Structure of the Ag/Si(111) Surface by Scanning Tunneling Microscopy

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We present the first real-space images, obtained by scanning tunneling microscopy, which show the ordered atomic structures of the Ag/Si(111) surface for several submonolayer coverages. The $(\sqrt{3}\times\sqrt{3})R30°$ surface is shown to be of the honeycomb structure, and the room-temperature coverage is determined to be $\theta=\frac{2}{3}$. The 1×3 overlayer consists predominantly of rows of Ag atoms separated by two empty rows. At low coverage the surface shows long-range 7×7 order, but patches occur within the 7×7 cells where Si adatoms are absent.

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The structure of metal-semiconductor interfaces has been of great technical and fundamental interest for many years. Fundamental interest arises because a wide variety of coverage-dependent structural arrangements occur, including ordered metal overlayers on reconstructed semiconductor surfaces, the formation of surface alloys, and the alteration of semiconductor reconstructions by trace amounts of metallic adsorbates. These interfacial rearrangements pose challenging problems for surface science, causing the application of many experimental and theoretical techniques to the determination of atomic positions, the nature of metal-semiconductor bonding, and the electronic structure of the interfaces.

In this Letter, we present results of scanning tunneling microscopy (STM) studies showing the first real-space images of the atomic structure of the Ag/Si(111) interface. We have chosen this well-studied surface because diffusion of the silver atoms into the bulk does not occur.[1] In addition the existence of structural models based on other techniques is helpful in interpreting STM images which involve an integral including the electronic density of states of both the tip and sample over a range determined by the gap voltage. Our results allow us to determine the lateral arrangement of silver atoms in the $(\sqrt{3}\times\sqrt{3})R30°$ layer and in the 1×3 structure, and to gain insight into the nature of the low-coverage surface. These data illustrate the already proven capabilities of STM[2-6] for obtaining surface structure and represent the first systematic STM study of a metal-semiconductor interface over a range of metal coverage.

Our measurements were carried out in an interconnected multichamber STM system with extensive surface preparation and analysis facilities.[7] Si(111) samples, $1\times1\times0.05$ cm^3, were cleaved from a p-type wafer, with $\rho\simeq0.01$ Ω-cm, and secured by tantalum clamps onto a tantalum carrier. The samples were loaded via an airlock into the system, which had base pressure $\leq10^{-10}$ Torr, and degassed at low temperatures by electron-bombardment heating from the rear. Subsequent heating to approximately 1030 °C for several minutes led to surfaces which had extended regions of 7×7 reconstruction as measured by STM. Traces of carbon ($\lesssim0.1$ ml) were usually detected by Auger-electron spectroscopy (AES). Sharp 7×7 low-energy electron-diffraction (LEED) patterns were observed. Silver was evaporated onto room-temperature samples from a liquid-nitrogen–shrouded tungsten-basket source. The deposition rate was maintained at approximately 0.5 ml/min by a quartz-microbalance servo. The coverages were estimated by comparing the Ag *MNN* and Si *LVV* Auger line intensities with the data of Hanbücken, Futamoto, and Venables.[8] The pressure in the deposition chamber remained below 3×10^{-10} Torr during evaporations, and no evidence for increased contamination was found with use of AES. Samples were subsequently annealed for various times and temperatures and monitored primarily by LEED. Temperatures were determined with an infrared pyrometer.

After the sample preparation, the sample and carrier were loaded onto a "louse"[9] in the STM, and an approach of the tip to the surface was made. Instrumental drifts typically settled to reasonable values (1.0 Å/sec) for atomic-scale measurements within one hour. All measurements presented here were carried out in a slow-scan mode[9] (100 Å/sec) with an image acquisition time of $\simeq5$ min and a constant tunnel current of $i_T=0.2$ nA.

It is generally agreed[1] that, at room temperature, silver grows on clean Si(111) in a layer by layer mode. At temperatures above $\simeq200$ °C, the growth mode changes, with Ag islands forming on an intermediate layer which gives a $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern. This same LEED structure, which we will refer to as $\sqrt{3}$, is observed if a sample, coated at room temperature with a few layers of silver, is annealed at temperatures between 200 and 500 °C, whereupon excess silver coalesces into islands. If annealing is carried out at higher temperatures, some silver desorbs and a 1×3 LEED pattern develops which transforms into a 1×6 pattern upon cooling to room temperature. Further annealing at elevated temperatures results in modified 7×7 LEED patterns and ultimately leads to the clean Si(111)(7×7) pattern.

