], convergent beam electron diffraction (CBED) [2], and dark field electron holography (DFEH) [3]. The second group includes techniques based on x-ray diffraction [4]. The third group includes techniques based on ion scattering [5].

From 1998 to 2000, x-ray diffraction techniques utilizing multiple-wave excitation phenomena were independently developed by two groups (Takahashi's group [6] and Akimoto's group [7]) to observe minute strain near a crystal surface. Yashiro *et al.* [8] observed the strain introduced to a Si substrate due to oxidization of the surface by focusing on the modulation of crystal truncation rod (CTR) scattering using the Bragg reflection. Emoto and Akimoto measured the strain near a Si surface due to reconstruction of the surface by removing a SiO₂ film or through the adsorption of Ag or Al atoms on the clean surface [9]. The strain field near an HfO₂/Si interface [10] was also evaluated by Emoto *et al.*

For the diffraction technique, curve-fitting of the rocking curve is a typical method used to determine the arrangements and kinds of atom in a unit cell. When the measured rocking curve has many features like sub peaks and interference fringes [11], a valid answer can be obtained in a relatively short time. In other case, an immense amount of time may be spent to get an answer.

This work focused on the peak intensity of the rocking

curve rather than the shape of the rocking curve. It was found that the relationship between the peak intensity and the wavelength of x-rays is uniquely decided by the distribution of the strain introduced to the crystal. This fact means that we can evaluate the strain more quickly and easily by focusing on the peak intensity rather than the shape of the curve when the rocking curve is featureless.

II. CALCULATION

The dynamical diffraction theory suggested by Darwin (the so-called Darwin's theory) [12, 13] has been used to calculate the reflectivity of x-rays for a single crystal. In this theory, an unstrained single crystal is treated as an aggregation of a homogeneous atomic layer (or unit cell) along the depth direction. When we focus on a certain atomic layer in the crystal, the field amplitudes of the incident and reflected beams at both surfaces of the layer must be related to each other with transmission and reflection coefficients that are calculated with the atomic arrangement of the layer using the kinematical diffraction theory. A sequential relating of the field amplitudes between neighboring atomic layers results in dynamical features. The relation of the field amplitudes can be summarized in a matrix form. In this equation, a characteristic matrix corresponding to the atomic layer is defined. In other words, if we desire to calculate the reflectivity of x-rays for a crystal including an irregular structure like a reconstructed semiconductor surface or strain, we can prepare the characteristic matrix corresponding to the irregular atomic layers, and then multiply this with the matrix for bulk [14].

In the optics of extremely asymmetric Bragg reflection, it is well known that Darwin's theory is no longer correct: the calculation of transmission and reflection coefficients for atomic layers using kinematical theory is not valid when the incident x-rays impinge on the atomic layer under the grazing angle. Yashiro *et al.* [15] success-

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FIG. 1: Geometry of extremely asymmetric x-ray diffraction under grazing incident condition. The (113) plane is inclined at $\alpha = 25.24^\circ$ with respect to the (001) plane.

fully resolved the problem by treating the mirror reflection and transmission of the grazing incident beam as multiple scattering. In this study, Darwin's theory as modified by Yashiro *et al.* was used.

In this work, a Si(001) surface was assumed to be the substrate. For structural analysis, the Si 113 reflection of the substrate was selected. The geometry of extremely asymmetric x-ray diffraction is shown in Fig. 1. It is noted that a mirror reflection is generated simultaneously with the 113 reflection because the incident x-rays impinge on the surface at grazing angle. In this optical geometry, the rocking curve is affected by a lattice deformation along the depth direction rather than one parallel to the surface because the (113) plane is inclined at 25.24° with respect to the (001) plane.

