RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 14 15 NOVEMBER 1989-I

Scanning tunneling microscopy and first-principles theory of the Sn/GaAs(110) surface

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(Received 14 August 1989)

Scanning tunneling microscopy of Sn overlayers on the GaAs(110) surface shows patterns with local order of nominal (3×3) periodicity and an absence of long-range order. Using first-principles calculations, we show that these observations can be explained in terms of a double-layer structure which consists of a complete (1×1) Sn layer covered by Sn adatoms. This structure results from a subtle balance between electronic energy and lattice strain. Spectroscopic studies indicate that this Sn overlayer exhibits a narrow gap (<0.2 eV) centered in the gap region of the GaAs substrate.

The structural and electronic properties of adsorbates on semiconductor surfaces are of great interest not only from the fundamental surface physics point of view but also for practical applications in heterostructure devices such as Schottky barriers and heterojunctions. In particular, overlayers of metals or semiconductors on the GaAs(110) surface are among the most extensively studied systems. Column V atoms deposited on GaAs(110) (e.g., Sb and Bi) (Refs. 1 and 2) form ordered (1×1) overlayers. In this case electronic energy is minimized due to saturation of surface dangling bonds and lattice strain is either relieved by relaxation (Sb/GaAs) (Ref. 1) or gives rise to a sparse dislocation network (Bi/GaAs).[2] In the case of Ge, which is a column IV atom, lattice strain appears to drive the formation of a (1×1) ordered overlayer on the GaAs(110) surface,[3] at the expense of high electronic energy which arises from unsaturated dangling bonds. The balance between electronic energy and lattice strain determines the structure of the overlayer. In the examples mentioned above one of these two factors dominates, resulting in simple (1×1) overlayer patterns.

In this work we present a study of Sn overlayers on GaAs(110), a system in which electronic energy and lattice strain both play important roles and their balance gives rise to a novel surface reconstruction. The observed structure has a nominal (3×3) local periodicity but no long-range two-dimensional order. The local order had not been previously revealed by low-energy electron diffraction (LEED) but is clearly observed in scanning tunneling microscopy (STM) images. To account for the STM observations we propose a structural model with two layers of Sn on the GaAs surface, forming a complete (1×1) Sn overlayer in contact with the GaAs surface and a Sn adatom layer on top. The atomic positions in the proposed reconstruction model were obtained through first-principles calculations and are in good agreement with experiment.

The experimental setup for STM has been described previously.[4] The system is also equipped with LEED and Auger spectroscopy for characterization of the sample. The GaAs samples are either *p* type (Zn doping of 1×10^{18} cm^{-3}) or *n* type (Si doping of 1×10^{18} cm^{-3}). The samples were cleaved in an ultrahigh-vacuum chamber with base pressure of $<4\times10^{-11}$ Torr. With the sample at room temperature, Sn was deposited from a filament evaporator with a deposition rate of 0.1 monolayers (ML)/min (1 ML = 8.85×10^{14} atoms/cm^2). STM images were acquired at a constant current of 100 pA.

In Figs. 1(a) and 1(b) we show perspective and top views, respectively, of a typical STM image of a cleaved GaAs(110) surface covered with 1 ML of Sn, taken at sample bias of −1.5 V. Areas corresponding to a Sn terrace and to the GaAs substrate can be clearly distinguished, with the Sn terrace at an apparent height of

