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In-plane structure of an arsenic-adsorbed Si(001) surface probed with grazing-angle x-ray standing waves

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The grazing-angle x-ray standing-wave technique has been employed for in-plane structure determination of an arsenic-deposited Si(001) surface with 1×2 and 2×1 domains. Experimental data were collected using the (220), $(\overline{2}\overline{2}0)$, and (040) Bragg planes nearly perpendicular to the surface under UHV conditions. Three arsenic-emission profiles were fit by calculations based on the x-ray dynamical theory for perfect crystals. The data analysis allows us to limit the possible ranges of an As-As dimer bond length L, an in-plane root mean-square thermal vibrational amplitude $\sqrt{\langle u_\parallel^2\rangle}$, and the two domain fractions, M_1 and M_2. The ranges of the structural parameters, such as L and $\sqrt{\langle u_\parallel^2\rangle}$, are consistent with other works. In particular, L and a two-domain area ratio M_2/M_1 are restricted within the narrow ranges from 2.57 to 2.52 Å, and from 1.35 to 1.29, respectively. Assuming domains are perfectly ordered, it is found that $L=2.52\pm0.05$ Å, $\sqrt{\langle u_\parallel^2\rangle}=0.22\pm0.07$ Å, $M_1=0.44\pm0.07$, and $M_2=0.56\pm0.07$. [S0163-1829(99)03747-9]

Papers reporting on As on Si(001) surface structures are classified into two groups: papers focused on step structures and papers describing atomic structures such as a bond length and atomic positions. The step structures of As/Si(001) have been investigated and understood using scanning tunneling microscopy[1–4] (STM) and theoretical calculations.[5] They are strongly related to the step structures of a clean Si(001), which have been investigated experimentally[6–8] and theoretically.[9–12] The Si surfaces with small misorientations, which need dimers to reduce the number of dangling bonds, show both 1×2 and 2×1 domains of the reconstructed surfaces. These domains are separated by single-layer height steps. The surfaces with large misorientations include domains having mainly double-layer height steps. Four distinct types of steps, S_A, S_B, D_A, and D_B are defined by Chadi.[10] The subscripts $_A$ and $_B$ indicate that the direction of dimer bonds on an upper terrace is normal (S_A, D_A) or parallel (S_B, D_B) to the step edge. S and D stand for a single-height step and a double-height step.

The step structures of As/Si(001) also depend on substrate misorientation and substrate temperature during As deposition. The results by Becker, Klitsner, and Vickers[1] show a nearly single domain surface consisting of D_B. This indicates that As dimers substitute Si dimers. Bringans, Biegelsen, and Swartz[3] prepared samples with a 4° misorientation using different sequences and conditions. Their low-energy electron diffraction (LEED) results showed that intensity ratios of the 2×1 to the 1×2 spots were very sensitive to the substrate temperature during As deposition. In addition, it was found that the intensity ratios changed as a function of time when the substrate temperature and As pressure were raised. Ide[4] reported the variation of the step structures with a 1° vicinal surface. His STM results showed arsenic-deposited surfaces changed their step structures depending on the substrate temperature and the As coverage.

X-ray measurements[13–15] revealed the atomic structure of As/Si(001). Zegenhagen *et al.*[13] registered a location for the vertical position of arsenic atoms relevant to the (004) Bragg planes using x-ray standing waves (XSW) in air. Franklin *et al.*[15] reported an arsenic dimer height and a bond length using XSW for the 004 and 022 reflections in a UHV condition. Their results showed an As-dimer bond length as well as thermal vibration amplitudes of As perpendicular to respective Bragg planes, but not parallel to the surface. The x-ray surface diffraction measurements by Jedrecy *et al.*[14] determined the As dimer bond length, the second layer Si displacement and the thermal vibration amplitude.

In this paper, we used grazing-angle standing waves[16–19] (GAXSW) to simultaneously determine the As-dimer bond length, the in-plane thermal vibrational amplitude which was not directly determined in Ref. 15, and the domain ratios of the 1×2 and 2×1 domains of Si(001):As. GAXSW were chosen instead of conventional XSW due to the fact that the former are more sensitive to the in-plane structure of crystal surfaces. This is because, in the grazing-angle geometry, the standing wave is phase-shifted in the nearly in-plane reciprocal-lattice vector $\mathbf{h}$ direction.