A strained Si layer with a thickness of H was assumed to exist on a perfect Si crystal. In this strained crystal model, uniaxial strain along the depth direction was assumed. Also assumed was a strain with values that changes for the depth in accordance with a Gaussian distribution: the magnitude of the strain takes a maximum value at a crystal surface and comes close to zero with increasing depth (examples of strain distribution can be seen in Fig. 6). The strain distribution with respect to the depth z from the crystal surface is expressed by the following equation:

$$\varepsilon(z) = \varepsilon_0 \exp \left\{ -\frac{z^2}{\alpha^2} \right\} \quad (0 \leq z \leq H), \quad (1)$$

where ε_0 is the maximum value of the strain. The value of ε_0 is expressed as $\varepsilon_0 = (d - d_0)/d_0$, where d and d_0 denote the lattice spacing of the (001) plane at the top surface and bulk, respectively. Note that the value of α is determined from the condition that $|\varepsilon| = 10^{-10}$ at the interface between the strained crystal and the perfect crystal ($z = H$). Therefore, α is related to ε_0 and H by the following equation:

$$\alpha = \frac{H}{\sqrt{10 \ln 10 + \ln \varepsilon_0}}. \quad (2)$$

One can also consider an amorphous film on the crystal surface. This film is characterized by the kinds of atomic species constructing the film, as well as the density and thickness.

FIG. 2: (a) Peak intensity of the rocking curve for strained and unstrained Si(001) substrates with respect to the x-ray wavelength. Note that the vertical axis is in logarithmic scale. For any symbols and lines, red, orange, green, aqua, and blue colors were calculated by assuming strain parameters $(\varepsilon_0, H) = (-0.5\%, 20 \text{ nm}), (-0.25\%, 20 \text{ nm}), (0\%, 20 \text{ nm}), (+0.25\%, 20 \text{ nm}),$ and $(+0.5\%, 20 \text{ nm})$, respectively. The symbols denote different kinds of interfaces: filled circles indicate 1.7-nm-thick SiO₂/Si, open circles indicate 2.5-nm-thick HfO₂/Si, filled triangles indicate 5-nm-thick HfO₂/Si, and crosses indicate 7.5-nm-thick HfO₂/Si interfaces, respectively. (b) Difference quotient of the peak intensity with respect to the x-ray wavelength. Symbols and colors are the same as in (a).

III. RESULTS AND DISCUSSION

In Fig. 2(a), the peak intensity of the rocking curves calculated for strained and unstrained substrates is plotted on a logarithmic scale with respect to the wavelength of x-rays. The intensities denoted by the filled circles were calculated for an interface of 1.7-nm-thick SiO₂/Si. The intensities denoted by the open squares, filled triangles, and crosses were for interfaces of 2.5-nm-thick HfO₂/Si, 5-nm-thick HfO₂/Si, and 7.5-nm-thick HfO₂/Si, respectively. Values of 2.33 g/cm³ and 9.87 g/cm³ were assumed for the densities of the SiO₂ and the HfO₂ films, respectively. The strain fields introduced to each substrate are distinguished by the color of the symbol and the line guiding the eyes. The intensities denoted by the symbols and the red, orange, green, aqua, and blue lines were calculated for strain parameters of $(\varepsilon_0, H) = (-0.5\%, 20 \text{ nm}), (-0.25\%, 20 \text{ nm}), (0\%, 20 \text{ nm}), (+0.25\%, 20 \text{ nm}),$ and $(+0.5\%, 20 \text{ nm})$, respectively.

FIG. 3: (a) Peak intensity of the rocking curve for a bare Si(001) surface with respect to the x-ray wavelength. (b) Difference quotient of the peak intensity with respect to the wavelength (see filled diamond). Penetration depth of x-rays with respect to wavelength is also shown (see open circle).

At longer wavelengths, there are no differences due to the strain among the peak intensities. The differences in intensity are purely caused by the differences in kind (or density) and thickness of amorphous films on the substrates. At shorter wavelengths, the peak intensities vary with respect to not only the parameters of the amorphous film (thickness and density), but also the strain parameters. Fig. 2(b) shows the difference quotient (DQ) of the peak intensities with respect to the wavelength. Flexion points are observed near the wavelength of 0.1397 nm (hereafter called the “critical wavelength λ_c ”). At wavelengths longer than λ_c , the value of the DQ agrees with respect to each kind and thickness of film on the substrate and has no relationship to the strain. On the other hand, at wavelengths shorter than λ_c , the value of the DQ is almost entirely determined by the strain parameters.