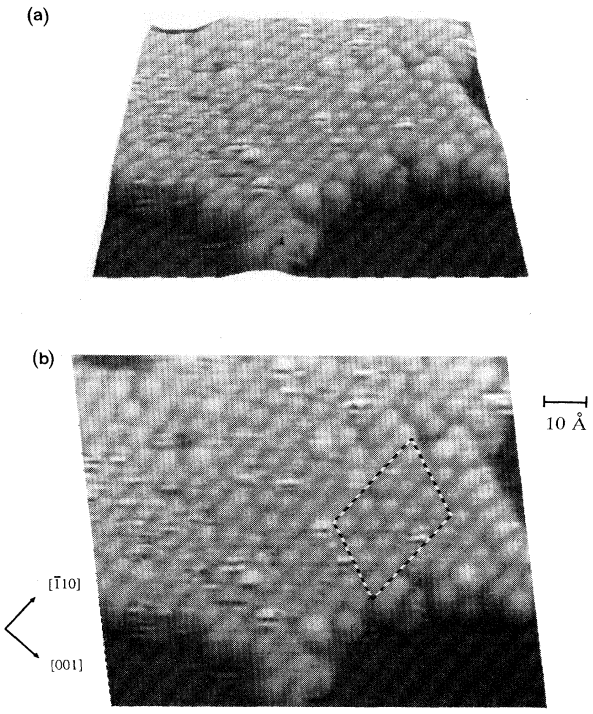

FIG. 1. (a) Perspective view and (b) top view of an STM image of a cleaved *p*-type GaAs(110) surface covered with 1 ML of Sn. The image is taken at sample bias of −1.5 V. A locally ordered region of the Sn overlayer is highlighted. The surface height is shown with a grey scale, ranging from 0 Å (black) to 9 Å (white).

about 5.4 Å with respect to the substrate. This apparent terrace height depends somewhat on the sample bias, it is always between 4.8 and 5.5 Å for sample bias ranging from −3 to +3 V. This range of height is considerably larger (by roughly a factor of 2) from the 2.5-Å terrace height of the (1×1) monolayer Sb/GaAs(110) system.[1] This comparison indicates that the Sn terrace is most likely a double-layer structure. Furthermore, at lower coverages (0.2 to 0.5 ML), the deposited Sn atoms form terraces of smaller area but with the same terrace height of about 5 Å, indicating that the double layer is indeed the energetically favorable structure. The bright spots in the image of Fig. 1 correspond to surface Sn atoms on the Sn terrace and As atoms on the uncovered GaAs region.[5] As the image shows, the surface Sn atoms on the top layer form rows along the $[\bar{1}10]$ direction. In the locally ordered regions, one of which is highlighted in Fig. 1(b), the top-layer Sn atoms are separated by 6 Å in the $[\bar{1}10]$ direction, corresponding to 1.5 times the periodicity of the (1×1) unit cell. Most ordered regions are about 20 Å on the side and contain from 6 to 10 top-layer Sn atoms. Between these locally ordered regions there exist disordered regions which are easily identified as irregularities in the STM images.

The apparent height of the overlayer terrace and the locally ordered arrangement of the top-layer Sn atoms can be explained by the following structural model: The ordered region is composed of a (1×1) Sn overlayer covered with Sn adatoms. The detailed structure of the model is shown in Fig. 2. The Sn atoms in the first (1×1) layer occupy sites close to an extension of the underlying zinc-blende lattice (the deviation from exact lattice sites is due to relaxation). We denote the Sn atoms of this layer, bonded to surface Ga and As atoms, as $Sn_{(Ga)}$ and $Sn_{(As)}$, respectively. Such a (1×1) layer will leave one unsatisfied dangling bond for each Sn atom [similar to the (1×1) Ge/GaAs(110) system]. On top of this layer Sn adatoms are placed, with each adatom bonded to three first-layer Sn atoms. There are two types of Sn adatoms denoted as $Sn_{(1)}$ and $Sn_{(2)}$, where $Sn_{(1)}$ is bonded to two $Sn_{(Ga)}$ and one $Sn_{(As)}$ and $Sn_{(2)}$ is bonded to two $Sn_{(As)}$ and one $Sn_{(Ga)}$. $Sn_{(1)}$ and $Sn_{(2)}$ alternate along the $[\bar{1}10]$ direction and are separated by 6 Å corresponding to 1.5 times the periodicity of the (1×1) cell along this direction. Thus, the translational vector between two $Sn_{(1)}$ adatoms along the $[\bar{1}10]$ direction is three times that of the (1×1) cell.