We consider an arsenic-adsorbed surface that is composed of ordered 1×2 and 2×1 domains with their area fractions, M_1 and M_2, respectively. It is assumed that more than two domains exist on the surface and are classified to 1×2 or 2×1 domains. In addition, we assume that there could exist randomly distributed atoms on the surface. M_i is proportional to the sum of the terrace areas which belong to 1×2 or 2×1 domains. For a surface with S_A, S_B, D_A, and D_B, we would expect that As dimers are located both exactly on the substrate (220) atomic planes, as well as well-defined distances l and $1-l$ away from the atomic planes (Fig. 1). Here, l is the distance normalized by the substrate-lattice spacing d_{220} and d_{040}. The As-As bond length L, is thus equal to $2ld_{220}$, and As atoms sit on distances l and $1-l$ from the substrate (040) planes using the same parameter l. It is noted that the bond length L, is independent of a surface

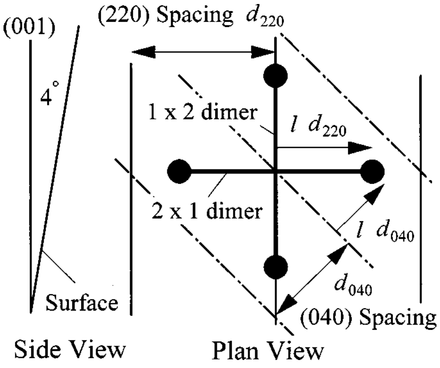

FIG. 1. Arsenic-atoms sitting in symmetry-related sites with respect to the (220) and (040) atomic planes of a substrate with its surface normal 4° off the (001) toward the $[\bar{1}10]$ direction. Drawn for our sample. *A* 2×1 dimer is shifted by integral number of the (220) spacing.

miscut angle since l is defined by crystallographic planes. As dimers on different domains should have the same bond length because As atoms are microscopically on the (001) planes.

X-rays with an amplitude of ε_0 are incident on the sample at a glancing angle ϕ_0, and also satisfy the Bragg condition on lattice planes nearly perpendicular to the surface. When ϕ_0 is close to the critical angle for total external reflection, specular x-rays with a complex amplitude of ε_s, and diffracted x-rays with a complex amplitude ε_h emerge out of the surface at ϕ_0 and ϕ_h, respectively. ε_0, ε_s, and ε_h coherently form an x-ray field on the surface, the intensity of which modulates in the direction of the **h** vector. Thus a tilt angle ρ between **h** and the surface must be smaller than several degrees when the GAXSW method is employed for determination of an in-plane structure of a surface. An emission yield from adsorbed atoms is proportional to the x-ray field intensity. The yield R_f in grazing-angle geometry has been expressed in Refs. 17, 18, and 19. In particular, for an adsorbate system involving atoms in symmetry-related sites as follows[20]

$$R_f = A + \eta_i G\sin(b+c+\delta), \tag{1}$$

where

$$A = |E_0 + E_s\exp(ia)\exp(i4\pi K\phi_0 Z)|^2 + |\varepsilon_h|^2, \tag{2}$$

$$c = \begin{cases} 2\pi K(\phi_0 - \phi_h)Z & \text{for real } \phi_h \\ 2\pi K\phi_0 Z & \text{for imaginary } \phi_h, \end{cases} \tag{3}$$

$$\delta = \tan^{-1}\left\{\frac{E_0 + E_s\cos(a + 4\pi K\phi_0 Z)}{E_s\sin(a + 4\pi K\phi_0 Z)}\right\}, \tag{4}$$

and

$$G = 2|\varepsilon_h||E_0 + \varepsilon_s\exp(i4\pi K\phi_0 Z)|. \tag{5}$$

E_0 and E_s are the real positive amplitudes of ε_0 and ε_s, respectively. The phases a and b stand for the phases for ε_s and ε_h, respectively. K is the wave number of x-rays used and the emission atoms are located at a surface-normal position Z. The η_i's depend on the reflections as follows,

$$\eta_1 = [M_1 + M_2\cos\{2\pi(1-l)\}]p^{-1}$$
$$\text{for the } 220 \text{ reflection}, \tag{6}$$

$$\eta_2 = [M_2 + M_1\cos\{2\pi(1-l)\}]p^{-1}$$
$$\text{for the } \bar{2}20 \text{ reflection}, \tag{7}$$

$$\eta_3 = (M_1 + M_2)\cos\{2\pi(1-l)\}p^{-2}$$
$$\text{for the } 040 \text{ reflection}, \tag{8}$$