Figures 2(a) and 2(b) show that the sensitivity of the peak intensity to the strain near the interface varies according to the wavelength of x-rays. This property can be explained in terms of the penetration depth of x-rays into crystal. Figures 3(a) and 3(b) show the wavelength dependence of the peak intensity and the DQ, respectively, for a bare Si(001)-(1×1) surface. In Fig. 3(b), the penetration depth of x-rays into the Si crystal is also shown with the DQ. The penetration depth of x-rays was evaluated as the depth of the intensity of incident x-rays reduced to $1/e$ (where e is a base of natural logarithm) of that

FIG. 4: (a) Peak intensity of the rocking curve for various strained substrates with respect to the x-ray wavelength. Note that the vertical axis is in logarithmic scale. The thick, black line is the intensity for the unstrained substrate. The filled symbols and the crosses colored in red are for the strained substrates under compressive strain: filled squares are for the strain parameters $(\varepsilon_0, H) = (-0.5\%, 20 \text{ nm})$, filled triangles for $(-0.25\%, 40 \text{ nm})$, filled diamonds for $(-0.125\%, 80 \text{ nm})$, filled circles for $(-0.0625\%, 160 \text{ nm})$, and crosses colored in red for $(-0.03125\%, 320 \text{ nm})$, respectively. The open symbols and the crosses colored in black are for the strained substrates under tensile strain: open squares are for $(\varepsilon_0, H) = (+0.5\%, 20 \text{ nm})$, open triangles for $(+0.25\%, 40 \text{ nm})$, open diamonds for $(+0.125\%, 80 \text{ nm})$, open circles for $(+0.0625\%, 160 \text{ nm})$, and crosses colored in black for $(+0.03125\%, 320 \text{ nm})$, respectively. A 1.7-nm-thick SiO_2 film was assumed for all substrates. (b) Difference quotient of the peak intensity with respect to the x-ray wavelength. Symbols are the same as (a).

at the crystal surface at the Bragg peak. In Fig. 3(b), the penetration depth of x-rays rapidly decreases from $\sim 115 \text{ nm}$ to $\sim 18 \text{ nm}$ as the x-ray wavelengths shorten from 0.1406 nm to 0.1397 nm. Up to the wavelength of 0.1397 nm, the penetration depth gently decreases from $\sim 18 \text{ nm}$ to $\sim 10 \text{ nm}$ because the total reflection of the incident x-rays occurs in this range of wavelengths. Therefore, structural information near the crystal surface, including the strain fields, is strongly reflected in the peak intensity of the rocking curve. Comparing the DQ spectrum with the graph of penetration depth in Fig. 3(b), it is clear that the value of the critical wavelength λ_c agrees with the critical value of the wavelength at which the dependence of the penetration depth on wavelength dras-

FIG. 5: Results of subtracting the intensity of unstrained substrates from that for strained ones: (a) for substrates under compressive strain. The filled circles colored in green are for the strain parameters $(\epsilon_0, H) = (-0.5\%, 20 \text{ nm})$, open squares in orange for $(-0.25\%, 40 \text{ nm})$, filled triangles in blue for $(-0.167\%, 60 \text{ nm})$, open circles in red for $(-0.125\%, 80 \text{ nm})$, crosses in aqua for $(-0.1\%, 100 \text{ nm})$, pluses in brown for $(-0.0833\%, 120 \text{ nm})$, open diamonds in green for $(-0.0714\%, 140 \text{ nm})$, filled squares in orange for $(-0.0625\%, 160 \text{ nm})$, open triangles in blue for $(-0.0556\%, 180 \text{ nm})$, and filled circles in red for $(-0.05\%, 200 \text{ nm})$, respectively. (b) Results for substrates under tensile strain. The filled circles colored in green are for the strain parameters $(\epsilon_0, H) = (+0.5\%, 20 \text{ nm})$, open squares in orange for $(+0.25\%, 40 \text{ nm})$, filled triangles in blue for $(+0.167\%, 60 \text{ nm})$, open circles in red for $(+0.125\%, 80 \text{ nm})$, crosses in aqua for $(+0.1\%, 100 \text{ nm})$, pluses in brown for $(+0.0833\%, 120 \text{ nm})$, open diamonds in green for $(+0.0714\%, 140 \text{ nm})$, filled squares in orange for $(+0.0625\%, 160 \text{ nm})$, open triangles in blue for $(+0.0556\%, 180 \text{ nm})$, and filled circles in red for $(+0.05\%, 200 \text{ nm})$, respectively. These graphs are called “difference spectra (DS)” in the main text.

