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Structural determination of the Si(111) $\sqrt{3}\times\sqrt{3}$-Bi surface by x-ray standing waves and scanning tunneling microscopy

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X-ray standing-wave measurements and tunneling microscopy have been combined to solve the atomic geometry of the $\sqrt{3}\times\sqrt{3}R30°$ honeycomb phase of Bi on Si(111). The standing-wave measurements utilize three different diffracting planes to triangulate the surface position of Bi atoms. The unoccupied surface sites required to completely determine the structure can be deduced from Rutherford-backscattering coverage and low-energy electron-diffraction symmetry arguments. These arguments are completely confirmed by a tunneling-microscope study, which is free of the ambiguities of previous studies. The final result is a $\frac{2}{3}$-ML $\sqrt{3}\times\sqrt{3}R30°$ structure with Bi atoms in the T_1 sites directly above first-layer Si atoms.

Due to their technological importance, the geometric structures formed when metal atoms are deposited on semiconductor surfaces have been a primary focus within surface science. While it is generally accepted that the group-III metals Al, Ga, In, and Tl form identical and stable $\sqrt{3}\times\sqrt{3}R30°$ (hereafter $\sqrt{3}\times\sqrt{3}$) structures on the Si(111) surface, in which $\frac{1}{3}$ ML of metal atoms adsorb in T_4 sites,[1] no such common stable bonding structure is observed for the group-V metals As, Sb, and Bi. The knowledge of these valence-five structures are crucial for issues concerning passivation, surfactant-assisted growth, and doping of Si surfaces and interfaces.

Utilizing photoemission and low-energy electron diffraction (LEED), Olmstead *et al.*[2] concluded that the structure formed when a Si(111) surface is exposed to As consists of an ordered 1×1 array, in which As atoms substitute for the top-layer Si atoms of the ideal Si(111) 1×1 surface. This presumption was later confirmed by x-ray standing-wave (XSW) measurements,[3] which measure directly the position of foreign or impurity atoms relative to the bulk diffracting planes of the host crystal.[4] For the heavier metal Sb, subsequent LEED studies[5] did not observe an ordered 1×1 structure on the Si(111) surface, but a well-ordered $\sqrt{3}\times\sqrt{3}R30°$ pattern commonly associated with the group-III metals was seen. The structure giving rise to this periodicity was later determined to be more complex than the T_4 geometry of the group-III metals, for it was found to consist of a full monolayer of Sb atoms adsorbed as trimers above the T_4 sites.[6]

Unlike the metals As and Sb, a consensus concerning the saturation structure of Bi adsorption on Si(111) has yet to be attained. In fact, various groups utilizing different structural techniques have arrived at conflicting models. For example, Takahashi *et al.*[7] suggested from an x-ray diffraction measurement that the Bi atoms adsorb as trimers terminated by a honeycomb array of top-layer Si atoms. On the other hand, Wan *et al.*[8] concluded from LEED intensity-voltage analysis that the identical trimer structure as found for the Si(111) $\sqrt{3}\times\sqrt{3}$-Sb surface best describes the Bi high-coverage phase. Although it is believed that at low coverages ($<\frac{1}{3}$ ML) the Bi atoms substitute for the Si adatoms of the 7×7 structure,[9,10] the structure of the saturation phase of Bi on Si(111) remains an open issue.

An additional complication hampering the determination of this geometry is the dependence on tunneling voltage of the scanning tunneling microscope (STM) images, which echo the complexity of similar $\sqrt{3}\times\sqrt{3}$ surface structures such as Si(111) $\sqrt{3}\times\sqrt{3}$-Ag.[11] This uncertainty is a direct reflection of the fact that the STM may not be imaging the atomic positions of adatoms, but it sees a complicated convolution of both the topography and the valence electronic density of states of both tip and sample. Early images of this surface reported by Park *et al.*[9] were attributed to two distinct high-coverage phases: a 1-ML trimer phase, which would be consistent with the trimer structure found for Sb and suggested by LEED,[8] and a $\frac{2}{3}$-ML honeycomb phase, which would be consistent with the Si-terminated structure

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proposed from x-ray diffraction.[7] Shioda *et al.*[10] later claimed that $\sqrt{3}\times\sqrt{3}$ images with one, two, or three protrusions per unit cell could be obtained from the same surface simply by varying the tunneling bias. It therefore seems impossible to conclude from these STM studies which of the various proposed models is in accord with the actual structure, and additional experimental input is paramount.