Disagreements exist regarding the structure of the $\sqrt{3}$ layer primarily because of the variations of the saturation coverage of silver with temperature and the surface preparation technique.[1] Similar disparities arise for the 1×6 structure and for low-silver-coverage surfaces.

The first structure which we discuss is observed on Si(111)(7×7) samples with initial coverage $\theta\sim2$ ml of silver, which were subsequently annealed for 5 min at 480 °C. Sharp $\sqrt{3}$ LEED patterns were obtained, and well-ordered regions of hexagonal structure, shown in Fig. 1, were observed in the STM at various sample-tip biases ranging between 0.39 and 2.8 V. Two proposed structures are illustrated in Fig. 2 for comparison. Trimer structures, shown in Fig. 2(a), which were suggested to account for $\theta=1$-ml (1 Ag atom per surface Si atom) measurements[1] are not consistent with the symmetry and spacing of the features observed in our STM images. The simple honeycomb model, shown in Fig. 2(b), agrees well with our results, provided that the bright spots in the STM image represent individual silver atoms. At somewhat higher tunneling currents, 0.6 nA, the bright dots are connected by ridges but no significant new features appear. Evidently the electronic structure is such that images at all voltages measured primarily reflect these same features, much as is the case for adatoms on the Si(111)(7×7) surface.[4] The cell edges are measured to be 6.8 ± 0.8 Å long and compare well with the expected value of 6.62 Å. Variants of the honeycomb model which propose additional silver atoms, either distributed randomly[10] or in sites at the centers of the honeycomb hexagons,[1] are also ruled out for the $\sqrt{3}$ layer at room temperature, and the coverage of the ordered overlayer is precisely $\theta=\frac{2}{3}$ ml.[8]

Among the honeycomb models, several variants describe the Ag atoms as embedded slightly below a reconstructed Si surface. The first of these models was based on observations of a decrease in the Ag ion surface scattering (ISS) signal after annealing of a sample coated with $\frac{2}{3}$ ml of Al.[11] Further work using LEED,[12] surface extended x-ray-absorption fine structure (SEXAFS),[13] and x-ray photoelectron diffraction (XPD)[10] supported these results. However, a recent measurement[14] showing that Ag ISS signals predominate at grazing incidence places the Ag atoms above the topmost Si layer. Although a simple topographic interpretation of our results favors the latter model, we cannot at present unambiguously resolve this issue because STM measurements involve both topography and density-of-states contributions.[4,5] In either case, the presence of metal atoms, with a large density of states, arranged in a honeycomb pattern near the surface plane offers a natural explanation of the images. Finally we note that an embedded trimer model[10,15] has recently been considered to explain $\theta=1$ coverage measurements and photoemission observations of a gap.[16] This model has top-layer Si atoms arranged in a honeycomb configuration which is consistent with our STM images but appears to be inconsistent with ISS and SEXAFS results and is not supported by LEED or XPD models. Our STM observations of extensive defects on Si(111)(7×7) surfaces cause us to question the precision of coverage measurements. Photoemission arguments also appear weak, relative to direct structural techniques, because of the possibility of charge transfer processes or the existence of a small, but finite, density of states in the gap observed by photoemission. We therefore support the honeycomb model.

To produce the 1×3 structure, we deposited a silver layer with $\theta\sim2$ ml and then annealed for several minutes at about 600 °C. LEED patterns, checked at 1-min intervals, showed a gradual evolution of a strong 1×3 pattern with very faint spots at the additional 1×6 positions and intermediate intensity at the $\sqrt{3}$ positions. An STM image and a proposed structure[1] for the 1×3

