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Adsorbate structure and vibrations on the Bi/Si(001)-(1×2) surface

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Abstract

X-ray standing wave measurements were undertaken to determine the bonding position and vibrational amplitude (normal to the surface plane) of Bi ad-dimers on the Bi-saturated Si(001)-(1×2) surface. Using the (004) Bragg reflection, we find that the center of the Bi ad-dimers lies 1.72 Å above the bulk-like Si(004) surface atomic plane. Using the (008) Bragg reflection, we find that the room temperature root-mean-square vibrational amplitude of the Bi adatoms normal to the surface plane is 0.13 Å. This direct determination of the adsorbate vibrational dynamics verifies earlier assumptions regarding the magnitude of adsorbate surface vibrations on Si surfaces, and suggests that the vibrational amplitude of dimerized group V/Si(001)-(1×2) structures is independent of the mass of the adsorbate.

1. Introduction

The adsorption of group V elements on Si(001) has garnered much attention due to its technological importance in heteroepitaxy, surface passivation, delta-doping and surfactant-mediated epitaxy (SME) [1–4]. Furthermore, the simple surface termination that often results in these systems [1, 5, 6] has stimulated fundamental interest in the surface bonding and configuration. Bismuth, the heaviest element in group V, has recently attracted more interest since a recent investigation (using reflection high-energy electron diffraction and secondary-ion mass spectrometry) concluded that Bi was the most ideal available surfactant for SME [7].

Evidently, two different adsorption phases exist for Bi/Si(001). Near the saturation coverage, the Bi adlayer displays a ($n \times 2$) superstructure, where the periodicity n is related to the coverage by $\theta = (1 - 1/n)$ [6, 8]. This observation is easily explained by a dimerized surface

with ordered missing-dimer-row defects; these defects are thought to be required for strain relief due to the size mismatch of the Bi adatoms and the substrate lattice. The local structure consists of dimers arranged with a (1×2)-like local geometry, similar to the clean surface [6]. This reasonable proposition was recently verified quantitatively by an X-ray standing wave (XSW) investigation of the adsorption height and dimer bond length [9].

At coverages lower than 0.5 ML, however, a different structure was predicted to occur (1 ML = 6.78×10^{14} atoms/cm²). A first-principles molecular cluster calculation predicted that the low-coverage structure consisted of Bi dimers residing on top of unbroken Si dimers with a (2×2) superstructure [10]. A scanning tunneling microscopy (STM) and low-energy-electron diffraction (LEED) study [11] of Bi adsorption at room temperature (RT) did observe a structure with (2×2) periodicity for Bi coverage below 0.5 ML. Coverage-dependent surface structures have never been reported for other group V elements (As and Sb) on Si(001). The lower-coverage surface will be treated in a separate publication, and we will focus here on the near-saturation case.

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We will present an XSW investigation of the structure and vibrations of the Bi-saturated Si(001) surface, employing reflections from the (004) and (008) bulk lattice planes. We thereby precisely determine two important Fourier components of the spatial distribution of Bi atoms relative to the Si lattice. From these parallel reflections, we can extract the room-temperature vibrational amplitude of the Bi adatoms normal to the surface plane.

2. Experimental procedure and results

The experiments were conducted at beamline X15A of the National Synchrotron Light Source at Brookhaven National Laboratory. The apparatus consists of several coupled ultrahigh vacuum (UHV) chambers (base pressure $\sim 9 \times 10^{-11}$ torr) allowing sample preparation (molecular beam epitaxial growth) and characterization [LEED, Auger electron spectroscopy (AES) and XSW]. The XSW technique as well as the experimental arrangement at X15A have recently been extensively reviewed by Zegenhagen [12].

The Si(001) sample was Syton-polished and chemically cleaned *ex situ* using the Shiraki process [13], and then mounted in a strain-free manner. After degassing the sample in UHV, the oxide was thermally desorbed at 900 °C. The sample was then cooled to room temperature (initial cooling rate ≈ 2.0 °C/s), resulting in a sharp, two-domain (2×1) LEED pattern. AES could detect no O and it could detect a small amount of C contamination (~ 0.03 ML). With the Si substrate held at 475 °C, ≈ 3 ML of Bi was deposited from the effusion cell over 10 min. The sticking coefficient for Bi adsorption, like that of other group V elements on Si(001) [14], goes to zero at coverages near 1 ML for this temperature [8]. Therefore, approximately 1 ML Bi was adsorbed on the surface. The Bi-saturated surface was further annealed for 5 min at 500 °C, resulting in a two-domain (1×2) LEED pattern with slightly diffused half-order spots. No clear *n*th order spots were observed.

The incident X-ray beam from the synchrotron radiation source was collimated and monochromated by a double-crystal monochromator and directed through a Be window into the UHV chamber. The single crystal sample was held at room temperature and placed so that the X-ray beam was Bragg reflected by either the (004) or (008) set of diffraction planes. We used 15 keV X-rays for both the (004) and (008) measurements, produced by reflection by the (004) or (008) diffraction planes of the monochromator crystal, respectively. This incident photon energy is above the Bi L_{III} edge, and the resultant Bi L fluorescence yield was detected by a solid-state Si(Li) detector. The intensity of the Bragg-reflected X-ray beam was measured by an *in vacuo* Si photodiode.