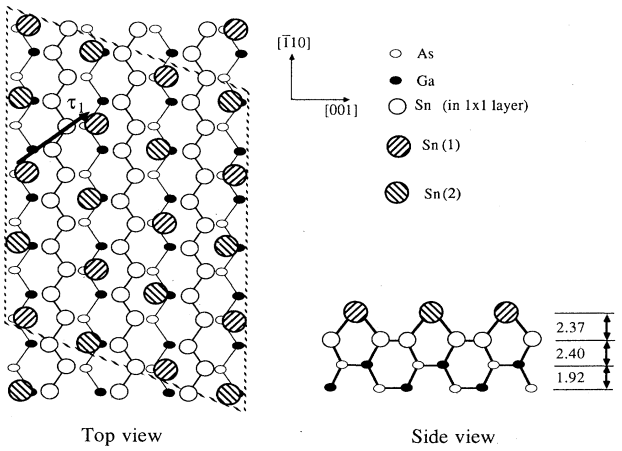

FIG. 2. Top view and side view of the proposed double-layer structure which is composed of a 1×1 Sn layer with a Sn adatom layer on top in a nominal (3×3) periodicity. The height (in Å) of the different Sn layers with respect to the GaAs substrate is indicated in the side view.

The addition of the adatom layer, with each Sn adatom bonded to three Sn atoms of the (1×1) layer, reduces the number of the unsatisfied dangling bonds by a factor of 3. This reduction of dangling bonds lowers the electronic energy of the system. The covalent bonding of the Sn adatoms to the Sn atoms of the (1×1) layer is made possible by the much larger covalent radius of Sn relative to that of GaAs (14% larger). Once a Sn adatom row is formed along the $[\bar{1}10]$ direction, there are two energetically and structurally equivalent ways of forming the next row: One corresponds to a translational vector of $\tau_1 = \frac{1}{2}[\bar{1}12]$, and the other corresponds to $\tau_2 = \frac{1}{2}[1\bar{1}2]$. Both τ_1- and τ_2-type stackings have translational periodicity along the [001] direction equal to three times that of the (1×1) cell. Thus, an ordered Sn overlayer is in registry with a (3×3) supercell on the GaAs surface, but its actual periodicity is (3×1) in a skewed unit cell. This peculiar arrangement will be called nominal (3×3) periodicity. A third stacking with periodicity $\tau_3 = [001]$ is also possible as far as saturation of dangling bonds by adatoms is concerned. However, our calculations show that the τ_3 stacking arrangement has higher energy [0.6 eV per (3×3) unit cell] than the τ_1 and τ_2 stackings. Consistent with the theoretical prediction, no locally ordered regions with the τ_3 stacking arrangement were observed in our STM images.

Figure 2 shows an example of a domain with τ_1 translational periodicity, which exhibits good agreement with the locally ordered region highlighted in Fig. 1(b). The exact atomic positions for this ordered bilayer were determined by performing total-energy calculations with the pseudopotential local-density-functional formalism[6] and a plane-wave basis. The atomic geometry is optimized by minimization of Hellmann-Feynman forces. The total terrace height above the GaAs substrate, as determined by the calculation is 4.77 Å (see Fig. 2, side view). For the range of bias voltage used (−3 to +3 V), the experimentally measured terrace height varies from 4.8 to 5.5 Å above the GaAs level. In comparing the experimental and theoretical terrace heights, one must recall that the experimental result reflects the electronic charge distribution on the surface, which certainly extends beyond the atomic core positions. With this in mind, we conclude that the experimentally measured height is in good agreement with the calculated atomic core position of 4.77 Å above the substrate. The Sn−Sn bond lengths are in the range 2.75–3.00 Å, close to the natural Sn−Sn covalent bond length of 2.81 Å in α-Sn. This is consistent with our argument that the bonding of the Sn adatom to the Sn atoms of the (1×1) layer is only made possible by the much larger covalent radius of Sn. This line of argument indicates that a similar geometry, with surface dangling bonds saturated by adatoms, is not possible in the Ge/GaAs(110) system, since the smaller covalent radius of

Ge would not allow proper bonding of the adatoms. We thus conclude that the driving mechanism for the formation of this novel structure is the subtle balance between electronic energy and lattice strain.

