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Adsorption of Sb on Ge(110) studied by photoemission and scanning tunneling microscopy

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The Ge(110) surface shows two possible reconstructions: the "16 structure" and the $c(8\times10)$. The adsorption of Sb on these surfaces at elevated substrate temperatures shows saturation behaviors. At 200 °C, the Sb saturation occurs at one-monolayer (ML) coverage, and the resulting surface exhibits a (1×1) diffraction pattern. Photoemission studies of the core levels suggest that this (1×1) surface is close to being an ideal Sb-terminated surface. This is consistent with direct observations by scanning tunneling microscopy (STM). At a higher substrate temperature of 400 °C, Sb saturation of the surface results in a (3×2) diffraction pattern. An Sb coverage of $\frac{2}{3}$ ML on this surface is determined from core-level-photoemission and Auger results. STM images for these surfaces are presented and discussed.

I. INTRODUCTION

The interaction and adsorption of group-V elements on the Si and Ge surfaces has been a subject of great interest. The group-V elements have a nominal chemical valence of three and can ideally terminate these surfaces by replacing a dangling bond with a fully occupied lone pair. This can result in a chemically passivated surface with a simple (1×1) or (2×1) geometry, which may be useful as a prototypical system for fundamental studies of surface properties and as a substrate for further growth. The possibility of δ doping and the growth of III-V materials on Si and Ge are also of technological importance. Previous studies of these systems have mainly focused on the (111) and (100) surfaces.[1-10] The present work is an investigation of the adsorption of Sb on the Ge(110) surface. The clean Ge(110) surface shows two possible reconstructions: the "16 structure" and the $c(8\times10)$.[11,12] Both of these have rather complicated structures which are subjects of some controversy. By saturating the surface with Sb, the structure becomes considerably simplified. Depending on the substrate temperature during Sb deposition, either a (1×1) or a (3×2) reconstruction is observed. This work is an investigation of the atomic ordering, chemical composition, and structure of these reconstructions with the use of synchrotron-radiation photoemission, scanning tunneling microscopy (STM), electron diffraction, and Auger spectroscopy.

II. EXPERIMENTAL DETAILS

The STM measurements were performed in a vacuum chamber with a base pressure in the 10^{-11} torr range. A tungsten tip electroplated with a layer of gold was used as the probe. Ge(110) samples were oriented with the Laue technique and polished to a mirror finish on a cloth pad loaded with alumina powder and lubricated with water. The samples were chemically etched just prior to insertion into the vacuum chamber. Cleaning of the Ge surfaces was performed by repeated cycles of 1-keV argon ion bombardment, followed by annealing. Sample heating was achieved by passing a current through the sample itself. The clean "16 structure" and the $c(8\times10)$ reconstruction were obtained by annealing at a temperature within the range of 380–430 °C and at about 750 °C, respectively.[11,12] After the annealing, the sample was allowed to cool down for several hours to near the room temperature before the STM measurements. This was necessary to minimize thermal drift effects. The scan sizes of our STM had been calibrated previously based on measurements of Si(111)-(7×7) and a variety of other surfaces of known structures. Taking thermal drift into account, size measurements with our STM were accurate to within a few percent.

The photoemission measurements were performed at the Synchrotron Radiation Center of the University of Wisconsin, Stoughton, Wisconsin. Synchrotron radiation from the 1-GeV storage ring Aladdin was dispersed by an extended-range monochromator and focused onto the sample. The photoemitted electrons were collected and detected by a large hemispherical analyzer. The overall instrumental resolution was better than 0.2 eV.

The quality of the starting surface was assessed by high-energy electron diffraction which showed a sharp diffraction pattern on a low background. Deposition of Sb on the sample surface was carried out by evaporation from a crucible containing ultrapure Sb, which was heated via electron beam bombardment controlled by a feedback system. The evaporation rate was measured by a water-cooled quartz thickness monitor.