In this work, we utilize the technique of XSW interferometry in conjunction with STM, Rutherford backscattering (RBS), and LEED to determine unambiguously the structure of the high-coverage Si(111) $\sqrt{3}\times\sqrt{3}$-Bi surface. Unlike the techniques mentioned above, XSW determines the precise positions of the atomic cores of adatoms using triangulation from different diffraction planes. Nearly ideal coherent positions and fractions for [111], [11$\bar{1}$], and [220] reflections establish that the Bi atoms are located on T_1 sites directly above first-layer Si atoms. Together with the accurate coverage determination from RBS and the $\sqrt{3}\times\sqrt{3}$ LEED periodicity, we can conclude that the Bi atoms are arranged in the honeycomb array observed by a subset of the STM images. In addition, we have confirmed this solution with an STM experiment that shows this to be the only high-coverage phase. This study also does not show the bias dependence reported by Shioda *et al.*[10]

Si(111) samples were chemically cleaned using the Shiraki[12] procedure prior to insertion into the vacuum chamber, where sample preparation and x-ray studies were performed. Si(111) 7×7 surfaces were prepared by flashing degassed samples to $\sim$900 °C, which rendered sharp 7×7 LEED patterns. Auger-electron spectroscopy found the samples to be free of carbon and oxygen. Approximately 3 ML (as determined from a quartz-crystal microbalance) of Bi was deposited from a degassed effusion cell onto the sample, which was held at 400 °C. The sample was then annealed for 15 min to 500 °C to desorb excess Bi, enhance the interfacial order, and arrive at the saturation coverage. This temperature is $\sim$50 °C below that at which all of the Bi desorbs from the Si surface ($\sim$550 °C). This procedure produced extremely sharp $\sqrt{3}\times\sqrt{3}$ LEED patterns with no residual 7×7 spots of the clean surface. The resulting Bi Auger intensity proved to be stable and independent of initial coverage. XSW measurements were made by cycling a double-crystal monochromator through the [111], [11$\bar{1}$], and [220] Si reflections and simultaneously recording the reflectivities, with a NaI detector, and the Bi $L\alpha$ fluorescence yield, with a Si(Li) detector, using 18-keV photons on beamline X15A of the National Synchrotron Light Source at Brookhaven National Laboratory. During the measurements, the sample was at room temperature.

Figure 1 shows the modulated Bi fluorescence yield for the [111] reflection in the field of the standing wave. The solid lines are the best fits, calculated from the dynamical theory of diffraction,[13] to the data points.[14] The independent parameters determined are P, the coherent position of the Bi atoms, and F, the fractional occupancy of Bi atoms at this position; they are found to be 0.98 ± 0.02 and 0.98 ± 0.02, respectively. It is clear from the near-unity value of F that the Bi atoms all lie in a single plane $0.98d_{111}$ above the center of the extrapolated surface bilayer, where d_{111} (=3.135 Å) is the lattice periodicity in the [111] direction.

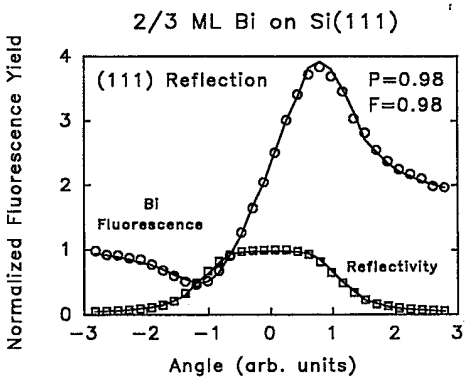

FIG. 1. The [111] reflectivity and fluorescence yield for $\frac{2}{3}$-ML Bi on Si(111) $\sqrt{3}\times\sqrt{3}R30°$.

Taking into account the distance between the bilayer, and assuming negligible contraction of the top Si layer, this places the Bi atoms 2.68 ± 0.03 Å directly above the first Si layer of the ideal 1×1 surface. This distance corresponds nearly identically to the sum of the Si and Bi covalent radii (1.17 and 1.54 Å, respectively), and therefore alone suggests that the Bi atoms are bonded in atop sites on the Si(111) surface[15] with little or no surface relaxation.[16] For completeness, we should mention that an "ideal" top-layer substitutional geometry would have a Bi perpendicular height of approximately $0.37d_{111}$.