tically changes. It is thought that the critical wavelength λ_c gives an indication of the wavelength at which the total reflection of the incident x-rays dominates the diffraction phenomena.

Figure 4(a) shows the peak intensity of the rocking curve for the various strained substrates under the 1.7-nm-thick SiO_2 film. The thick, black line indicates the intensity for the unstrained substrate. The series of filled symbols and crosses colored in red are calculated for the substrate under compressive strain. The series of open symbols and crosses colored in black are calculated for the substrate under tensile strain. In these calculations,

FIG. 6: (a) The change in the difference spectra (DS) with a change in the maximum strain value ϵ_0 around -0.0625% , keeping H constant at 160 nm. The filled squares are for $\epsilon_0 = -0.0525\%$, crosses for $\epsilon_0 = -0.0575\%$, filled triangles for $\epsilon_0 = -0.0625\%$, filled circles for $\epsilon_0 = -0.0675\%$, and filled diamonds for $\epsilon_0 = -0.0725\%$, respectively. (b) The changes in the DS with a change in the thickness of the strained layer H around 160 nm, keeping ϵ_0 constant value of -0.0625% . The open squares are for $H = 120 \text{ nm}$, crosses for $H = 140 \text{ nm}$, filled triangles for $H = 160 \text{ nm}$, filled circles for 180 nm , and open diamonds for $H = 200 \text{ nm}$, respectively.

the strain parameters of ϵ_0 and H are determined so as to satisfy the next relation, $|\epsilon_0| \times H = 10\% \cdot \text{nm}$, to observe the behavior of the peak intensity for relatively wide ranges of ϵ_0 and H (in particular, $0.03125\% \leq |\epsilon_0| \leq 0.5\%$ and $20 \text{ nm} \leq H \leq 320 \text{ nm}$). In Fig. 4(a), the profile of the peak intensity seems to be uniquely determined with respect to the strain parameters. It is noted that the intensity is enhanced or reduced with respect to the intensity of the unstrained substrate when the introduced strain is compressive or tensile, respectively. Fig. 4(b) shows the DQ of the peak intensity with respect to the wavelength. The wavelength of the flexion point (or the critical wavelength λ_c) is different from each strain parameter because the introduced strain slightly varies the density of the crystal near the interface, i.e., the condition for total reflection slightly varies because of the introduction of strain.

The difference spectra (DS) extracted by subtracting the peak intensity for the unstrained substrate from that for the strained substrate obviously shows a relationship between the intensity change and the strain parameters

FIG. 7: (a) Series of strain distributions with a change in the maximum strain value ε_0 around -0.0625% , keeping $H = 160$ nm. The filled squares are for $\varepsilon_0 = -0.0525\%$, crosses for $\varepsilon_0 = -0.0575\%$, filled triangles for $\varepsilon_0 = -0.0625\%$, filled circles for $\varepsilon_0 = -0.0675\%$, and filled diamonds for $\varepsilon_0 = -0.0725\%$, respectively. (b) Series of strain distributions with a change in the thickness of the strained layer H around 160 nm, keeping $\varepsilon_0 = -0.0625\%$. The open squares are for $H = 120$ nm, crosses for $H = 140$ nm, filled triangles for $H = 160$ nm, filled circles for $H = 180$ nm, and open diamonds for $H = 200$ nm, respectively.

ε_0 and H . Figures 5(a) and 5(b) show the DS when the compressive strain and the tensile strain, respectively, are introduced. A systematic behavior of the DS with respect to the parameters of the strain is clear: when the magnitude of the maximum strain $|\varepsilon_0|$ is small and the thickness of the strained layer H is large, the peak or dip of the DS appears at a large wavelength and the absolute value of the intensity for the DS is small.