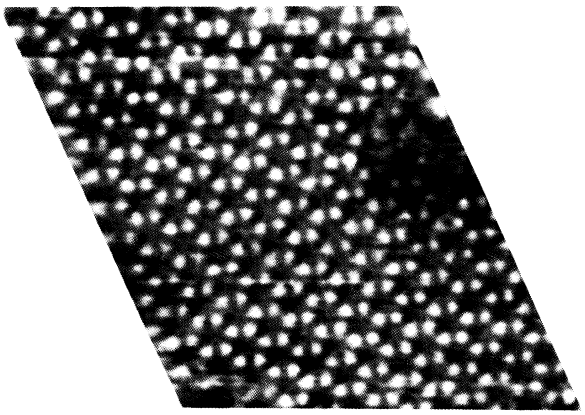

FIG. 1. STM image of a 90×90 Å^2 region of the $(\sqrt{3}\times\sqrt{3})R30°$ Ag/Si(111) interface. The corrugation of the ordered area is about 1 Å at a tip bias of $V_T=-0.39$ V. All gray scale representations in this Letter use white to represent elevated features.

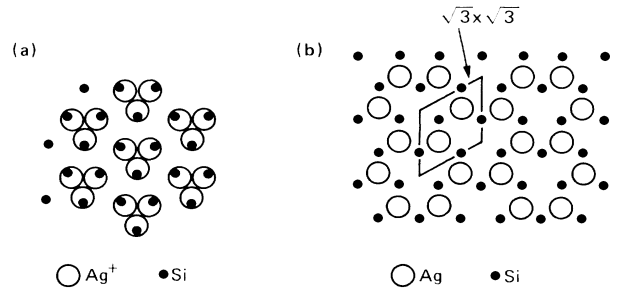

FIG. 2. Models for the $\sqrt{3}$ Ag/Si(111) overlayer. (a) Simple trimer model with 3 Ag atoms per unit cell on an unreconstructed Si(111) surface. (b) Simple honeycomb model with 2 Ag atoms per unit cell sitting in threefold-hollow sites of the unreconstructed surface.

overlayer are shown in Fig. 3. The bright lines in Fig. 3(a) are consistent with the spacing and symmetry of a structure where Ag atoms align in rows separated by two empty rows as shown in Fig. 3(b). The coverage of this structure agrees with all coverage measurements[1,11,12,16,17] of $\theta = \frac{1}{3}$ for the 1×3 overlayer. Striations along the rows in some images indicate that individual Ag atoms are barely resolved. The rows of this image are rotated by $\simeq 30°$ with respect to the $\sqrt{3}$ lattice observed in other images during the same run. The 1×6 character of the reconstruction, which appears in LEED only below 200 °C,[1] has been atrributed to small displacements of alternate rows along the row direction on the basis of reflection high-energy electron-diffraction measurements.[17] LEED studies[18] have contradicted this result and given a model where alternate rows are depleted when the coverage falls below $\theta = \frac{1}{3}$. Our LEED observations on this sample suggest a well developed 1×3 structure with only very weak 1×6 character, and our STM images predominantly show 1×3 rows. For the alternating displacement model we would expect significant 1×6 LEED intensity even for a 1×3 row arrangement. This result argues against the alternating displacement model, and our occasional observations of regions of depleted alternate rows support the latter model.

In attempts to observe structure on samples with low Ag coverage, we again annealed samples at 600 °C until $\theta \simeq 0.1$ ml. LEED patterns for such samples generally show modified 7×7 patterns with the most intense spots around the (01) positions and along the line between them. For such samples, we typically observe partial 7×7 cells, together with disordered features which cannot readily be interpreted. This result can be better understood by consideration of Ag adsorption on Si(111) in the context of Takayanagi's dimer-adatom-stacking fault model[19] for the Si(111)(7×7) reconstruction. An examination of this model reveals that Si adatoms occupy threefold-hollow sites and eliminate all but nineteen of the dangling bonds in the 7×7 cell. The remaining threefold-hollow sites involve three top-layer Si atoms, two of which are bonded to adatoms. Evidently, Ag and

