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Brief Reports

Observation and low-energy-electron-diffraction structure analysis of the Ge(111)-($\sqrt{3}\times\sqrt{3}$)R 30°-Bi system

K. J. Wan, W. K. Ford, G. J. Lapeyre, and J. C. Hermanson
Advanced Materials Center and Department of Physics, Montana State University, Bozeman, Montana 59717
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Surface reconstruction of the submonolayer Bi/Ge(111) system was investigated by low-energy diffraction and Auger-electron spectroscopy. It was found that an ordered ($\sqrt{3}\times\sqrt{3}$) superstructure is formed at $\sim\frac{1}{3}$ monolayer Bi deposition on the ~320 °C surface. The data were analyzed by full dynamical low-energy-electron-diffraction calculations. A quantitative comparison between experiment and calculated I-V spectra suggests that the Bi adatoms are located at the T_4 site 1.324 Å above the first Ge layer. Our results imply that substrate atoms in the first two atomic layers are significantly displaced from their ideal bulk positions. Details of the atomic coordinates are given.

The interaction of metallic films with elemental semiconductor substrates is currently of interest for both practical applications and theoretical considerations.[1] The epitaxial growth of column-III and -V metals on nonpolar semiconductor substrates is believed to fully passivate the surface dangling bonds, leading to the high quality of epitaxy of the III-V compounds on the Si or Ge substrate. To facilitate an understanding of the electronic structure of the interface, including issues such as the formation of Schottky barriers in electronic devices, the knowledge of the atomic geometry of the interface in the initial stages of formation appears necessary. Among the several techniques for locating atoms at surfaces low-energy electron diffraction (LEED) is a well-established tool for the determination of surface structure, though other techniques such as photoelectron diffraction and electron holography are advancing rapidly.[2]

In this paper, we present detailed structural information for the incipient growth of Bi films on a Ge(111) substrate obtained by LEED. As noted in earlier observations of Ga, Pb, Sb, etc. films on Si and Ge(111) surfaces,[3–5] a ($\sqrt{3}\times\sqrt{3}$) LEED pattern induced by the Bi overlayer occurs for Bi coverages of less than 1 monolayer (ML) on Ge(111) substrates. This places the Bi/Ge(111) system in the same class with a large group of metal-semiconductor overlayer structures with a ($\sqrt{3}\times\sqrt{3}$) unit cell. By contrast, the chemically similar metal As has been shown to form a simple (1×1) not ($\sqrt{3}\times\sqrt{3}$) structure resulting from the substitution of the topmost Si atomic layer.[6] Proposed models so far for the ($\sqrt{3}\times\sqrt{3}$) surfaces include simple overlayer,[7] honeycomb,[8] trimer,[9] and bilayer models[4] corresponding to adatom coverages of $\frac{1}{3}$, $\frac{2}{3}$, 1, and $\frac{4}{3}$ ML, respectively.

The experiments reported here were carried out in an UHV chamber equipped with a four-grid LEED optics which was also used as a retarding field analyzer for Auger-electron spectroscopy (AES) measurements. The base pressure of this chamber was less than 8×10^{-11} Torr. The computer-controlled video LEED optics and the experimental conditions were the same as we described in previous work.[10] The n-type Ge single crystals with 40-Ω cm resistivity were cut into 5-mm square bars oriented to within 0.5° along the (111) direction. Using a diamond saw, notches 0.051 in. deep and 0.020 in. wide were cut into the side of each bar at 0.085-in. intervals to assist in the cleaving process under UHV. Bi films were deposited by sublimating high-purity (99.9999999%) polycrystalline material from the bulk at a background pressure of less than 5×10^{-10} Torr and at a slow rate, typically less than 1 Å per minute. The film deposition was monitored with a quartz-crystal oscillator and calibrated using Rutherford backscattering in another chamber.[11] One ML is defined in substrate units, i.e., as one deposited atom per surface germanium atom: 7.22×10^{14} atoms/cm^2. The sample could be heated to a temperature in excess of 500 °C, and cooled to −125 °C while the spot intensities as a function of incident electron energy (I-V curves) were recorded. The incident beam was aligned within ~0.5° of the sample normal as permitted by our instrument.[10]

TABLE I. AES measurement of Bi coverage (θ) as a function of annealing temperature (T).