In order to determine the lateral registry of the Bi atoms, the surface standing-wave data were taken for both the [11$\bar{1}$] and [220] planes. The resulting fluorescence yields are shown in Fig. 2, and Fig. 3 shows their corresponding registration. These planes are inclined 70.53° and 35.27° from the Si(111) surface, respectively. The [11$\bar{1}$] data are ideal in as-

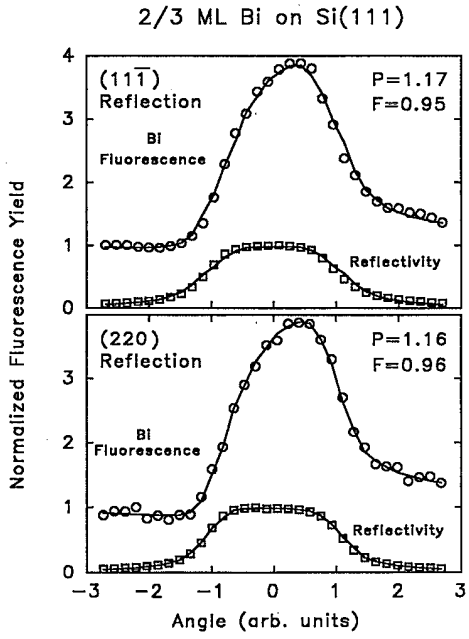

FIG. 2. Same as Fig. 1 for the [11$\bar{1}$] and [220] reflections.

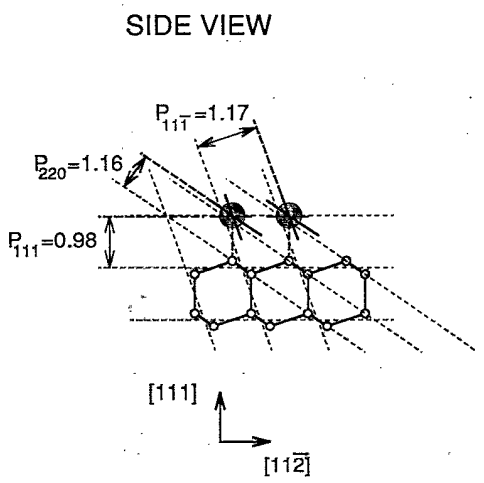

FIG. 3. The registration of the Bi atoms relative to the Si [111], [11$\bar{1}$], and [220] planes.

sessing the lateral arrangement of Bi atoms, for this reflection measures mostly in-surface registry. The values determined from both are $P=1.17\pm0.02$ and $F=0.96\pm0.02$. The fact that both off-normal reflections have such high coherent fractions allows a straightforward triangulation to determine that the Bi atoms lie directly above the first-layer silicon atoms in T_1 sites. Had the Bi atoms deviated from bulk Si sites, the coherent fractions in the off-normal directions would be significantly less than unity. For example, in the trimer model where the Bi-Bi bond length is 3.1 Å [i.e., the natural Bi-Bi length and an equivalent situation to that found for Sb (Ref. 15)], either coherent fraction would be reduced to 0.85.

To our knowledge, this system is the only one studied to date with this complexity that has yielded coherent fractions so close to unity in all directions. The group-III metal Ga is similar in this regard,[17] although high coherent fractions are expected since the Ga atoms occupy the T_4 sites for coverages below $\frac{1}{3}$ ML. As a counterexample, the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag interface was found to have a coherent fraction close to unity in the [111] direction, but due to the lateral reconstruction of the honeycomb-chained trimer model, the coherent fraction in the [11$\bar{1}$] direction was found to be as low as 0.5.[8] Even a small deviation from the high-symmetry sites of the Si lattice can produce dramatic reductions in the coherent fraction.

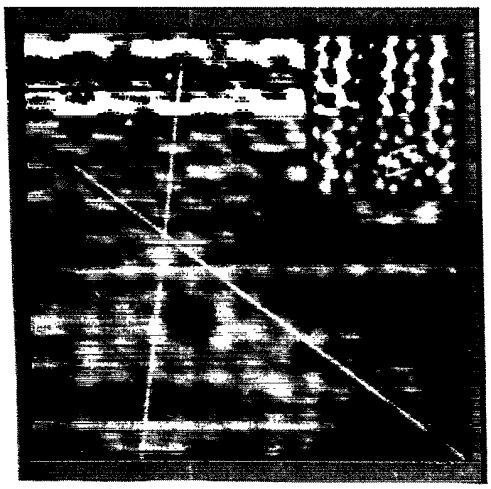

FIG. 4. STM image of two $\sqrt{3}\times\sqrt{3}$ phases. The lower part corresponds to the $\frac{1}{3}$-ML $\sqrt{3}\times\sqrt{3}$ phase, in which each bright spot corresponds to a Bi atom situating at a T_4 site. The upper part is the high-coverage phase, forming the ordered honeycomb structure. In better images of the honeycomb structure (inset), there are two bright spots and one dark hole in each $\sqrt{3}\times\sqrt{3}$ unit cell. A unit cell is also outlined.

