## Surface polymerization of epitaxial Sb wires on Si(001)

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Measurements of the local density of states of epitaxial antimony structures on Si(001) are reported and related to surface polymerization. Scanning tunneling spectroscopy was used to investigate the electronic structure of Sb<sub>4</sub> clusters, Sb<sub>2</sub> dimers, and short epitaxial Sb lines. We find these nanostructures of the semimetal Sb on Si to be nonmetallic. The electronic structure in the center of the Sb line is similar to that of the Si surface. In contrast, the ends of the Sb lines show a finite density of states at the Fermi level. These observations are consistent with theoretical predictions for surface polymerization in similar systems.

Atoms of metallic elements often show one-dimensional (1D) self-assembly on a reconstructed semiconductor surface like silicon (001). Recently, Brocks, Kelly, and Car<sup>1</sup> have predicted that the self-assembly of aluminum on Si(001) is a surface polymerization reaction. They theoretically investigated the growth of Al on Si(001) using an *ab initio* technique. The polymerization reaction is analog to an organic polymer where a monomer bonds to the radical end of a chain and becomes the new reactive site to continue the reaction. In the case of Al the building block, "monomer," is a single Al atom and the reactive site involves dangling bonds of the substrate. Reference 1 predicts that the radical should be observable as a low-energy feature in the local density of states (LDOS) at the end of the Al line. In this report we show the key effect of such a surface polymerization, namely the enhanced charge density at the extremities of the structure, using the example of self-assembled antimony lines on Si(001).

Deposition in UHV combined with inspection by a scanning tunneling microscope (STM) can be used to create and study nanostructures of (e.g., metallic) elements on a substrate involving various sizes and geometries down to the atomic scale. Since the separation of the atoms in a nanostructure is partly controlled by the atom-substrate interaction and partly by the atom-atom interactions there will be deviations from bulk behavior. In addition, the reduced dimensionality of the nanostructure will also alter the electronic properties. It is *a priori* unclear whether the structure will behave like a metal, semiconductor, or an insulator. Tunneling spectroscopy with the STM is the appropriate technique to investigate the LDOS (basis of the conduction properties) of such a nanostructure.

Two atom wide lines of antimony on the Si(001) surface have been investigated. They represent a well-defined 1D model system. A detailed study of such a model system will enhance the understanding of confined electronic states at the molecular scale<sup>2</sup> and surface phenomena such as epitaxial growth. In this report, we place particular focus on the electronic structure of these epitaxial Sb lines and present evidence for a radical state (finite density of states at the Fermi level,  $E_F$ ) at the ends of the Sb lines. The self-assembly of Sb on Si, where the building block is a Sb<sub>2</sub> dimer, is discussed in the context of surface polymerization. A Sb<sub>2</sub> dimer bonds to the reactive end of the Sb line and the reactive site moves to the new end of the line. The observation of the radical state has a strong bearing on recent theoretical work on surface growth by self-assembly e.g., Ref. 3.

For our experiments we used *p*-type Si(001) wafers (0.2  $\Omega$  cm) cut from standard stock which were cleaned in isopropanol before loading into UHV. The base pressure of the system in which the samples are prepared and scanned was below  $5 \times 10^{-11}$  mbar. After loading, the sample was degassed up to 1000 K while keeping the pressure below  $5 \times 10^{-10}$  mbar for several hours. After this the substrate was briefly flashed up to 1500 K and after a few minutes at 1100 K was cooled to room temperature at a rate of 1 K/s or slower to produce a  $2 \times 1$  reconstructed surface.

The Sb was deposited at a rate of less than 0.01 monolayers (ML) per second from an electron gun evaporator onto the room-temperature substrate. The rate was established by monitoring the ion current of the Sb flux which was calibrated by STM observation of a submonolayer coverage of Sb<sub>2</sub> dimers. The sample was heated by passing a direct current through the silicon. Temperatures were measured with a pyrometer and extrapolated below 650 K based on the heating current.

For the STM we used electrochemically etched tungsten tips which were degassed by electron bombardment after loading into UHV. The tips were further cleaned and sharpened by self-sputtering in neon as discussed in Ref. 4. All the voltages referred to are referenced to the sample.