T (°C/5 min)	20	167	225	250	280	300	320	350	370	390	420
θ (ML)	1.514	1.452	1.112	1.134	0.789	0.479	0.398	0.312	0.302	0.210	0.199

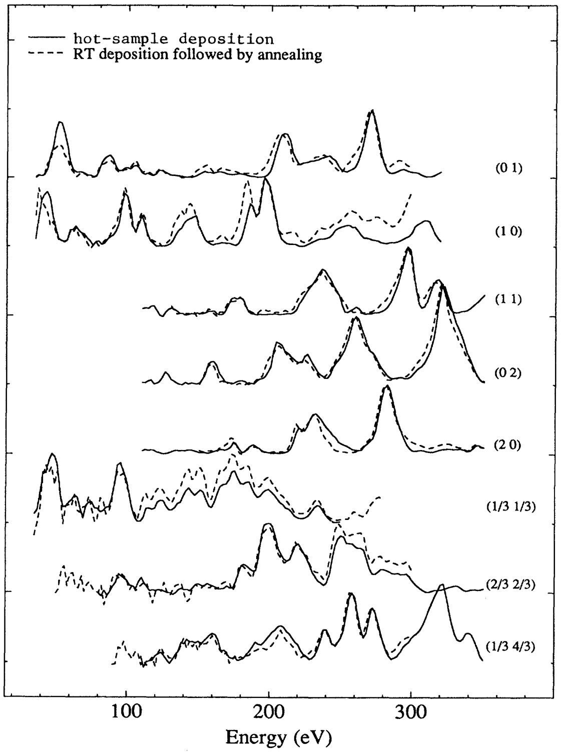

FIG. 1. *I*-*V* spectra for two different sample preparations to demonstrate the similarity of the LEED structures. The relative intensities of the beams are retained within each panel.

It is well known that the surface atomic structure of Ge(111) is strongly dependent on the sample preparation.[13] Our room-temperature as-cleaved Ge(111) surface exhibited a very clear (2×1) diffraction pattern. Slight annealing to about 100 °C results in a (2×8) structure and further annealing up to 200 °C transforms the (2×8) to a (1×1) superlattice. Starting from the Ge(111)1×1 clean surface, about 1.5-ML Bi was deposited at room temperature. After this deposition, the (1×1) LEED pattern persisted with a strong background, which indicates no ordered Bi overlayers can be prepared at room temperature without annealing. AES results of Table I show the coverage of Bi versus the annealing temperature. A $(\sqrt{3}\times\sqrt{3})$ LEED pattern appeared at 200 °C and became sharpest at about 320 °C. No other structure but $(\sqrt{3}\times\sqrt{3})$ was observed during gradual annealing up to 500 °C. Evidence suggests that the reconstructions induced by the submonolayer film, and the corresponding coverages, depend mainly on the substrate temperature.[12] Thus, the Bi/Ge(111)-$(\sqrt{3}\times\sqrt{3})$ surface structure should also be produced by Bi deposition on a high-temperature substrate. The *I*-*V* spectra shown in Fig. 1 by solid lines were obtained after deposition of 2-ML Bi on the 320 °C substrate. Although 2-ML bismuth was deposited at this temperature, AES measurement indicated that only $\frac{1}{3}$ ML Bi remained on the surface, the other atoms being desorbed from the hot substrate. This behavior is similar to that of the Bi/Si(111) system studied in our previous work.[12] The dashed curves in Fig. 1 were obtained for a film deposited at room temperature, followed by annealing to 320 °C. The two sets of data are essentially identical; this result strongly suggests identical surface atomic geometries. We find that the $(\sqrt{3}\times\sqrt{3})$ structure achieved by deposition on the hot-sample surface gives better reproducibility; accordingly, we used these data for the multiple-scattering analysis.