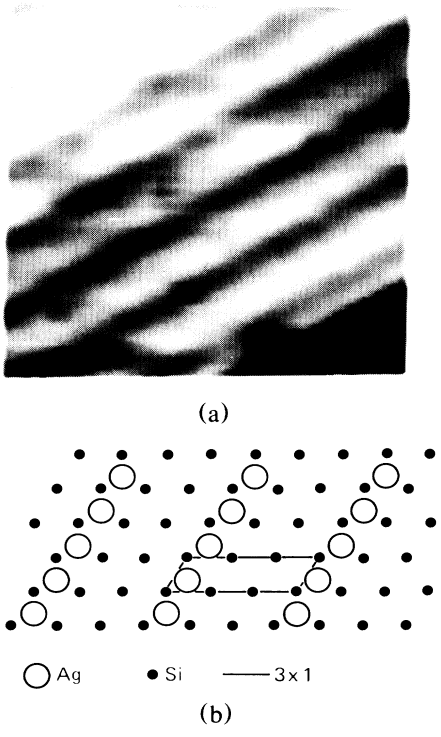

FIG. 3. (a) STM image of a Ag/Si(111) surface which shows a 1×6 LEED pattern. The image is over a 40×100 Å^2 area with $V_T = +2.8$ V. The corrugation is 0.4 Å at a current of 0.2 nA. The rows run parallel to a (110) step seen in the upper corner. The structure and origin of the contrast near the step edge is not sufficiently understood or resolved to establish the registration of the Ag. (b) Model of the 1×3 Ag/Si(111) surface with Ag atoms in threefold-hollow sites.

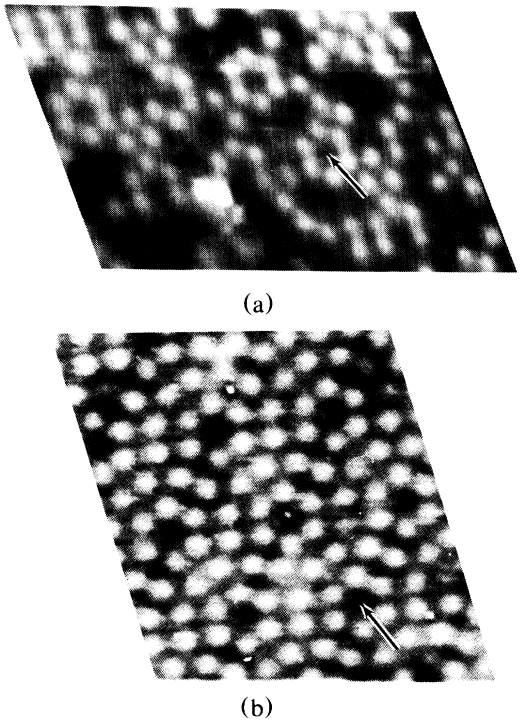

FIG. 4. (a) STM image of a low-coverage Ag/Si(111) surface produced by annealing. $V_T = -0.9$ V and the gray scale range is 9 Å. (b) STM image of the Si(111)(7×7) surface taken at $V_T = 1.9$ V. The corrugation is about 1.6 Å. The sides of the unit cell are known to be 26.7 Å long. Holes with six surrounding adatoms are identified by arrows in both (a) and (b).

Si adatoms are both in competition for dangling bonds. In the context of the dimer-adatom-stacking model, it then becomes apparent that the complete erasure of the 7×7 structure by the $\sqrt{3}$ or the 1×3 Ag/Si(111) structure involves both transport of Si adatoms and extensive rearrangements of the topmost Si double layer. Conversely, if one obtains low coverage by evaporating Ag from a $\sqrt{3}$ layer, a critical coverage arises where Si adatoms are promoted above the surface and local subsurface rearrangements begin to appear. These phenomena can result in a roughening of the surface which frustrates attempts of Ag atoms to order and may explain the relatively frequent appearance of defects in our images of 1×3 structures.

The STM image shown in Fig. 4(a), obtained on such a low-coverage sample, supports this notion. A careful inspection of this image shows that nearly every corner hole of the 7×7 can be identified and, in fact, that nearly every bright feature can be associated with an adatom position of the clean Si surface, shown in Fig. 4(b). Evidently, the silver atoms have reacted with the surface and result in the local displacement of Si adatoms from the affected regions of the surface. We conclude that, although there is a deficiency of Si adatoms and deep defects occur which correspond to missing portions of the top double layer, the long-range (7×7) order of the corner structures is remarkably good. We assert that the stability of the 7×7 structure must arise in part from long-range effects in addition to local order[20] and note that the stabilization of the surface by adatoms can evidently proceed in the presence of vacancies in the topmost double layer.