where $p = \exp(2\pi^2\langle u_\parallel^2\rangle/d_{220}^2)$ and p^{-1} is a Debye-Waller factor. $\sqrt{\langle u_\parallel^2\rangle}$ is the root mean-square thermal vibrational amplitude for the 220 reflection. We assume that the thermal vibrational amplitude is isotropic in the (001) planes. The subscript $\parallel$ means an in-plane component of the thermal vibrational amplitude. If $\langle u_\parallel^2\rangle$ is known,

$$l = 1 - \frac{1}{2\pi}\cos^{-1}\left\{\frac{\eta_3 p^2}{(\eta_1 + \eta_2)p - \eta_3 p^2}\right\}. \tag{9}$$

If l is known,

$$\sqrt{\langle u_\parallel^2\rangle} = \left[\frac{d_{220}^2}{2\pi^2}\ln\left\{\frac{(\eta_1+\eta_2)\cos(2\pi l)}{\eta_3\{1+\cos(2\pi l)\}}\right\}\right]^{1/2}. \tag{10}$$

If neither $\langle u_\parallel^2\rangle$ nor l are known, a relation between $\langle u_\parallel^2\rangle$ and l can be obtained from data. The area fractions are also expressed using η_i's and p,

$$M_1 = p(\eta_1 - g\eta_2)/(1-g^2), \tag{11}$$

$$M_2 = p(\eta_2 - g\eta_1)/(1-g^2). \tag{12}$$

Here, $g = \eta_3 p^2/\{(\eta_1+\eta_2)p - \eta_3 p^2\}$.

The sample surface was cut 4° away from the (001) plane toward the $[\bar{1}10]$ axis.[21] The Shiraki-etched surface was cleaned by heating 3 times at a temperature of about 1000 °C for a few minutes in a UHV environment ($\sim 10^{-7}$ Pa). The substrate temperature reached about 580 °C and was kept at this temperature during arsenic deposition. This deposition was done using an outgassed Knudsen cell operated at about 300 °C. The vapor pressure of As was $\sim 10^{-3}$ Pa. The sample was annealed at about 350 °C for more than 3 min to remove any loosely bound As on the surface. After this process, LEED patterns showed stronger 2×1 spots than 1×2 spots.

The sample transfer technique and the horizontal scattering geometry used in the x-ray measurements at the Photon-Factory synchrotron-radiation source, Japan, were similar to those of the previous experiment.[19] The pressure of a UHV chamber[22] used for the x-ray measurements was maintained at better than 10^{-7} Pa during sample transportation and introduction, and 10^{-8} Pa during the 3 days of our measurements. Measurements were performed at the 14B vertical wiggler. X-rays of 17.0 keV photon energy were extracted with a double-crystal beamline silicon monochromator. A Si(220) monochromator with a symmetric reflection was used in the beamline hutch. We used the (220), $(\bar{2}20)$, and (040) planes nearly perpendicular to the surface. The tilt angles ρ's were 0.0, 4.0, and 2.83° for the (220), $(\bar{2}20)$, and (040) planes, respectively, and had errors of 0.02°. We re-

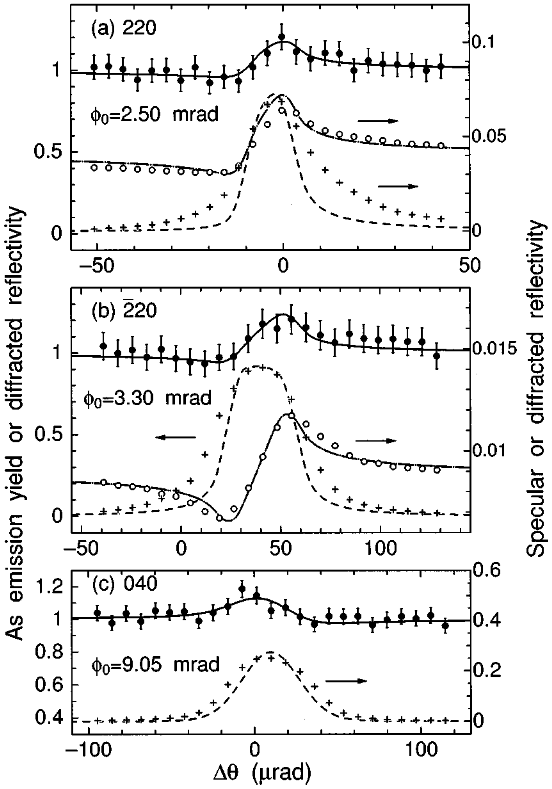

FIG. 2. Symbols represent experimental data and lines show calculations including an experimental resolution function: arsenic-emission yields (●), specular reflectivities (○), and diffracted reflectivities (+). The reflections and the glancing angles used are indicated. The critical angle of total external reflection is 1.8 mrad.

