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Observation of the strain field near the Si(111) 7 × 7 surface with a new X-ray diffraction technique

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A new X-ray diffraction technique has been developed in order to measure the strain field near a solid surface under ultrahigh vacuum (UHV) conditions. The X-ray optics use an extremely asymmetric Bragg-case bulk reflection. The glancing angle of the X-rays can be set near the critical angle of total reflection by tuning the X-ray energy. Using this technique, rocking curves for Si surfaces with different surface structures, *i.e.* a native oxide surface, a slightly oxide surface and an Si(111) 7 × 7 surface, were measured. It was found that the widths of the rocking curves depend on the surface structures. This technique is efficient in distinguishing the strain field corresponding to each surface structure.

Keywords: X-ray diffraction; dynamical theory; Si(111) 7 × 7; strain field; asymmetric Bragg case.

1. Introduction

Strain fields introduced into the interface of a crystal are of interest in surface science and the semiconductor industry because they can affect thin-film growth. In particular, it is clear that strains introduced into interfaces in the hetero-epitaxial growth of thin films contribute to the growth mode at the initial stage of growth (Williams *et al.*, 1991).

X-ray techniques utilizing dynamical diffraction phenomena are suitable for the precise observation and measurement of such minute strain fields. Kishino & Kohra (1971) considered dynamical theory in the case of extremely asymmetric reflection at a small glancing angle near the critical angle of total reflection; here mirror reflection is no longer insignificant. They expected that such optics would be sensitive to the strain field near the surface because the X-ray glancing angle is very small. These optics have been used with synchrotron radiation, leading to a continuous setting of the incident angle. Kitano *et al.* (1992) successfully observed minute surface defects (which could not be observed by conventional techniques) on a silicon surface using plane-wave X-ray topography. Strain fields introduced by thermal oxidation of a silicon surface have also been evaluated by investigating the oxide-layer-thickness dependence of measured rocking curves (Hasegawa *et al.*, 1995). However, until now there has been no such surface-science technique which can be used under ultrahigh vacuum (UHV) conditions.

In this work, we have developed a new X-ray technique which is able to measure strain fields under UHV conditions. Moreover, we report for the first time the correlation of surface structures with strain fields.

2. Experimental

A UHV chamber was set up on beamline 15C of the Photon Factory, KEK, Tsukuba, Japan. This chamber was equipped with a precision manipulator which could be moved by a pulse motor in steps of 0.0036°. The experimental apparatus is shown in Fig. 1. The X-rays from the synchrotron source were monochromated by an Si(111) double-crystal monochromator symmetric reflection and were then collimated by an Si(111) crystal using an extremely asymmetric reflection from the (311) plane, which is at an angle of 29.496° with respect to the (111) plane. The collimator crystal surface was at an angle of 5° with respect to the (111) plane and 24.496° with respect to the (311) plane. Therefore, the total reflection width of the diffracted X-rays from this crystal was sufficiently narrow. An Si(111) sample crystal was mounted on the manipulator and aligned to satisfy the diffraction condition for the (311) plane. This is a (+,−) non-dispersive parallel setting with an asymmetric reflection. In order to enhance the sensitivity for the measurement of strain fields near the surface, the glancing angle of the X-rays was set near to the critical angle of total reflection and the wavelength was tuned continuously. (Note that the measured rocking curves must be treated within dynamical theory because the experimental set-up utilizes bulk reflection.) The incident and reflected beam intensities were monitored using an ionization chamber and a scintillation counter, respectively. In order to minimize the contribution of a warp of the wafer due to annealing processes, an indirectly annealing method was adopted and a slit of a few mm width was set in front of the scintillation counter. Surface structures were also observed *in situ* by reflection high-energy electron diffraction (RHEED) in the same chamber.