This work demonstrates the unique capabilities of the STM as a tool for understanding surface structure. Images of the $\sqrt{3}$ structure of Ag/Si(111) allow us to rule out trimer models and to establish the honeycomb model with room-temperature silver coverage of $\theta=\frac{2}{3}$ without model calculations. For the 1×6 structure, our results imply that Ag vacancies in alternate rows do occur and explain the appearance of a weak 1×6 character to a predominantly 1×3 overlayer. Observations at low coverage provide valuable insight into the competition between the structures preferred by the metal overlayer and the clean silicon surface. Further work including scanning tunneling spectroscopy techniques[9] together with more detailed accounts of the electronic structure than those presently available[1,16] may ultimately allow us to use metal-derived electronic states as indicators of the atomic species on the surface.

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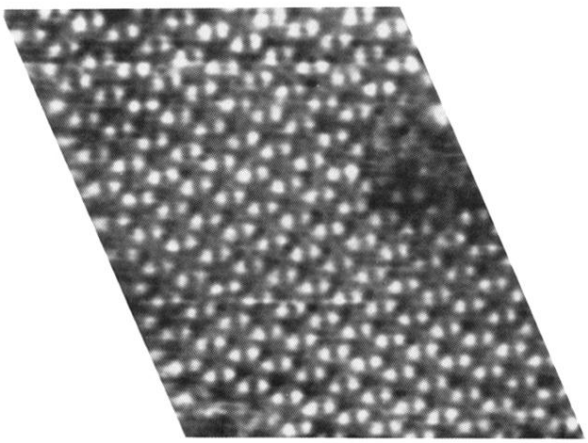

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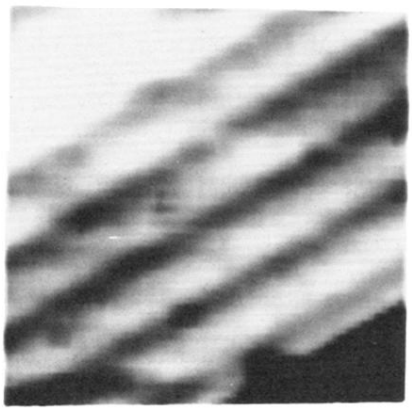
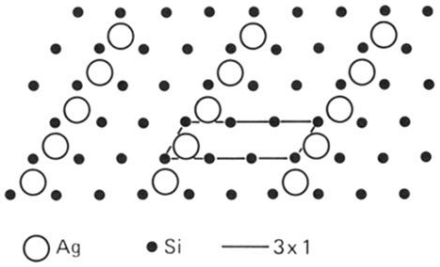


(a)



(b)

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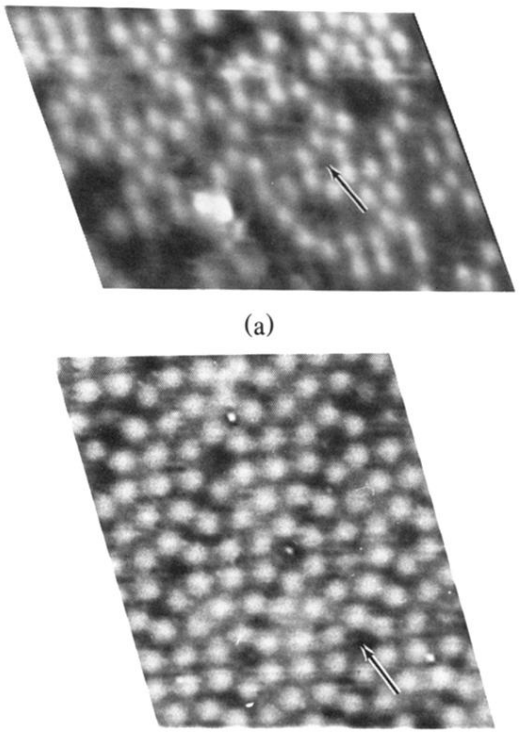

(a)

(b)

FIG. 4. (a) STM image of a low-coverage Ag/Si(111) surface produced by annealing. $V_T = -0.9$ V and the gray scale range is 9 Å. (b) STM image of the Si(111)(7×7) surface taken at $V_T = 1.9$ V. The corrugation is about 1.6 Å. The sides of the unit cell are known to be 26.7 Å long. Holes with six surrounding adatoms are identified by arrows in both (a) and (b).