III. RESULTS AND DISCUSSION

A. Electron-diffraction patterns and Sb-coverage determination

Sb deposition was performed first on a sample at room temperature. The intensity of photoemission from the Sb core level and the intensity of the Sb-derived *MNN* Auger transition were monitored as a function of exposure which was derived from the evaporation rate as determined from the quartz thickness monitor and the exposure time. These intensities provided a relative measurement for the Sb coverage on the surface for coverages less than 1 monolayer (ML). Here, 1 ML is defined as 8.84×10^{14} atoms/cm^2, the site density for unreconstructed Ge(110) plane. It was expected that the deposited Sb would condense on the surface at room temperature; namely, the coverage should equal the exposure. The photoemission and Auger intensities were observed to be linearly proportional to the exposure at exposures less than 1 ML (for exposures greater than 1 ML, the intensities show a sublinear dependence on the exposure due to self-attenuation associated with the multilayer configuration). The results from these measurements formed the basis for Sb-coverage determination in later measurements.

When the sample temperature during evaporation was maintained at 200 °C, the coverage was still nearly the same as the exposure for deposition below 1 ML. However, the coverage was observed to saturate at 1 ML as the deposition progressed to higher exposures. This saturation behavior can be attributed to reevaporation of Sb in excess of 1 ML. The bulk solubility of Sb in Ge is extremely low, and bulk Ge-Sb alloy or compound formation is not expected based on the known chemistry of these materials. At this saturation coverage, a (1×1) electron-diffraction pattern was observed. Similar saturation behaviors have been reported before for Sb on Ge(100), Si(111), Si(100), and Si(110).[9,10]

When the sample temperature was maintained at 400 °C during evaporation, a similar saturation behavior was observed except that the saturation coverage was $\frac{2}{3}$ ML at this higher substrate temperature. The resulting saturated surface exhibited a sharp (3×2) electron-diffraction pattern. The same surface could also be produced by first depositing more than $\frac{2}{3}$ ML of Sb on the surface at room temperature, followed by annealing at 400 °C. Figure 1 shows Auger electron spectra taken from the (1×1) and (3×2) Sb-saturated surfaces. The Sb Auger signal from the (3×2) surface is $\frac{2}{3}$ of that from the (1×1) surface.

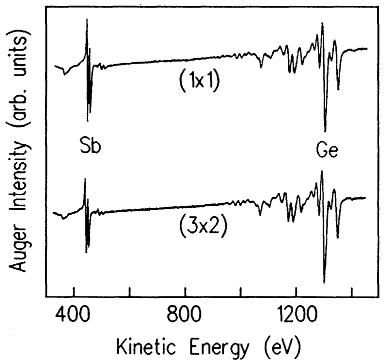

FIG. 1. Auger spectra for the Sb-saturated Ge(110) surfaces. The top spectrum is for the low-temperature (1×1) surface and the bottom spectrum is for the high-temperature (3×2) surface. The Ge- and Sb-derived Auger transitions are indicated.

B. Photoemission from the core levels

The general technique and data analysis related to photoemission studies of core-level line shapes have been discussed quite extensively in the literature.[1,8–10,13] Briefly, surface atoms may show shifts in core-level binding energies relative to the bulk due to the different environments of the surface atoms (such as the possession of a dangling bond). The surface shifts are usually a short-range effect. With ideal Sb termination, we can expect that the surface core-level shifts for the clean Ge(110) surface, if any, will be quenched, because the Ge surface atoms, now below the Sb adlayer, will sense a bulklike environment. Similar studies of As and Sb terminations of various Si and Ge surfaces have been reported before.[1,8–10] The readers are referred to the cited references for details.

Figure 2 shows the Ge 3*d* photoemission line shapes for the Ge(111) "16 structure" and for the same surface after saturation coverage with Sb at 200 °C resulting in the 1-ML-Sb-covered (1×1) surface. These spectra are surface-sensitive because of the photon energy of 90 eV used in the measurement. The appearance of two peaks in each spectrum is due to the spin-orbit splitting. The spectrum for the (1×1) surface is considerably sharper than that for the "16 structure." Figure 3 shows a similar set of spectra for the Ge(110)-$c(8\times10)$ and the same surface after saturation coverage of Sb at 200 °C resulting