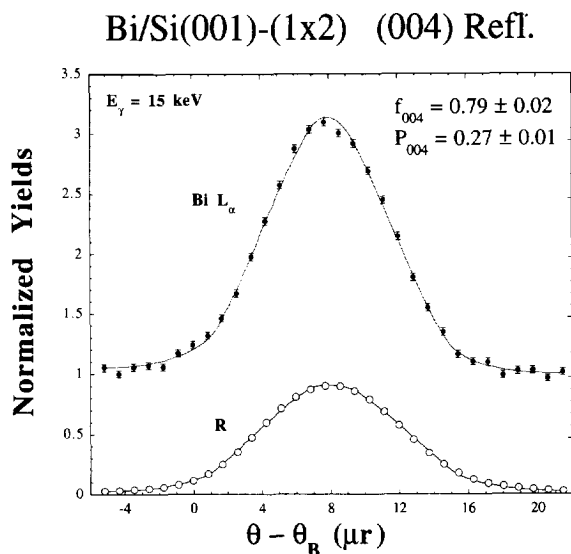


Fig. 1. The experimental and theoretical angular dependence for the X-ray reflectivity and Bi L fluorescence yield for the (004) reflection at $E_\gamma = 15$ keV.

A rocking curve about the Bragg condition was accomplished by scanning the incident X-ray energy (using angular piezoelectric drives on both monochromator crystals). This is equivalent to scanning the angle of the sample substrate about the Bragg angle, and the abscissas of the data are therefore expressed as angular deflections. At each (equivalent) angular step, the reflected X-ray intensity and fluorescence spectrum were recorded simultaneously.

Fig. 1 shows the Si reflectivity and Bi L fluorescence yields (normalized to unity at off-Bragg angles) as a function of the Bragg reflection angle θ for the (004) reflection (diffraction vector normal to the sample surface). The solid line through the reflectivity data is a fit to standard dynamical diffraction theory [15]; the line through the fluorescence yield is a fit to a parametrization that will be discussed below. A similar scan (Fig. 2) was acquired for the same surface using the (008) reflection, whose diffraction vector is *also* normal to the surface plane.

3. Discussion

The interference of the coherently coupled incident and Bragg-reflected X-ray plane waves generates in XSW in and above the crystal, with the XSW nodal planes parallel to and having the same periodicity as the diffraction planes. The phase of the standing wave with respect to the diffraction planes shifts by 180° as the Bragg angle θ is scanned from the low-angle side of the rocking curve

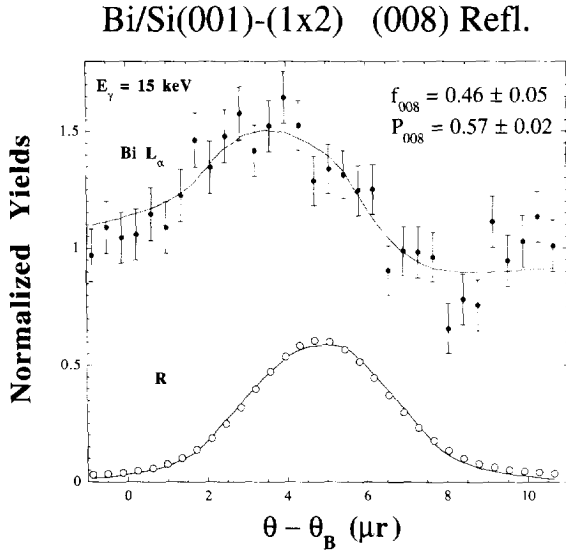


Fig. 2. The experimental and theoretical angular dependence for the X-ray reflectivity and Bi L fluorescence yield for the (008) reflection at $E_\gamma = 15$ keV.

to the high-angle side. This phase shift moves the anti-nodal planes of the standing wave inward by one-half of the d -spacing d_{hkl} . Thus, the angular dependence of the fluorescence yield $Y(\theta)$ from an adatom layer can be described as

$$Y(\theta) = 1 + R(\theta) + 2\sqrt{R(\theta)}f_H \cos[v(\theta) - 2\pi P_H], \quad (1)$$

where $R(\theta)$ is the reflectivity and $v(\theta)$ is the relative phase of the diffracted plane wave. The coherent fraction f_H and coherent position P_H correspond to the amplitude and phase, respectively, of the H th Fourier component of the time-averaged spatial distribution of the nuclei of the adatoms (projected into a unit cell). H is the reciprocal lattice vector for the (hkl) diffraction planes. More specifically, the coherent fraction can be expressed, due to the convolution theorem, as the product of three factors [16]:

$$f_H = C a_H D_H, \quad (2)$$

where C is the fraction of adatoms at ordered positions, a_H is a geometrical factor, and D_H is the Debye–Waller factor. The Debye–Waller factor can be written as $D_H = \exp(-2\pi^2 \langle u_H^2 \rangle / d_H^2)$, where $\langle u_H^2 \rangle$ is the mean-squared thermal vibrational amplitude of the adatom in the H direction.