When Sb is directly evaporated from the bulk at a low rate it is mainly deposited as nonepitaxial Sb<sub>4</sub> clusters onto the room-temperature Si(001) surface.<sup>5</sup> Already at room temperature Sb<sub>4</sub> clusters convert spontaneously into different precursor states of the final equilibrium condition of two free Sb<sub>2</sub> dimers. Full conversion of Sb<sub>4</sub> to Sb<sub>2</sub> can be achieved by annealing the sample at 430 K for a few minutes.<sup>6</sup> In contrast to this work most earlier investigations of Sb on Si(001) have been done starting from saturation coverage of one ML evaporated at elevated temperature.<sup>7,8</sup> The low coverages studied by us, show comparatively long Sb dimer rows and

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FIG. 1. STM image of Sb  $1 \times 2$  growth on the  $2 \times 1$  Si(001) surface at 575 K (0.1 nA, bias referred to substrate) Sb lines extend from two to about 12 dimers (5 nm). Note the splitting of the Sb dimer row into a "double" line similar to the Si  $\pi^*$  orbital in the empty state image. Most of the Sb dimer rows terminate between the  $\pi$  chains of the Si. In the schematic the Sb line is shown with the two possible termination types: on a former Si dimer row (left) and between dimer rows (right, occurs much more frequently).

no three-dimensional growth up to the desorption temperature of the Sb.

When the surface is annealed at 575 K the Sb orders into short lines (up to 5 nm) orthogonal to the Si dimer rows as shown in Fig. 1. We observe  $1 \times 2$  epitaxial growth of Sb on the  $2 \times 1$  reconstructed Si which is consistent with the study by Richter *et al.*<sup>7</sup> of 820 K annealed Sb layers (0.6 ML and more), leading to three-dimensional growth. The schematic in Fig. 1 shows the structure of the Sb<sub>2</sub> adsorption and the  $1 \times 2$  growth of the Sb dimer rows. We have varied the Sb<sub>2</sub> coverage from <1% to 70% and the annealing temperature from 525 to 600 K as well as the annealing time and always find the same maximum length of Sb lines.

It is essential to demonstrate that we indeed observe Sb structures on Si and not Si on Si. Starting from a low coverage of Sb Garni et al.<sup>9</sup> also observed the formation of dimer rows on the surface. However, in contrast to our work and earlier studies they argue that these consist of Si which was replaced by Sb in the terrace structure at temperatures above 460 K leading to Si<sub>2</sub> ad-dimers. The key observations of Ref. 9 are the chemical contrast observed at low negative sample bias and a high defect density on the Sb:Si(001) surface. We performed these experiments in the temperature and coverage range stated in the previous paragraph and observe no increase in the number of defects after annealing. Furthermore, we observe no chemical contrast: no dark disordered regions appear when scanning at low bias as shown in Fig. 2. Additionally, the observed epitaxial lines are limited to a maximum length of <5 nm which is inconsistent with Si on Si(001). Much longer epitaxial lines are observed for Si on Si.<sup>10</sup> We conclude that we observe Sb<sub>2</sub> dimers and dimer rows on Si which is consistent with earlier studies.<sup>6–8,11,12</sup>

Further annealing of the sample at 700 K leads to the conversion of the Sb dimer rows to islands. The amount of Sb on the surface does not change during the conversion of Sb<sub>2</sub> dimers to the islands. This was confirmed by annealing a sample with a certain Sb coverage from free Sb dimers to Sb dimer rows and then to the Sb islands while analyzing the Sb surface coverage in the STM images. The maximum length of Sb rows in these islands is about 8 nm which is considerably longer than the Sb lines with a maximum of 5 nm. A clean  $2 \times 1$  Si surface reestablishes after an anneal at 775 K



FIG. 2. STM image of 0.23 ML of Sb on Si(001) at  $-1.2V_{subs}$  and 0.1 nA annealed at 600 K. The inset shows the upper left region at -1 V. No dark disorder patches are observable as well as no chemical contrast. This is consistent with Sb on Si; however, different from what Garni *et al.* reported in their Figs. 4(c) and 4(d) under similar conditions.

for 5 min. We speculate that the Sb has desorbed from the surface and is not incorporated into the substrate which is consistent with work done by Wasserfall and Ranke.<sup>13</sup>

We have performed local density of states measurements of the Sb clusters, lines, and islands by means of scanning tunneling spectroscopy. The feedback loop is opened after stabilizing the tunneling gap ("freezing" the tip position) and we record the current as a function of voltage, I(V). This is done in a grid of points on the surface and several of these curves were averaged at distinct features (e.g., Sb<sub>2</sub> dimer).