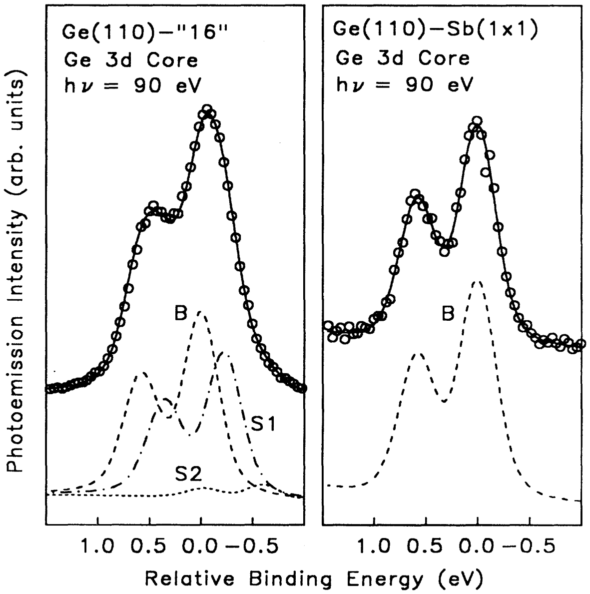

FIG. 2. Ge 3*d* core-level spectra obtained with a photon energy of 90 eV. The spectrum on the left is for the "16 structure" of clean Ge(110), and the spectrum on the right is for the same surface after Sb-saturation coverage to produce the (1×1) surface. The circles are data points, and the solid curves are fits. The long-dashed, dash-dotted, and short-dashed curves below the spectra indicate the decomposition of the line shape into the bulk (*B*) and surface (*S*1 and *S*2) components, respectively. The relative binding energy scale is referred to the Ge $3d_{5/2}$ bulk component.

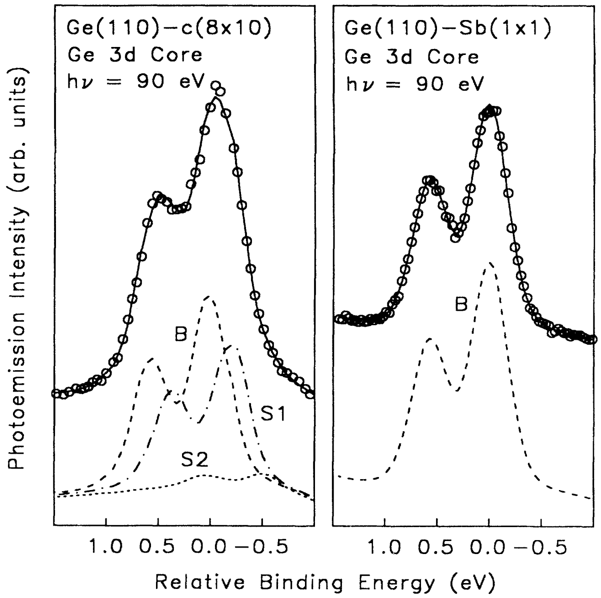

FIG. 3. Same as Fig. 2 except that the starting surface is Ge(110)-$c(8\times10)$.

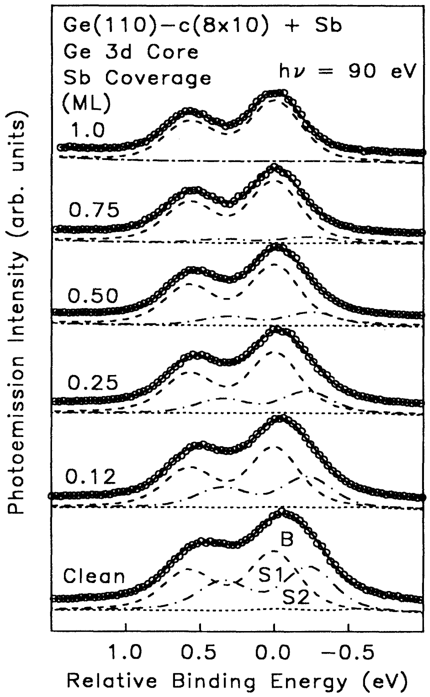

FIG. 4. Ge $3d$ core-level spectra for Ge(110)-$c(8\times10)$ deposited with various amounts of Sb at 200 °C. The photon energy used was 90 eV. The circles are data points, and the solid curves are the fits. The long-dashed, dash-dotted, and short-dashed curves below the spectra indicate the decomposition of the line shape into the bulk (B) and surface ($S1$ and $S2$) components, respectively. The relative binding energy scale is referred to the Ge $3d_{5/2}$ bulk component.