Group V adatoms on Si(001) and Ge(001) surfaces have been demonstrated to occur as dimers. Furthermore, it appears that these dimers are not buckled, i.e., tilted, with respect to the surface [9, 17–20]. Thus, both

Bi atoms in the unit cell are at the same adsorption height relative to the surface plane (for symmetric Bi dimers). The coherent position P_{004} equals h'/d_{004} , where h' locates the height of the Bi ad-dimer relative to the Si(004) bulk-like atomic plane. Since the period of the XSW for the (008) reflection is half that for the (004) reflection, the value of P_{008} should be $2P_{004}$ (modulo 1). (If the adatom spatial distribution normal to the surface is asymmetric, however, some deviation from this relationship is expected. This can occur in the case of an anharmonic bonding potential.) Since all adatoms occupy equivalent positions for symmetric dimers, the geometrical factor a_{004n} for diffraction vectors perpendicular to the surface is unity (i.e., $a_{004} = a_{008} = 1$).

The close relationship of the (004)- and (008)-derived Fourier components of the spatial distribution (for simple structures like the dimers considered here) can be exploited to render information on the disorder $1 - C$ and the root-mean-squared thermal vibration amplitudes $\langle u_\perp^2 \rangle^{1/2}$ perpendicular to the surface plane. Assuming the ordered fraction C as a constant, Eq. (2) for the (004) and (008) reflections can be solved (using $d_{008} = 0.5d_{004}$) for $\langle u_\perp^2 \rangle^{1/2}$ and C :

$$\langle u_\perp^2 \rangle^{1/2} = \frac{d_{004}}{\sqrt{6\pi}} \sqrt{\ln \frac{f_{004}}{f_{008}}} \quad (3)$$

and

$$C = \frac{f_{004}}{D_{004}(u_\perp)}. \quad (4)$$

Thus, using XSW with higher-order harmonics, a direct measure of the thermal vibrational amplitude and surface disorder becomes possible [16].

The coherent fractions (f_{004}, f_{008}) and coherent positions (P_{004}, P_{008}) shown in Figs. 1 and 2 are determined by χ^2 fits of Eq. (1) to the Bi L fluorescence data. The measured value of $P_{004} = 1.27 \pm 0.01$ indicates that the Bi ad-dimer height $h' = P_{004} d_{004} = 1.72 \pm 0.02$ Å above the Si(004) bulk-like atomic planes. The measured value of P_{008} is 0.57 ± 0.02 . This value is equivalent to twice the P_{004} value (0.54), indicating that the Bi atomic spatial distribution is not markedly asymmetric.

The coherent fractions can immediately be used in Eqs. (3) and (4) to indicate the degree of disorder present in the Bi atom population and the Bi thermal vibrational amplitude. Given our results of $f_{004} = 0.79 \pm 0.02$ and $f_{008} = 0.46 \pm 0.05$, we find the ordered fraction C to be a reasonably high 0.95 ± 0.05 . This experimental determination of the Bi order provides quantitative confirmation of STM reports of highly ordered Bi, with a small, but finite, defect concentration [6]. It should be kept in mind, however, that STM and XSW have different sensitivities to different types of disorder. Our measurement

reports the fraction of the Bi atoms present that reside in sites with a particular registration. It is essentially insensitive to the presence of vacancies, which are evident in STM.

Our value for the RT root-mean-squared vibrational amplitude perpendicular to the surface $\langle u_{\perp}^2 \rangle^{1/2}$ is 0.13 ± 0.015 Å. This direct determination can be compared to prior determinations of other dimerized group V adsorbates on Si(001). It corroborates a value inferred indirectly using XSW for As/Si(001)-(1 × 2) of 0.12 Å at RT [21]. Furthermore, it is consistent with a direct determination of $\langle u_{\perp}^2 \rangle^{1/2}$ made by our group for Sb/Si(001)-(1 × 2) of 0.14 ± 0.01 Å [22]. Empirically, then, it appears that the amplitude of the thermal vibrations of these similar structures is not sensitive to the mass of the adsorbed species. We hope that the availability of experimentally determined values of adsorbate vibrational amplitudes aids and stimulates theoretical investigations of surface dynamics on semiconductor surfaces.

4. Conclusion

We have directly studied the geometry, order and vibrational amplitude of Bi atoms on the saturated Bi/Si(001)-(1 × 2) surface using the XSW technique, employing higher-order reflections. We find that the centers of Bi ad-dimers are located 1.72 ± 0.02 Å above the bulk-like Si lattice plane. The RT vibrational amplitude normal to the surface was found to be 0.13 ± 0.015 Å, and a high degree of surface order was observed. Combined with previous work, this result indicates that the vibrational amplitude of group V adatoms on Si(001) is nearly independent of the mass of the adsorbate.

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