Figures 6(a) and 6(b) show the DS for various strained substrates with strain parameters around $(\varepsilon_0, H) = (-0.0625\%, 160 \text{ nm})$. Figure 6(a) shows the change in the DS with a change in ε_0 , with H kept at 160 nm. The intensities of the DS up to a wavelength of 0.1398 nm become large as the magnitude of the maximum value of the strain $|\varepsilon_0|$ increases. Figure 6(b) shows the change of the DS with a change in H as ε_0 kept at -0.0625% . The intensities around the peak become large as the thickness of the strain layer H increases. Interestingly, there is a different response of the DS to the strain parameters ε_0 and H . This difference may be interpreted as follows. As shown in Fig. 3(b), the penetration depth of incident x-rays is shallower as the x-ray wavelength decrease. This means that the sensitivity of the crystal structure near the surface is increased when short x-ray wavelengths are used. On the other hand, the actual structural changes of the strained crystal model are different when changing only ε_0 compared to changing only H in the strain distribution function $\varepsilon(z)$. Figures 7(a) and 7(b) show the changes in the strain distribution resulting from changing only ε_0 and H , respectively. When only the parameter

FIG. 8: (a) Difference spectra (DS) for a Gaussian strain distribution (filled diamonds), a Lorentzian strain distribution (open circles), and an exponential attenuation distribution (filled triangles), respectively. (b) Strain distribution function for a Gaussian (blue line), a Lorentzian (red line), and an exponential attenuation (green line), respectively. Note that the maximum value of strain ε_0 and the half-width of half-maximum of these curves have the same value ($\varepsilon_0 = -0.03\%$, HWHM = 9 nm).

ε_0 is changed, a significant change in the spacing between atomic layers occurs in the upper atomic layers as shown in Fig. 7(a). However, when only the parameter H is changed, a change in the spacing occurs at deeper areas with respect to the surface of the crystal, as shown in Fig. 7(b). Observing the two factors overall, it is thought that the DS reflects the strain distribution by regarding the axis of the wavelength of x-rays as the depth direction. However, the shape of the distribution may be modified by the contribution of the penetration depth.

The sensitivity of the DS to strain distribution was confirmed by comparing the DSs for a Gaussian-like strain distribution, for a Lorentzian-like distribution, and for an exponential attenuation distribution, as shown in Fig. 8(a). The actual distribution of the strain for each case is shown in Fig. 8(b). Note that the three distribution functions have the same values of ε_0 ($\varepsilon_0 = -0.03\%$) and the half-width-of-half-maximum (HWHM = 9 nm). It is clear that the DS successfully distinguishes among the three distributions.

The obvious difference in the response of the DS to the parameters ε_0 and H , as shown in Fig. 6, seems to make the evaluation of strain easy and quick. The parameter ε_0 can be determined by the value of the DS near the shortest x-ray wavelength, and then the parameter H can be determined by the peak position and peak height of peak or depth of dip.

IV. SUMMARY

Using the dynamical x-ray diffraction theory, the relations of the peak intensity of the rocking curve for asymmetric Bragg reflection with the strain parameters ε_0 and H were studied. The peak intensity of the rocking curve was found to be dominated by the strain as long as an amorphous film exists on the substrate when using x-rays with wavelengths up to the critical wavelength λ_c . It was found that the difference spectrum (DS) extracted by subtracting the peak intensity for the unstrained substrate from that for the strained substrate was uniquely determined by the strain parameters ε_0 and H . It was also found that the DS shows a different response to the strain parameters ε_0 and H : (i) the entire intensity of the

DS varies with a change in the maximum strain value ε_0 up to the critical wavelength λ_c , and (ii) the position of a peak or dip, as well as the height of the peak or depth of the dip, varies with a change in the thickness of the strain layer H . Therefore, we can evaluate the strain distribution quickly and easily by focusing on the DS rather than by focusing on the rocking curve when the curve is featureless.

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