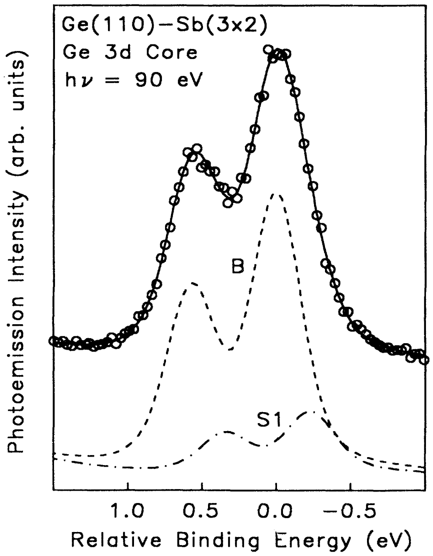

FIG. 5. Ge $3d$ core-level spectrum for the Ge(110)-Sb(3×2) surface taken with a photon energy of 90 eV. The circles are data points, and the solid curve is a fit. The dashed and dash-dotted curves show the bulk (B) and surface ($S1$) contributions, respectively. The relative binding energy scale is referred to the Ge $3d_{5/2}$ bulk component.

in the (1×1) surface. Again, the (1×1) spectrum is considerably sharper than that of the $c(8\times10)$. The two (1×1) spectra in Figs. 2 and 3 have the same line shape within our experimental resolution. The fact that the line shapes for the "16 structure" and the $c(8\times10)$ are wider indicates that these surfaces exhibit surface-induced core-level shifts, although these shifts are small and not resolved in the spectra (no clear additional peaks or shoulders are seen). The sharpness of the Ge core-level spectra for the (1×1) surfaces suggests, as expected, there is very little surface-induced shift. The line shape can be compared with the bulk contribution of the Ge(111) and Ge(100) surfaces previously studied.[14,15]

The line shapes in Figs. 2 and 3 have been analyzed by a nonlinear-least-squares fitting procedure.[13] The (1×1) line shapes are fitted by a single component consisting of two spin-orbit split Voigt functions (convolution of a Lorentzian and a Gaussian). The resulting line-shape parameters, including the spin-orbit splitting, the intensity branching ratio between the two spin-orbit split lines, the Gaussian width, and the Lorentzian width, are used for fitting the line shapes for the "16 structure" and the $c(8\times10)$ reconstruction. In each case, two surface-shifted components ($S1$ and $S2$) were needed in addition to the bulk component (B) for a satisfactory fit. The results of the fit are indicated in Figs. 2 and 3 by the various curves for the different components. Figure 4 illustrates the evolution (sharpening) of the Ge core-level line shape as Sb is gradually built up on the Ge(110)-$c(8\times10)$ surface. Each spectrum is fitted by the same procedure, and the two surface components are seen to diminish for increasing Sb coverages. The top spectrum with a 1-ML coverage corresponds to the (1×1) Sb-saturated surface.

Figure 5 shows the Ge $3d$ line shape for the (3×2) surface with a $\frac{2}{3}$-ML Sb coverage. It is not as sharp as that for the (1×1) surfaces, as revealed by the filling-in in the valley between the two spin-orbit split peaks, indicating the presence of surface-shifted components. The same analysis is applied here; the line-shape parameters obtained from the fit to the (1×1) surfaces are used. The results of the fit are shown in Fig. 5; a surface component $(S1)$ is found in addition to the bulk component (B). By using the standard layer attenuation model for the relative intensities of the surface and bulk components,[13,14] we obtain the coverage corresponding to the $S1$ component to be 0.44 ± 0.11 ML for assumed values of the electron escape depth in the range of 5 ± 1 Å. Due to the uncertainty in the electron escape depth and the approximations inherent to the layer attenuation model, one can only say that the $S1$ component corresponds to a coverage in the range of $\sim\frac{1}{3}-\frac{1}{2}$ ML.