2 inch diameter *n*-type wafers 350 μm thick with 10.0–20.0 Ω cm resistance grown by Czochralski (CZ) method, were used as sample crystals. We measured rocking curves with the technique mentioned above for a changing surface structure by annealing the native oxide silicon surface. RHEED observations and rocking curve measurements were performed at room temperature.

3. Results

Annealing of the sample crystal was carried out at about 1273 K for several seconds. The temperature of the substrate was monitored using a thermocouple. After annealing several times and slowly cooling, the Si(111) 1 × 1 pattern was observed. Since the 1 × 1 pattern became clear at higher glancing angle, it was concluded that the oxide layer remained on the silicon surface. Hereafter we refer to this surface as the 'slightly oxide' surface. The Si(111) 7 × 7 pattern was observed after further annealing.

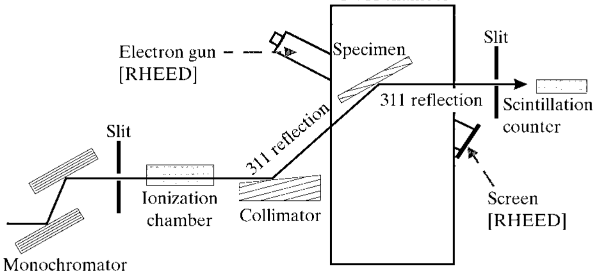

Figure 1
The experimental apparatus.

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The rocking curves corresponding to each surface structure are shown in Figs. 2 and 3. Fig. 2 shows the rocking curves measured for the native oxide and slightly oxide surfaces, and Fig. 3 for the slightly oxide and Si(111) 7 × 7 surfaces, with subtracted background intensities. Note that the wavelengths used for the measurements are different for Fig. 2 and Fig. 3. The sensitivity to the strain field is enhanced at shorter wavelengths as mentioned in the next section. Because of the difference of the strain field for the slightly oxide surface and Si(111) 7 × 7, which is less than that for the native oxide surface and the slightly oxide surface, we used a shorter wavelength for comparing these rocking curves to emphasize the differences.

The asymmetric feature of the rocking curves is intrinsic for these experimental optics. The widths of the rocking curves are different for each surface structure. The width of the native oxide surface is larger than that of the slightly oxide surface shown in Fig. 2, and that of the slightly oxide surface is larger than that of Si(111) 7 × 7 shown in Fig. 3.

4. Discussion

The wavelength dependence of the X-ray penetration depth is shown in Fig. 4; this is a theoretical result from dynamical diffraction theory (Kishino & Kohra, 1971). The penetration depth was evaluated as the depth of the 1/e intensity for the incident X-ray beam. The penetration depth decreases as the wavelength shortens. A drastic change occurs near the critical angle of total reflection. This means that the volume of the bulk crystal contributing to diffraction becomes small when the wavelength shortens. As a result, the effect of dynamical diffraction is suppressed and the kinematical diffraction arising from the strain field appears more clearly (Chikawa *et al.*, 1970).

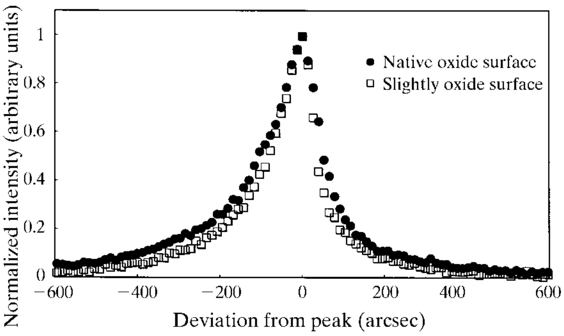

Figure 2
The rocking curves corresponding to the native oxide surface and the slightly oxide surface. The wavelength used was 0.16101 nm, calculated from the monitored angle of the monochromator.