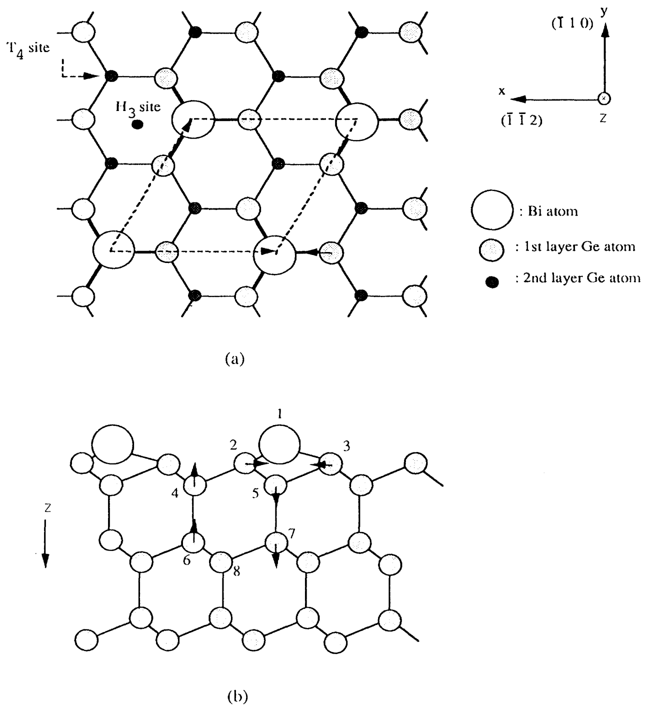

FIG. 2. (a) Top and (b) side views of the optimized structure.

The most important goal of our analysis is to establish the atomic configuration responsible for the $(\sqrt{3}\times\sqrt{3})$ reconstruction of Bi/Ge(111). To this end, the full dynamical LEED intensity calculations were performed. The computer source code was an extended version based on the method of Duke and Laramore[14] and reported elsewhere.[11] We summarize here only the features of the method salient to our studies.[12] The energy-dependent phase shifts of Bi and Ge were computed relativistically using the Hartree-Fock-Slater muffin-tin model; the substrate potential was treated by superposing atomic charge densities within the neighboring sixteen shells of atoms.

TABLE II. Atomic coordinates of the T_4 structure; the Cartesian coordinates and atom numbers are defined according to Fig. 2(b). The origin is placed at the topmost Bi atom.

Atom no.	$\hat{x}$ (Å)	$\hat{y}$ (Å)	$\hat{z}$ (Å)	Displacement from bulk position (Å)
1	0.000	0.000	0.000	
2	0.808	1.400	1.324	$-0.346\hat{x}+0.600\hat{y}$
3	−1.617	0.000	1.324	$0.693\hat{x}$
4	3.465	2.001	2.186	$0.046\hat{z}$
5	0.000	0.000	2.585	$0.445\hat{z}$
6	3.465	2.001	4.726	$0.135\hat{z}$
7	0.000	0.000	5.014	$0.423\hat{z}$
8	1.155	2.001	5.831	