Figure 6 shows the line shapes of the Sb 4*d* core level for various Sb-covered Ge(110) surfaces, including the fully saturated (1×1) and (3×2) surfaces. The line shape is the same for all of the sample configurations. Thus, the Sb adatoms are located in similar sites on the surface. If an alloy has formed over a few layers, we can expect the line shape to be much more complex or broader.

C. STM study of the Sb-saturated (1×1) surfaces

The coverage study and the core-level line-shape analysis presented above suggest that the Sb-saturated (1×1) surface is close to being the ideal Sb-terminated surface. A top view of a model for the ideal structure is presented in Fig. 7(a). Each Sb atom on the surface is bonded to one subsurface Ge atom and two other Sb atoms, satisfying the chemical valence of Sb. Each Sb atom thus possess a filled lone pair. Based on this model, we expect that the STM pictures should reveal the positions of the Sb atoms on the surface. The Ge atoms, being located below the surface, should be invisible. A rectangular (1×1) unit cell connecting four Sb atoms is indicated in Fig. 7(a) on the left; within this unit cell is an Sb atom biased toward one side of the rectangle.

Figure 8 shows a grey-scale STM picture of the (1×1) surface taken over a large area. A unit cell connecting four protrusions is indicated. The unit cell does not appear to be exactly rectangular due to thermal drift effects. In each unit cell, there is one additional protrusion near the center. The position of this additional protrusion is obviously shifted relative to the model shown in Fig. 7, so the resulting pattern resembles a centered rectangular net. This shift in atomic position is not surprising since the Sb atoms on the surface are not necessarily located at the ideal bulk-truncated Ge positions. The covalent radius of Sb is significantly larger than that of Ge, and it is conceivable that the Sb atom within the (1×1) rectangle shown in Fig. 7 may move toward the center of the rectangle for a better fit.

Another interesting feature of the picture in Fig. 8 is

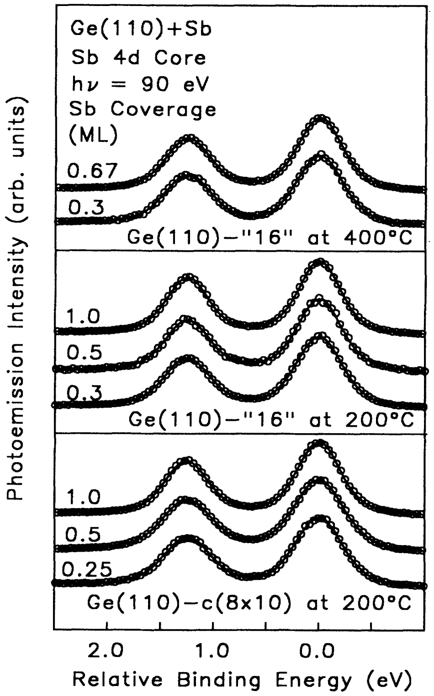

FIG. 6. Sb 4*d* core-level spectra taken with 90-eV photons for Ge(110) deposited with various amounts of Sb at either 200 °C or 400 °C. The Sb coverages, the starting surface reconstruction, and the sample temperature during deposition are indicated. The relative binding energy scale is referred to the Sb $4d_{5/2}$ component.

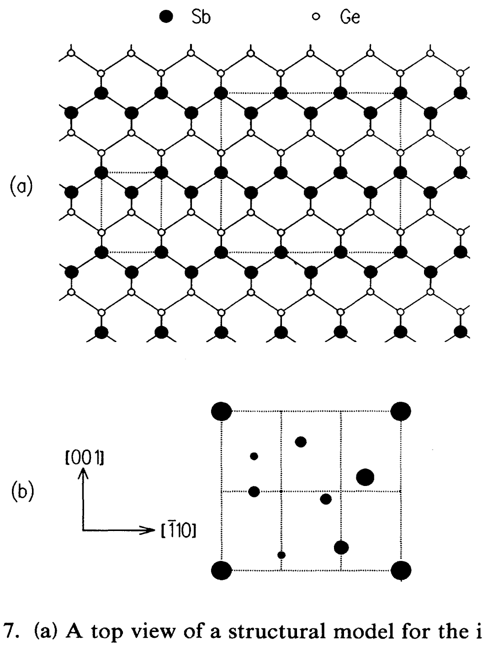

FIG. 7. (a) A top view of a structural model for the ideal Sb-terminated Ge(110) (1×1) surface. The surface layer consists of Sb atoms only. The Ge atoms shown are located in the layer below the surface layer. A (1×1) and a (3×2) unit cell are indicated by the dashed rectangles. The size of the (1×1) unit cell is 4.00×5.66 Å^2. (b) A schematic rendition of the STM image showing the locations of the protrusions in a (3×2) unit cell. The sizes of the circles indicate roughly the relative intensities.