corded K fluorescence emission from As atoms with an energy of 10.54 keV using a germanium detector. Simultaneously we collected specular intensities and diffracted intensities using Na(I) detectors. A typical arsenic-emission intensity was 650 counts for an acquisition time of 500 s for the 220 reflection at $\phi_0 = 2.50$ mrad for a 1 mm×15 mm irradiated area on the sample.

Figure 2 shows the experimental data together with the fitted curve. These calculations include an experimental resolution function, which has two divergence angles, $\delta\phi_0$ for the glancing angle and $\delta\theta$ for the lattice planes considered. We used $\delta\phi_0 = 0.4$ mrad and $\delta\theta = 11.5\,\mu$rad for the 220 reflection, $\delta\phi_0 = 0.2$ mrad and $\delta\theta = 11.5\,\mu$rad for the $\bar{2}$20 reflection, and $\delta\phi_0 = 0.4$ mrad and $\delta\theta = 38.5\,\mu$rad for the 040 reflection. Different $\delta\phi_0$ values indicate that the sample has anisotropic curvature. The calculations also take into account the miscut angle ρ as well.

Experimental-specular data are in quite good agreement with the calculations on the basis of the x-ray dynamical theory for perfect crystals, while experimental-diffraction curves are not in very good agreement with such calculations. The experimental-diffraction curves imply that crystal lattices in surface layers of the substrate may be bent. These distortions could be induced by a thermal-cleaning process.

Z is not a fitting value since GAXSW are not sensitive[19] to a Z position close to 0 Å. This is due to the long-wavelength modulation of a GAXSW field in the perpendicular direction induced by total-external reflection. Published Z values are −1.43 (Ref. 13), −1.40 (Refs. 15 and 23), −1.37 (Ref. 24), −1.32 (Ref. 25) Å. To check the dependence of fitting parameter (η) on Z, we tried to fit the As emission yields with calculations using Eqs. (1), (6), (7), and (8) for the four Z values. We obtained the identical η_i's values for the four Z values within the estimated standard deviations: $\eta_1 = 0.10 \pm 0.05$, $\eta_2 = 0.25 \pm 0.05$, and $\eta_3 = -0.32 \pm 0.07$.

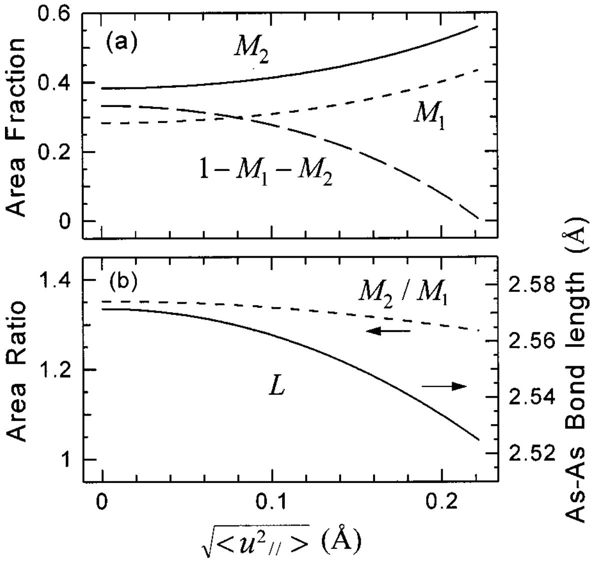

FIG. 3. Area fractions, M_1, M_2, and $1-M_1-M_2$ dependence on the in-plane root mean-square thermal vibrational amplitude $\sqrt{\langle u_{\parallel}^2\rangle}$ (a). As-As dimer bond length L and area ratio M_2/M_1 as a function of $\sqrt{\langle u_{\parallel}^2\rangle}$ (b).