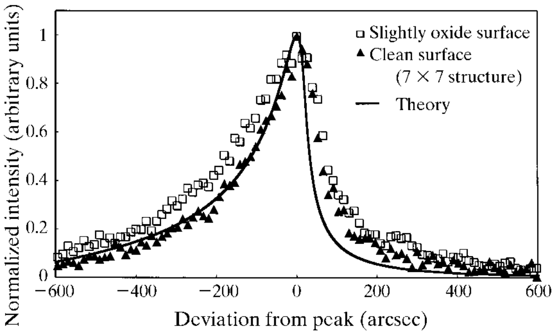

Figure 3
The rocking curves corresponding to the slightly oxide surface and the clean surface [*i.e.* the Si(111) 7 × 7 surface]. The solid line is the theoretical curve of the best agreement with the 7 × 7 curve. The wavelength used was 0.16093 nm.

We can see from Figs. 2 and 3 that the rocking curves clearly depend on the surface structures, as a change of surface structure results in a change in the rocking-curve width. It is expected that the widths of rocking curves change owing to the expansion and contraction of the lattice parameter and the bend of the diffraction plane with respect to those of the bulk. Therefore, we conclude that we can observe the strain field near the surface or interface of interesting systems through measuring the rocking curves.

We deduce from the smallness of the widths of the rocking curves that the Si(111) 7 × 7 structure has a smaller strain field than the slightly oxide surface, and that the slightly oxide surface has a smaller strain field than the native oxide surface. This means that the Si(111) 7 × 7 reconstructed structure has the smallest strain field, but does not mean that the structure has no strain field. In Fig. 3, the theoretical curve which shows the best agreement with the rocking curve for the Si(111) 7 × 7 structure is shown. The disagreement which is seen on the-high angle side may imply the existence of a strain field.

Hasegawa *et al.* (1995) suggested that the interface of SiO_2/Si(100) consisted of a thin oxide layer (about 2–6 nm) with a larger strain field than that of a thicker layer (more than 7 or 8 nm) because of the existence of the structural transition layer which is formed by the volume expansion on thermal oxidation. By investigating oxide layers up to several nm thick, *i.e.* corresponding to the native oxide layer thickness, our work has demonstrated that oxide layers show a large strain field.

Kelires & Tersoff (1989) calculated the equilibrium properties of an Si–Ge alloy by direct simulation. They found an oscillatory variation of the composition with depth near the surface. They suggested that the reconstruction of the surface leads to such an oscillatory feature through induced strain. Strain fields near surfaces or interfaces have become an important problem for the field of surface science today.

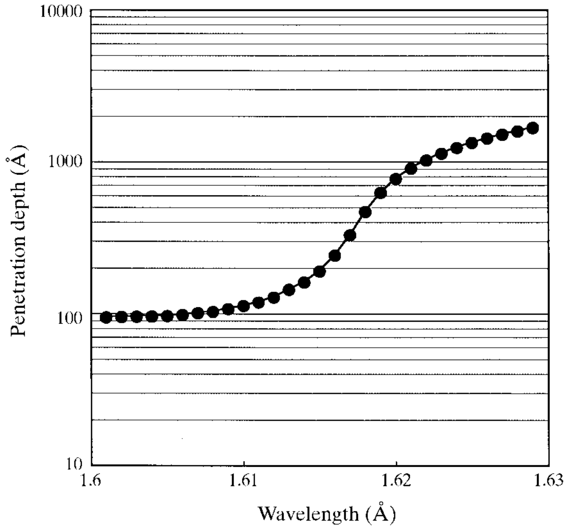

Figure 4
The wavelength dependence of the X-ray penetration depth calculated using dynamical theory.

5. Summary

We have measured the rocking curves of an Si(111) surface for three surface structures: a native oxide surface, a slightly oxide surface, and an Si(111) 7 × 7 surface. We have used a new X-ray diffraction technique under extremely asymmetric Bragg-case conditions and UHV. The widths of the rocking curves clearly depend on the surface structures. It is suggested that an Si(111) 7 × 7 reconstructed surface structure has a smaller strain field near the surface than the native oxide or the slightly oxide surfaces.

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