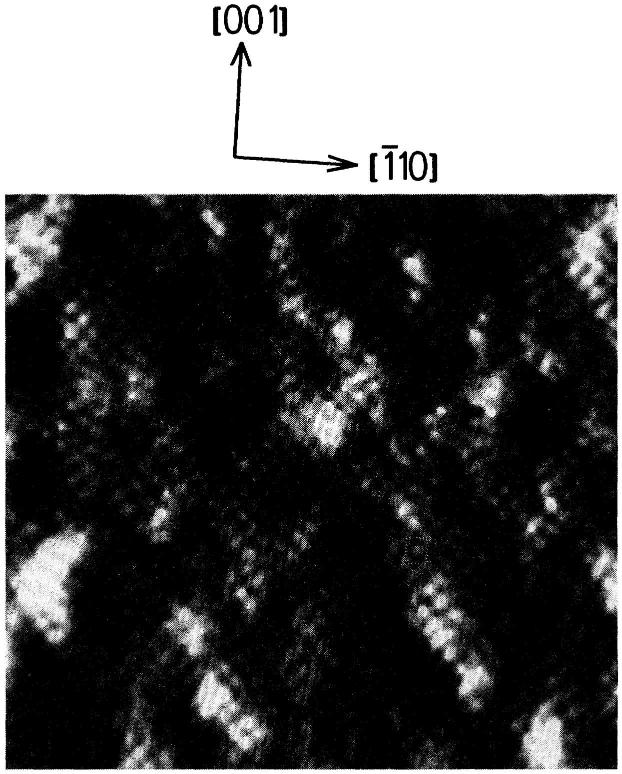

FIG. 8. A grey-scale STM image of Ge(110)-Sb(1×1). A (1×1) unit cell of size 4.00×5.66 Å^2 is indicated. The sample bias voltage and current are 50 mV and 0.4 nA, respectively.

the apparent disorder in the form of ripples and bumps superimposed on the (1×1) pattern. The Sb atoms are well resolved over most of the areas despite the underlying ripples and bumps. Even in the apparently black regions, the Sb atoms are mostly resolved and can be seen if a different grey scale is chosen for presentation. Two possible explanations exist for this kind of disorder. The first is the surface strain associated with the size mismatch between Ge and Sb. The strain can cause topographical distortion and associated electronic redistribution. The second explanation is the nonuniform work function or nonuniform doping of the surface by Sb (Sb will dope the surface to become *n* type, and in our experiment, the starting substrate is *p* type). In a previous study of oxygen adsorption on GaAs(110), a similar kind of disorder was discovered and was attributed to similar effects.[16] The effects of nonuniform strain, doping, and work function might not destroy the local atomic order.

D. STM study of the Sb-saturated (3×2) surface

The measurements of the Auger and photoemission intensities and of the core-level lineshapes indicate that $\frac{2}{3}$ ML of Sb atoms are on the (3×2) surface and $\sim\frac{1}{3}-\frac{1}{2}$ ML of Ge atoms are located in significantly different sites. The Sb coverage is less than that of the (1×1) surface; this is expected since raising the substrate temperature tends to drive off the more volatile Sb. Some Ge atoms are expected to be exposed due to the reduced Sb coverage. To first order, we might expect the structure to be described by the one shown in Fig. 7(a) with $\frac{1}{3}$ ML of Sb in the surface plane now replaced by Ge.