We next discuss the absence of long-range order observed in the STM image. Since the *local* bonding arrangement is identical in τ_1 and τ_2 periodicities, and a τ_1 ordered domain is actually a mirror image of a τ_2 ordered domain, it is energetically allowed to pack the rows of adatoms with randomly alternating τ_1 or τ_2 periodicity. This randomness along the [001] direction will destroy long-range order. Moreover, at room temperature different islands grow incoherently which also results in defects at the boundaries. The probability for growth of an extended ordered area is small since this would require both continuous stacking sequence within islands and coherent growth of different islands.

Spectroscopic studies on this surface reveal some interesting results. Figure 3 shows typical spectra taken on a locally ordered terrace and on the *n*-type GaAs substrate about 20 Å away from the terrace edge. Spectroscopic data are taken by interrupting the feedback loop used for the topographic image, with the tip to sample separation (s) decreased as the sample bias is reduced in order to establish a large dynamic range. The data are then normalized to constant s and plotted in a logarithmic scale, giving a measurement independent of the s contour

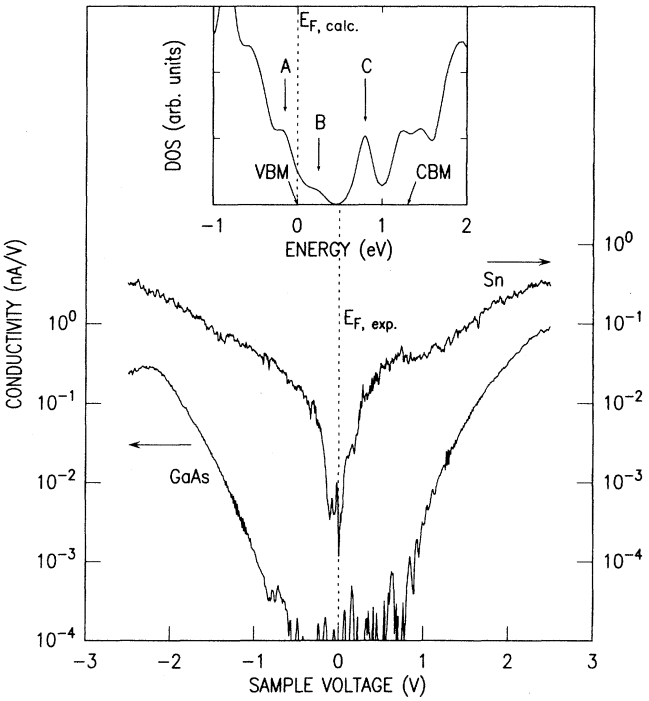

FIG. 3. Conductivity at a constant tip-sample separation vs voltage measured on a Sn-covered locally ordered region and on a neighboring region of clean *n*-type GaAs substrate. The inset shows the calculated density of states for the ordered layer. The calculated positions of the VBM and CBM of bulk GaAs, as well as the position of the Fermi level (E_F) are indicated. Features *A*, *B*, and *C* correspond to adatom states (see text).

(for details on this method see Ref. 7). The onset of the conductivity for the GaAs surface occurs at sample bias of -0.65 ± 0.15 V for the occupied states and 0.80 ± 0.15 V for the unoccupied states. These values correspond to the band edges [valence-band maximum (VBM) and conduction-band maximum (CMB)] of GaAs, the positions of which agree very well with the reported Fermi-level pinning position in photoemission experiments.[8] The band edges of the Sn terrace are found at -0.2 ± 0.1 V and 0.0 ± 0.1 V for occupied and unoccupied states, respectively. Thus the Sn layers exhibit a narrow gap of about 0.2 eV. A second feature which appears consistently in the data is a peak at about 0.5 ± 0.2 V above the top of the Sn band gap.

In the proposed structural model, the adatom dangling bonds are expected to form a half-filled metallic band. Indeed, the calculated density of states (DOS) for the ordered layers (given as inset in Fig. 3) shows no gap at the Fermi level (indicated by a dashed line in Fig. 3, inset). The character of the states near the Fermi level was investigated by charge-contour plots. This revealed that the states immediately below the Fermi level have most of the charge in the $Sn_{(2)}$ dangling bond (marked as *A* in Fig. 3, inset), whereas the states immediately above the Fermi level have most of the charge in the $Sn_{(1)}$ dangling bond (marked as *B*). However, a small gap of about 0.2 eV exists at 0.5 eV above the Fermi level, as well as a peak at 0.3 eV above the top of the gap (marked as *C*). The latter, again from charge-contour plots, was identified as antibonding states on the Sn adatoms (both $Sn_{(1)}$ and $Sn_{(2)}$).