STM and RBS measurements on similarly prepared samples were performed at Harvard University. In all cases, greater than 1 ML of Bi was deposited onto the clean 7×7 surface. For the STM measurements, two deposition methods were employed. During the cold deposition, the sample was kept at room temperature and annealed afterwards to temperatures ranging from 390 °C to 540 °C. If the annealing temperature is above 510 °C, Bi atoms slowly desorb from the high-coverage $\sqrt{3}\times\sqrt{3}$ phase. This produces mixed phases, which allows the determination of adatom registry by STM as pointed out previously.[19] For the hot deposit, the sample was kept at 500 °C during the deposition. STM images revealed that samples prepared by the hot-deposition method (i.e., those whose temperature never exceeded 500 °C) were completely covered with a single high-coverage $\sqrt{3}\times\sqrt{3}$ phase without Bi islands or a $\frac{1}{3}$-ML $\sqrt{3}\times\sqrt{3}$ phase.

Figure 4 shows an STM image from a sample that was prepared by cold deposition and annealed to 510 °C for 10 min. The resulting surface contains primarily the high-coverage $\sqrt{3}\times\sqrt{3}$ phase, with less than 5% of the $\frac{1}{3}$-ML $\sqrt{3}\times\sqrt{3}$ structure that appears near step edges. The high-coverage $\sqrt{3}\times\sqrt{3}$ phase consists of a honeycomb pattern with two bright spots and one dark hole in each $\sqrt{3}\times\sqrt{3}$ unit cell. Similar images were obtained by both Park *et al.*[9] and Shioda *et al.*[10] Unlike the previous STM study by Shioda *et al.*,[10] which suffers from a strong tunneling condition dependence, this honeycomb pattern is consistently found in our images with sample biases ranging from +0.5 to +1.7 V and from −0.4 to −1 V. In general, a pattern in a STM image caused by some electronic artifact will be highly bias dependent. Since the same honeycomb pattern is obtained for this sample preparation over a wide range of tunneling biases with both polarities, it is natural to assign each bright spot to a surface Bi atom. Comparison with the $\frac{1}{3}$-ML $\sqrt{3}\times\sqrt{3}$ region of the sample finds that each Bi atom is situated at a T_1 site, and there is one vacant T_1 site per $\sqrt{3}\times\sqrt{3}$ unit cell. Figure 5 shows the geometric structure associated with this image. The Bi coverage of this particular sample was determined by RBS to be 0.66 ± 0.03 ML, consistent with the ideal $\frac{2}{3}$ ML for this structure. We found no other high-coverage $\sqrt{3}\times\sqrt{3}$ phase. Cold-deposited samples were annealed at lower temperatures (as low as 400 °C) for testing. The STM images contained only the honeycomb pattern and scattered Bi clusters; no higher-coverage $\sqrt{3}\times\sqrt{3}$ phase was found.

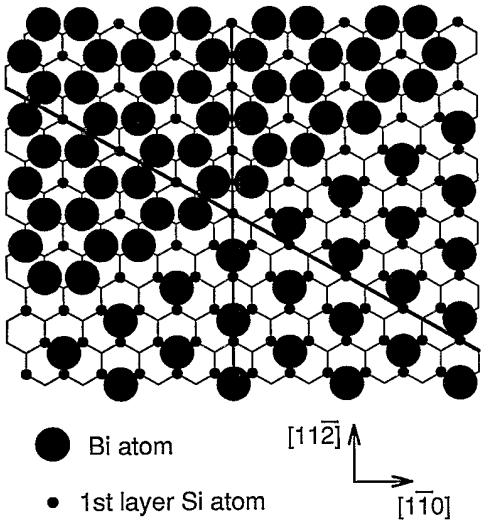

FIG. 5. An exact atomic model for the two phases shown in Fig. 4.

In conclusion, through a combination of x-ray standing waves, scanning tunneling microscopy, and Rutherford backscattering, we have determined the high-coverage phase of the Si(111) $\sqrt{3}\times\sqrt{3}$-Bi surface to correspond to $\frac{2}{3}$ ML of Bi atoms adsorbed at T_1 sites directly above the first-layer Si atoms. These Bi atoms correspond to the bright spots seen in STM images, which show a honeycomb reconstruction. The equivalence of the perpendicular distance, as determined by the standing-wave measurement of the Bi atoms to the first Si plane with the sum of the Si and Bi covalent radii, suggests that the Si surface is not relaxed.

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