Figure 9 shows a grey-scale STM picture of this surface. A (3×2) unit cell is indicated. The periodic pattern is disrupted by a line fault running across the picture at about $\frac{1}{3}$ height. There is a nonuniform background in the picture which renders the equivalent protrusions to have varying intensities across the picture, and the two crystallographic axes are not exactly mutually perpendicular due to thermal drift and nonideal behaviors of the piezoelectric scanner in our microscope. The picture shows a total of 8 protrusions per (3×2) unit cell. To aid visualization, this is depicted in Fig. 7(b) with circles indicating the positions of the protrusions, and the sizes of the circles indicate roughly the relative intensity. The observed density of 8 protrusions per (3×2) unit cell of 12 sites agrees well with the $\frac{2}{3}$-ML coverage of Sb on this surface, and it is natural to make such association.

Thus, we propose that the protrusions seen in Fig. 9 correspond to the Sb adatoms. The varying intensities of the protrusions in the STM picture and the position offsets relative to the ideal model shown in Fig. 7(a) suggest significant atomic rearrangement relative to the ideal positions. Such rearrangement may be a response of the surface to the size mismatch between Sb and Ge, and/or other effects such as the redistribution of valence charges

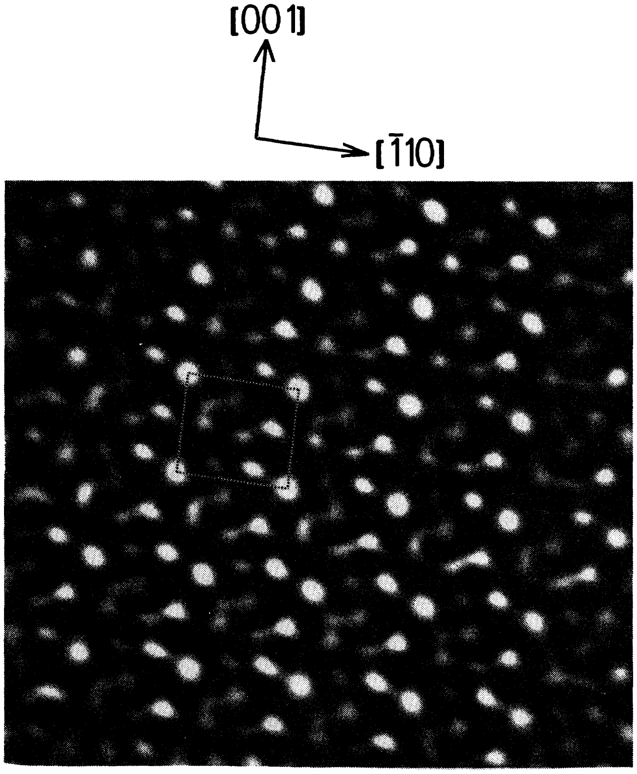

FIG. 9. A grey-scale STM image of Ge(110)-Sb(3×2). A (3×2) unit cell of size 12.0×11.3 Å^2 is indicated. The sample bias voltage and current are −75 mV and 0.5 nA, respectively

associated with the dangling bonds of the Ge atoms exposed on the surface. A detailed understanding of this structure awaits theoretical treatments.

Note that the disorder in the form of underlying bumps and ripples seen in Fig. 8 is not detected for the (3×2) surface. If we assume that surface strain as a result of the size mismatch plays a major role in the reconstruction, we can offer a qualitative explanation for this effect. By reducing the Sb coverage on the surface from 1 ML to $\frac{2}{3}$ ML, it is now possible to accommodate the strain within each unit cell in the form of atomic displacement without any leftover strain to cause long-range disorder.

IV. SUMMARY

STM, photoemission, Auger, and electron-diffraction measurements have been preformed for an investigation of the Sb-saturated Ge(110) surfaces. The Sb saturation results in considerable simplification of the surface structure, from the "16 structure" or the $c(8\times10)$ reconstruction to either a (1×1) or (3×2) reconstruction, depending on the substrate temperature during Sb deposition. At 200 °C, the (1×1) reconstruction is obtained, which exhibits properties characteristic of a 1-ML-Sb-terminated surface. The atomic positions are displaced from the ideal positions of a bulk-truncated Ge surface, and long-range partial disorder is observed. At a higher substrate temperature of 400 °C, the (3×2) structure is obtained with a reduced amount of Sb ($\frac{2}{3}$ ML) on the surface. STM appears to reveal the positions of Sb adatoms, which are significantly displaced from the bulk-truncated positions, but the partial disorder seen on the (1×1) surface is absent. The size mismatch between Sb and Ge and the resulting strain may be an important factor in determining the structure.