The discrepancy between theory and experiment concerning the position of the Fermi level may be attributed to two different factors. It is possible that electron correlations result in single occupation of each adatom dangling-bond state, due to on-site Coulomb repulsion (Hubbard U). A similar mechanism has been proposed to explain the STM results of Al/Si(111).[9] This would shift the Fermi level to the region where a gap appears in the theoretical DOS (see Fig. 3, inset). Our calculations, based on local-density-functional theory, underestimate the magnitude of self-energy corrections and correlations, and would not capture the effect described above. A second possibility is that the presence of disorder in the system may open a gap near the Fermi level by breaking the translational periodicity and localizing surface states. The presence of disorder is consistent with our STM images: The largest ordered regions we have found consist of approximately 10 adatoms and have defects in their immediate neighborhood. Finally, the possibility of a different structural model with a gap at the Fermi level is an open question.

In conclusion, we have found that Sn atoms on the GaAs(110) surface form a locally ordered double-layer structure which is composed of a (1×1) Sn layer covered by Sn adatoms, with nominal (3×3) periodicity. The driving mechanism of this novel structure is a subtle balance between electronic energy and lattice strain. The observed absence of long-range order in the overlayer is explained by the existence of two different translational periodicities with identical *local* bonding arrangement.

Structural features of the STM images are in good agreement with the calculated relaxed atomic configuration. The theoretical position of the Fermi level in the proposed structural model falls in a partially occupied band, which apparently disagrees with the experimentally observed small gap. The theoretical results may be rendered consistent with experimental measurements by postulating single occupancy for the adatom dangling-bond states due to electron correlation arising from on-site Coulomb repulsion. Alternatively, the observed gap may be the result of Fermi-level pinning due to local disorder which is always present in our STM images. The need for a different model cannot be excluded, although it seems improbable given the good agreement between theory and experiment for the structural features of the proposed model.

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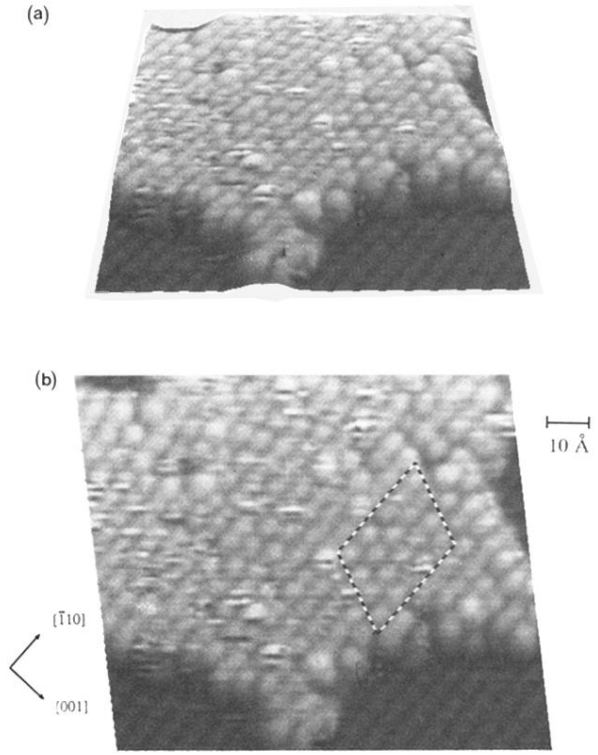

FIG. 1. (a) Perspective view and (b) top view of an STM image of a cleaved p-type GaAs(110) surface covered with 1 ML of Sn. The image is taken at sample bias of -1.5 V. A locally ordered region of the Sn overlayer is highlighted. The surface height is shown with a grey scale, ranging from 0 Å (black) to 9 Å (white).