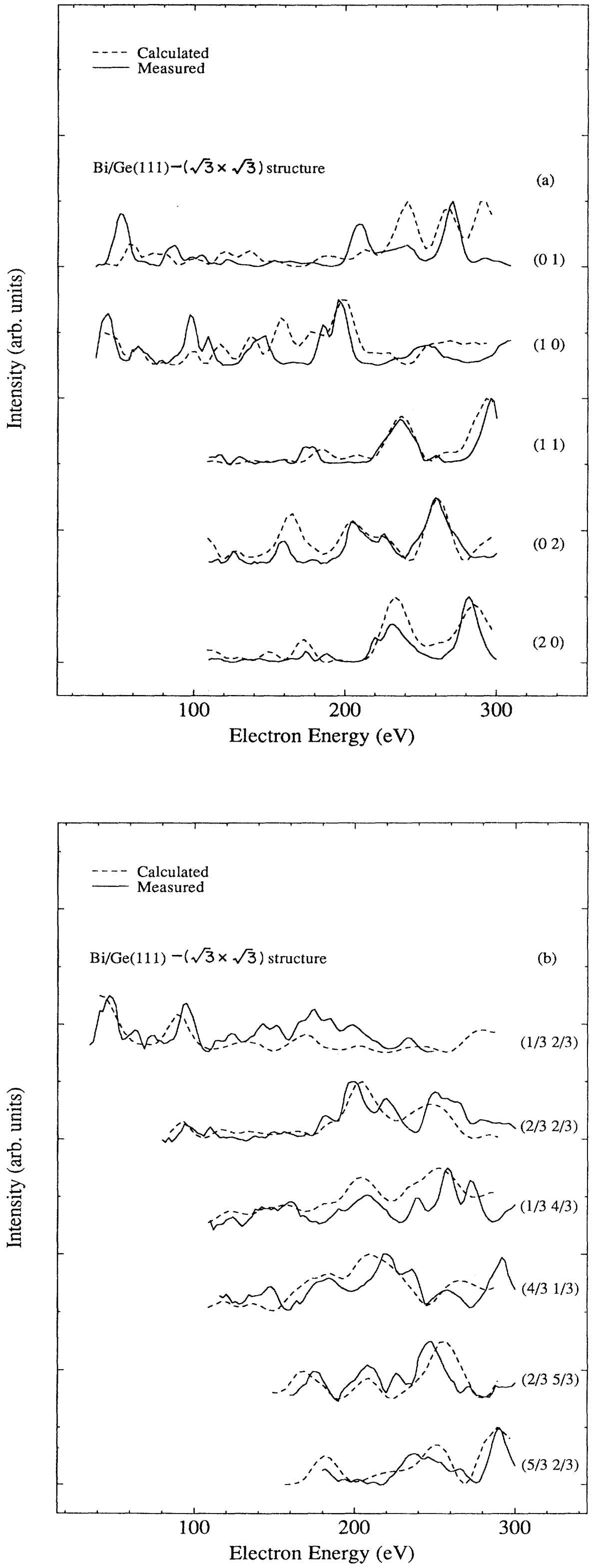

FIG. 3. Comparison between experimental and calculated *I*-*V* spectra; solid curves are from experimental data and dashed lines are the computed intensities of the best-fit structural model in Fig. 2. (a) Integral-order spots; (b) fractional-order spots. Averaged R_x (eleven beams) is 0.244.

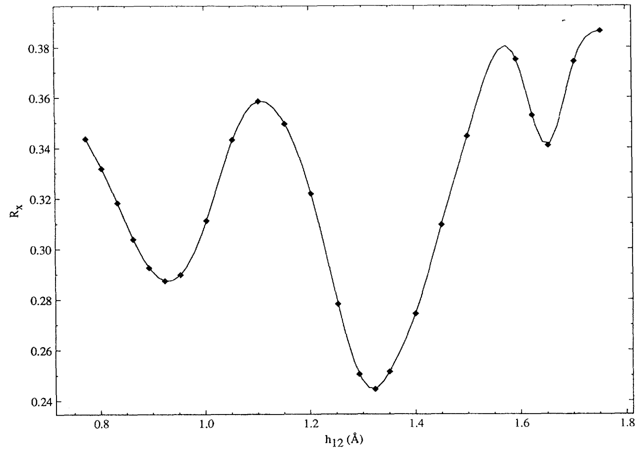

FIG. 4. Variation of R_x with the vertical height of Bi atom for the best-fit structure to demonstrate the occurrence of local minima.

Six phase shifts were used over an energy range of 50–300 eV. The electron attenuation inside the crystal was described by an imaginary part of the inner potential, which was allowed to vary along with the real part of the inner potential in the fitting procedure. The semi-finite substrate was replaced by a slab of six Ge bilayers, five of which were treated exactly. A set of structural parameters was selected to describe atomic displacements in the top two Ge bilayers, including the vertical relaxation and lateral displacements of the first atomic layer. The calculation was run efficiently on the Cray XMP at the National Center for Supercomputing Applications.