Figure 3 shows the spatially resolved density of states of an epitaxial Sb line on Si. This spectroscopy data were taken after an anneal at 575 K. These topography of the 3D image reflects the constant current scan with several free Sb<sub>2</sub> dimers and a Sb dimer row. The brightness indicates the density of states at the Fermi level. The area with a finite density of states is always restricted to the end of Sb lines. The dI/dV spectra of free Sb<sub>2</sub> dimers show a gap similar to Si. The I(V) inset shows the region around the Fermi energy where the ends of the Sb dimer row show a finite slope in contrast to the Sb line center and the Si.

The normalized numerical derivative of the spectroscopy data in Fig. 3 is presented in Fig. 4 over the full acquired energy range. It shows three distinct classes of curves: first, the Sb<sub>2</sub> dimer with a low state density near  $E_F$  and a peak in the LDOS at a valence energy deeper than the Si; second, the enhanced LDOS near  $E_F$  (0.5 eV) and finite LDOS at  $E_F$  for the Sb-line end; and third, the center of the Sb line with almost identical LDOS as the bare Si(001) 2×1. Not shown in the figure is spectroscopy averaged over a Sb<sub>4</sub> cluster. Spectroscopy curves of Sb<sub>4</sub> clusters display very little structure and are lower in amplitude compared to the Si and the other Sb structures. This may be attributed to weak bonding/ coupling to the substrate of this nonepitaxial cluster. The results demonstrate a significant change of the observed LDOS when the Sb<sub>2</sub> is incorporated in a Sb dimer row.

The Si(001)  $2 \times 1$  surface shows the bonding  $\pi$  and antibonding  $\pi^*$  state as shown clearly in Fig. 4. The observations confirm the identical behavior of the center of the Sb line and the Si in contrast to the end state which peaks closer



FIG. 3. (Color) Epitaxial Sb line on Si 2  $\times$  1. The apparent height reflects the topography at  $+2V_{sample}$  and the color the magnitude of dI/dV at 0 V as shown in the I(V) inset (from blue over red to white for 0 to 2pA/V). Only the ends of the Sb line show a finite density of states at the Fermi level marking the reactive sites of the surface polymerization in contrast to the free Sb<sub>2</sub> dimers (the two dimers on the upper left are separated by a  $\pi^*$  chain and not bonded like a Sb line). The vertical scale is exaggerated, the Sb<sub>2</sub> dimers and Sb line appear as 0.1 nm features in the scan.

to the Fermi level. It is interesting to note that the Sb lines show a more pronounced  $\pi^*$ -like feature than the Si which is consistent with the clear antibonding like character of the Sb line as shown in the empty state image of Fig. 1. This is surprising since one could expect an occupied  $\pi^*$  orbital when the lone pairs of the Sb atoms hybridize. Thus, the state we observe is most likely not just a  $\pi^*$  state but a different antibonding orbital of the complicated Sb on the Si system. The ends of the Sb line show a finite density of states at  $E_F$  but we still observe a peak in the LDOS at -0.5 eV. We speculate that this may be due to the interaction between the two dangling bonds of the reactive site.

A central result of the spectroscopy work is the observation of a finite density of states at the Fermi level for the ends of the Sb dimer rows. A finite density at the Fermi level is the signature of a reactive site like a dangling bond. A dangling bond is half filled and so is expected to result in a finite slope of the I(V) curve at zero bias (finite LDOS). To our knowledge this is the first direct observation of the reactive end of a structure leading to surface polymerization as predicted by Brocks *et al.* Ganz *et al.* studied the 1D growth of Si on Si(001) and speculated that "sticky ends" may be responsible for the unexpected growth direction and studied



FIG. 4. The normalized spectrum (dI/dV)/(I/V) showing similar behavior of the center of the Sb line and the clean Si surface. The Sb line end displays a finite LDOS at  $E_F$  and peaks between  $E_F$  and the Si  $\pi$  state.

the growth kinetics. We think that the findings for Si on Si(001) must be attributed to a similar origin as for Sb on Si(001). The 1D growth of Sb on Si(001) is based on the higher probability of an ad-dimer to stick to the end of the Sb line versus the side of the line. The observation of a finite density of states at the Fermi level uniquely links the growth mode to the microscopic electronic properties of the structure.