If we assume $\sqrt{\langle u_{\parallel}^2\rangle} = 0.17$ (Ref. 14) Å, then L, M_1, and M_2 calculated using Eqs. (9), (11), and (12) are 2.54 ±0.04 Å, 0.36±0.07, and 0.48±0.08, respectively. If we assume $L = 2.55$ (Ref. 14) Å, then $\sqrt{\langle u_{\parallel}^2\rangle} = 0.15 \pm 0.07$ Å, $M_1 = 0.35 \pm 0.07$, and $M_2 = 0.46 \pm 0.08$ from Eqs. (10), (11), and (12).

Figure 3(a) shows the M_1 and M_2 dependence on $\sqrt{\langle u_{\parallel}^2\rangle}$ calculated from Eqs. (11) and (12). M_1 and M_2 increase from 0.28 to 0.43 and from 0.39 to 0.56, respectively, with $\sqrt{\langle u_{\parallel}^2\rangle}$. They are sensitive to $\sqrt{\langle u_{\parallel}^2\rangle}$. The fraction of randomly distributed atoms, $1-M_1-M_2$, which should be positive, allows us to limit a range of $\sqrt{\langle u_{\parallel}^2\rangle}$. Accordingly L and M_2/M_1 vary between 2.57 and 2.52 Å and 1.35 and 1.29, respectively [Fig. 3(b)]. From these results, it is found that L and M_2/M_1 do not strongly depend on the thermal vibrational amplitude. This indicates that we were able to determine the As-dimer bond length and the area ratio. The attained L is consistent with those of other works, by calculations;[24] by the combination of calculations and use of the angle-resolved photoelectron spectroscopy[25] as well as the results of x-ray measurements.[14,15] If a relative intensity ratio of 2×1 spots to 1×2 spots in LEED results is equivalent to the domain ratio, our M_2/M_1 ratio is different from the value as obtained by Bringans, Biegelsen and Swartz[3] (they measured about 8). The difference might be ascribed to the slight difference of temperature in the thermal-cleaning process and the arsenic-deposition process since they showed that the intensity ratio is sensitive to the substrate temperature. The x-ray irradiated area on the sample was much larger than the area observed by LEED. This also implies that the domain ratios may not be identical over the x-ray irradiated area and our M_2/M_1 is the average value of the domain ratio over the area.

From a previous STM study,[1] it seems clear that the dimerized surface is highly ordered and thus we assume the ordered fraction is equal to $1 (M_1+M_2=1)$. This assumption was also used to determine the thermal vibrational amplitude in the previous XSW study.[15] We obtain that $L=2.52\pm 0.05$ Å, $\sqrt{\langle u_\parallel^2\rangle}=0.22\pm 0.07$ Å, $M_1=0.44\pm 0.07$ and $M_2=0.56\pm 0.07$. This L is slightly smaller than 2.58 (Ref. 15) Å. It is noted that the in-plane root mean-square thermal vibrational amplitude is larger than the 0.14 (Ref. 15) Å, which is the surface-normal one. It is difficult to separate the surface-normal and the in-plane component of the thermal vibrational amplitude using the usual XSW technique. This is because intensity modulations of these XSW have a considerably large surface-normal component as well as the in-plane component. In addition, the x-ray field intensities are modulated in the both direction as a function of the periodicity of the d spacing used (this modulation is short compared with that in the normal direction of GAXSW fields). The in-plane component of the thermal vibrational amplitude should be different from the surface-normal component since the surface is truncated. The GAXSW method was able to extract the in-plane component $\sqrt{\langle u_\parallel^2\rangle}$ of the thermal vibrational amplitude. We also have to note that the analysis based on the x-ray dynamical theory for perfect crystals gave us reasonable surface structure information, such as the dimer bond length and the in-plane thermal vibrational amplitude. These results were valid even if the surface layer may include some crystal distortions.

We have employed the GAXSW method for determining a dimer bond length and an in-plane thermal vibrational amplitude. The dimer bond length is in good agreement with the results obtained by the x-ray diffraction measurements,[14] conventional XSW measurements,[15] and theoretical calculations.[24,25] The obtained in-plane root mean-square thermal vibrational amplitude is slightly larger than the surface normal one in the XSW study[15] when domains are assumed to be perfectly ordered. Moreover, we have obtained the average domain ratio over a large area of the sample, which might be difficult to determine with other techniques. The GAXSW method is promising for in-plane structure determination of adsorbed atoms because the third-generation synchrotron-radiation sources with brighter x-rays allow us to obtain better statistics of the fluorescence from adsorbed atoms.

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