Quantitative understanding of Bi/Ge(111) interface formation requires accurate information on the location of the Bi atoms, within the framework of a trial geometric model used to interpret the LEED data. Since the Bi coverage was estimated at around $\frac{1}{3}$ ML and the Bi/Ge(111)-$\sqrt{3}$ surface exhibits C_{3v} symmetry, we considered a simple adatom model, in which the Bi atom adsorbs at the T_4 site with a coverage of $\frac{1}{3}$ ML. The T_4 model together with the directions of substrate relaxation are illustrated in Fig. 2. (a) is a top view which shows that the T_4 site is aligned laterally with the second Ge layer and that the H_3 site is at the first-layer hollow position above the fourth Ge layer; panel (b) is a side view of the T_4 model and arrows show the directions of relaxation. The *I*-*V* curves calculated from the T_4 model give the best fit of experimental values, with the x-ray reliability factor R_x averaged over all eleven beams being 0.244. The comparison between experiment and theory of the eleven *I*-*V* curves of this optimized structure is shown in Fig. 3 for five integral-order and six fractional-order beams. The beam index convention is that commonly used in the literature.[12] In Table II, we list the atomic coordinates of this structure.

During the dynamical LEED calculation, a wide range of values for each individual parameter was scanned to avoid local minima.[15] Figure 4 shows an example of the occurrence of multiple local minima when the *R* factor is plotted versus the vertical height of the Bi layer from the substrate while fixing the other model parameters at their

TABLE III. Surface atom deformation induced by the Bi adatom [cf. Fig. 2(b)].

Bond length	b_{12} (Å)	b_{25} (Å)	b_{24} (Å)	b_{57} (Å)	b_{46} (Å)
Deformation	2.090	2.051	2.857	2.429	2.534
Bulk	2.680[a]	2.450	2.450	2.450	2.450

[a] Sum of covalent radii.

best fit values. The local minima occurred at 0.923 and 1.6529 Å. Each parameter search was carried out through a point by point analysis to avoid misleading conclusions.

From the calculated results, we can see that the three first-layer Ge atoms surrounding the adsorbed Bi atom (atoms 2,3 in Fig. 2 and another one not pictured) are strongly squeezed together, and the second-layer atom (atom 5) beneath the Bi atom is moved downward. This, in turn, causes the third-layer atom (atom 7) beneath the Bi atom to be displaced downward also. Thus the bond length between the atoms at the hollow site (e.g., atom 4) and the first-layer atoms (e.g., atom 2) is increased to 2.860 Å compared with the bulk value of 2.450 Å; the bond angle changes accordingly. As a result, the bond length between atoms 4 and 6 is elongated to 2.543 Å, and that between atoms 5 and 7 is shortened to 2.429 Å, relative to the bulk value of 2.45 Å. Note that the bond length between the Bi and Ge atoms is 2.090 Å, 27% shorter than the sum of the covalent radii of Bi and Ge atoms. Table III shows the bond length deformation compared with the bulk values.

We have performed the calculation for another simple adatom model, in which the Bi atom adsorbs at the H_3 site. In the H_3 model, no lateral displacements of those atoms in the first Ge layer were considered because of the equivalent bonding configuration of every substrate atom in this model. However, agreement between the experimental and calculated spectra was poor in the H_3 model, with the minimum R_x value of 0.42, which is not small enough to reliably predict the true surface geometry.

In summary, we observed the Bi-induced Ge(111)-$(\sqrt{3}\times\sqrt{3})$ LEED structure at a Bi coverage of about $\frac{1}{3}$ ML and substrate temperature around 320 °C; this structure can be produced either by hot-sample deposition or by room-temperature sample deposition followed by annealing. Bi adatoms were determined to adsorb on the T_4 site with a vertical distance of 1.324 Å above the first Ge layer, with large substrate relaxations in both the lateral and perpendicular directions. The two relaxation parameters for the $(\sqrt{3}\times\sqrt{3})$ Bi-covered Ge(111) surface are (1) the separation of atoms 2 and 3 in Fig. 2, 2.801 Å, 30% shorter than the bulk separation of 4.001 Å and (2) the angle between two neighboring Bi—Ge bonds, 86.13°. This deformation is expected when Bi atoms are bonded to the topmost Ge atoms due to the strong surface tensile stress. Meade and Vanderbilt[16] performed a first-principles calculation to illustrate the correspondence of Ge(111) surface relaxation, induced by an adlayer, and the surface stress. They concluded that many factors contribute to the surface relaxation such as the size of the adsorbate and substrate atoms, the chemical bond between atomic species at the surface, etc. The results from our study should present an interesting example for those who study the factors that lead to the surface stress and the energetic properties of interface formation.

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