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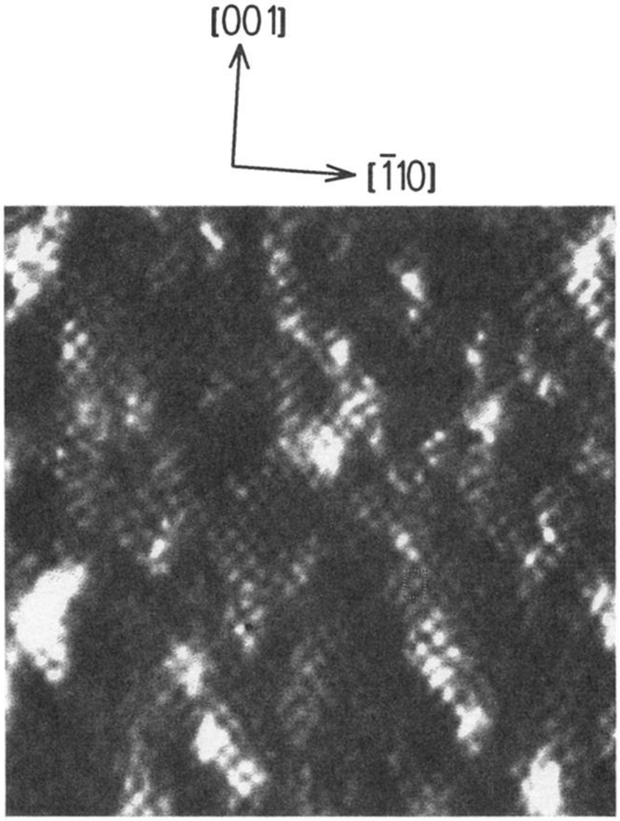

FIG. 8. A grey-scale STM image of Ge(110)-Sb(1×1). A (1×1) unit cell of size 4.00×5.66 Å^2 is indicated. The sample bias voltage and current are 50 mV and 0.4 nA, respectively.

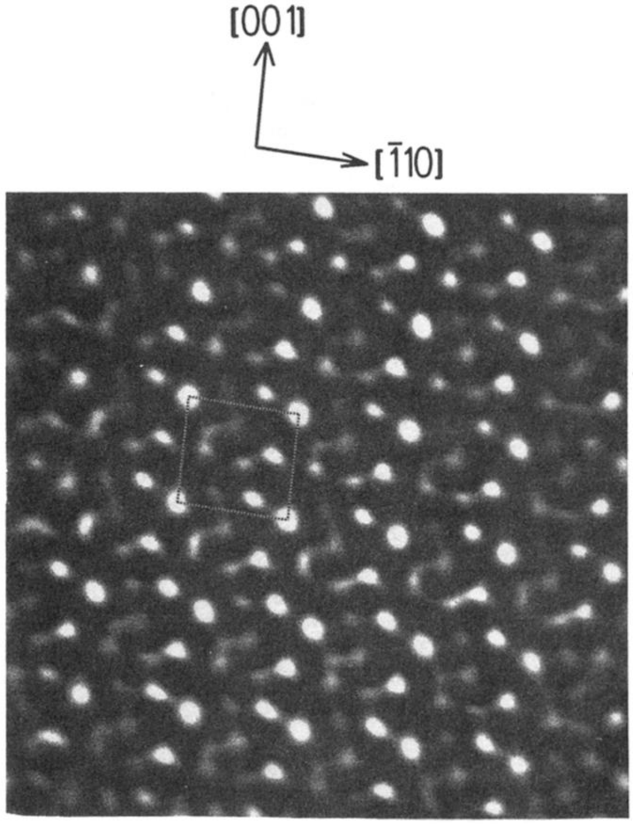

FIG. 9. A grey-scale STM image of Ge(110)-Sb(3×2). A (3×2) unit cell of size 12.0×11.3 Å^2 is indicated. The sample bias voltage and current are −75 mV and 0.5 nA, respectively