The reactive end is the nucleation site for the next building block of the polymer chain as shown in the schematic of Fig. 1 at, e.g., the left end of the Sb line. A Sb<sub>2</sub> dimer can bond to the two dangling bonds and extend the chain by breaking the  $\pi$  bond of the next Si<sub>2</sub> dimer. The next step is identical to an addition on the right end of the Sb line in Fig. 1 where the strained  $\sigma$  bond needs to be broken to add a dimer to the Sb line. The process then repeats until the added strain (discussed below) in the Sb line is larger than the gain in energy due to the bonding.

The existence of the end state does not depend on the total length of the Sb line as we have observed in Sb lines ranging from two to a maximum length of about 12 Sb<sub>2</sub> dimers. We find the crossover from single dimer behavior abruptly at the shortest possible "Sb line" with two dimers where one is located between the  $\pi$  chains of the Si. A two dimer Sb line already shows the end-state behavior which is consistent with the reactive sites shown for the four dimer Sb line in Fig. 1.

The Sb dimer rows preferentially terminate between the Si  $\pi$  chains as shown in Fig. 1 resulting in an odd number of Sb<sub>2</sub> dimers in most of the Sb lines. Apparently this configuration (right end in Fig. 1) is more favorable since the next growth step would require the break of the  $\sigma$  bond of the Si<sub>2</sub> dimer in the next chain which is probably already strained but not broken. In the empty state image of Fig. 1 some of the Sb row ends show a rounded feature which seems to extend the Sb line partly into the next  $\pi$  chain of the Si. We speculate that this may be an impurity atom, terminating the reactive end of the Sb line.

In contrast to Sb lines of two dimers or more a single Sb<sub>2</sub> could be bonded via the  $\pi$  orbital of the Si 2×1 reconstruction leaving the Si dimer  $\sigma$  bond intact. The alternative is the

breakup of the  $\sigma$  bond even for a free dimer. To our knowledge this question has not been addressed carefully. Our spectroscopy data show the similarity of the Sb<sub>2</sub> states to the Si<sub>2</sub>  $\pi$  orbitals, only 0.2 eV shifted to lower valence energy. Since we observe states at relative low energy (<2 eV) this suggests that the remaining two electrons per Sb atom are not involved in a  $\sigma$  like bond to the Si leaving the Si-Si  $\sigma$ bond intact. Based on this observation we propose that the Sb<sub>2</sub> is chemisorbed by breaking only the  $\pi$  bond of the Si<sub>2</sub> dimer.

When a Si(001) surface with Sb<sub>2</sub> dimers is annealed at sufficiently high temperature (we achieved this at approximately 575 K) the  $\sigma$  bond of the Si dimer is definitely broken<sup>7</sup> and the growth of the Sb dimer row continues until it is terminated by strain induced in the Sb line. At lower temperatures the Sb<sub>2</sub> is diffusing on the surface by bonding to the  $\pi$  orbitals. The higher temperature makes it possible to break the  $\sigma$  bond resulting in the reactive ends leading to the one-dimensional growth discussed here. Considering the ratio of the covalent radii of Sb and Si,  $r_{\rm Sb}/r_{\rm Si}=1.21$ ,<sup>14</sup> it is quite remarkable that the epitaxial Sb lines of Sb grow up to a maximum length of approximately 5 nm considering the strain of  $\Delta l/l = 17\%$  in the Sb line (corresponding to approximately two atoms over 5 nm). This shows that the simple covalent radius model is not sufficient to explain the growth. It is necessary to include the energy gain of bonding an additional dimer to the Sb line to explain the extended growth.

In conclusion, we presented spectroscopy data on epitaxial Sb nanostructures on Si(001). The ends of the Sb dimer row show a finite density of states at the Fermi level in contrast to the center of the Sb line which is semiconducting with characteristics similar to Si(001)  $2 \times 1$ . We found no evidence for the replacement of Si by Sb in the surface. We propose that the end state is the experimental evidence for the surface polymerization model.<sup>1</sup> The self-assembly of the Sb line begins by breaking the  $\sigma$  bond of the Si and a very reactive site is formed. This site enhances the density of states at  $E_F$  (Fermi level) and propagates the surface polymerization.

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