

Role of Si adatoms in the Si(111)-Au(5×2) quasi-one-dimensional system

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The unoccupied electronic states of the Si(111)-Au(5×2) system have been studied, using inverse photoemission. Striking similarities exist between the unoccupied bands of the Si(111)-Au(5×2) system and the Si(111)-(7×7) and Si(111)-Au($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ systems. We argue that these similarities suggest that the Si(111)-Au(5×2) system contains Si adatoms, and that the adatom-induced surface states dominate both the inverse photoemission and photoemission spectra in the vicinity of the Fermi level. If this suggestion is correct, it means that the bands crossing the Fermi level may not be derived from the overlap of Au wave functions. The Au atoms may actually inhibit the formation of a Si adatom-induced band in the direction perpendicular to the Au chains. [S0163-1829(97)04023-X]

INTRODUCTION

Recent photoemission studies of quasi-one-dimensional systems, in their metallic phase, have demonstrated that there is vanishing emission intensity in the vicinity of the Fermi level.¹⁻⁵ This is in contrast to the behavior of two- and three-dimensional metals, where well-defined Fermi edges are observed.¹ Although the studies mentioned above have been performed on bulk quasi-one-dimensional systems, it is also possible to fabricate quasi-one-dimensional, chainlike systems on surfaces. One example is the Si(111)-Au(5×2) system^{6,7} (Fig. 1). Although the details of this surface structure are still being worked out, it appears that the interchain spacing is significantly larger than the interatomic spacing along the chains.⁶ So, at least from a structural point of view, the ordering of the Au atoms, on the Si surface, is quasi-one-dimensional. In agreement with bulk quasi-one-dimensional systems, photoemission studies have found evidence for a strong anisotropy in the band dispersion. However, in contrast, they have observed a well-defined Fermi edge.⁸ This difference in electronic properties begs the question, do bulk and surface quasi-one-dimensional metals belong to the same physical class?

To investigate these questions further, we have performed inverse photoemission studies of the Si(111)-Au(5×2) system. We have paid particular attention to the region in the vicinity of the Fermi level, in an attempt to detect the Fermi edge, and the surface band identified in the photoemission studies⁸ which crosses the Fermi level.

EXPERIMENT

The experiments were performed in a μ -metal ultrahigh vacuum chamber with a base pressure of 7×10^{-11} torr. The inverse photoemission apparatus consists of a low-energy electron gun of the Erdman-Zipf design,⁹ and a bandpass photon detector that utilizes a CuBe mesh electron multiplier (Johnston Laboratories MM1) and a CaF₂ entrance window as described by Schäfer *et al.*¹⁰ In contrast to Schäfer *et al.* we evaporated KCl onto the first dynode, to act as the photoemissive material. Angular dispersion is achieved by rotating the electron gun while the sample and detector remain

fixed. The overall energy resolution of this system was estimated to be 0.6 eV full width at half maximum from the Fermi level emission onset of sputtered polycrystalline Ta, using the method described by Dose to extract the instrument pass function.¹¹ The overall momentum resolution of the system is both energy and angle dependent and has been esti-

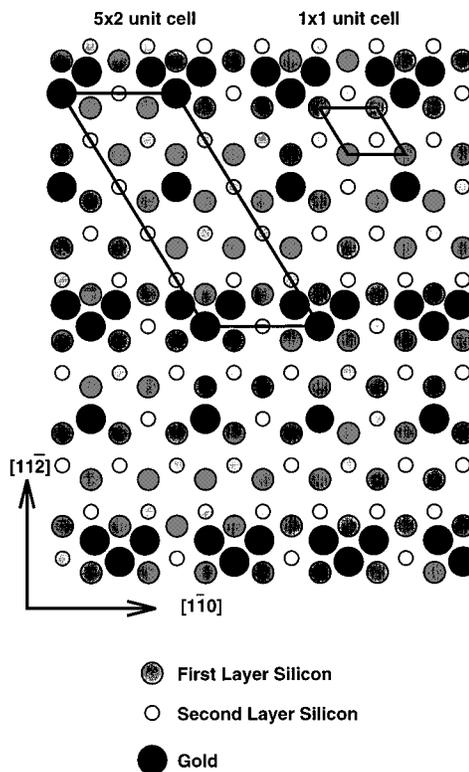


FIG. 1. The Si(111)-Au(5×2) structure proposed by Bauer includes chains of Au atoms, which are common to many other models. The figure is included to define the crystallographic directions referenced in the text. In addition to the structure shown, Bauer also suggests that there are extra gold atoms on top of the chain rows, which increase the coverage from 0.4 to 0.45 ML. The spacing between these extra atoms is $4 + 2n$ bulk lattice constants along the chains, where n is a positive integer. The two parallelograms are the oblique 5×2 and 1×1 unit cells.

mated to be between 0.1 and 0.2 Å⁻¹ for the energies and angles in this study. A Princeton Research Instruments RVL 8-120 reverse view low-energy electron diffraction (LEED) system was used for sample alignment and surface characterization.

The rotational symmetry of the diamond crystal structure about the [111] axis defines three equivalent 5×2 domains. However, it has been demonstrated that a single domain sample can be prepared using a vicinal surface.¹² The intentional vicinal miscut breaks the threefold degeneracy and favors the nucleation of a single domain, specifically that with Au chains parallel to the surface steps.

The samples used in this experiment were cut from vicinal Si(111) wafers, miscut by $4 \pm 0.5^\circ$ towards $[11\bar{2}]$. All of the samples were *p* type, with resistivities of $\approx 5 \Omega \text{ cm}$. The overlayers were prepared *in situ* by direct current heating of the sample and deposition of Au from a Knudsen cell evaporator. All currents were applied in the $[\bar{1}\bar{1}2]$ (uphill) direction to avoid step bunching on the surface.¹³ A clean, well-ordered Si(111) surface was prepared by flashing the Si sample to $\approx 1100^\circ\text{C}$. The sample was heated to $\approx 650^\circ\text{C}$ during the Au deposition. The quantity of Au deposited was calibrated using a quartz crystal rate meter. Coverages were measured by timed exposures to be between 0.40 and 0.45 ML, where 1 ML is defined to be the number of silicon atoms per unit area in the top layer of an ideally terminated Si(111) plane, $7.83 \times 10^{14} \text{ cm}^{-2}$. The pressure during evaporation typically remained below 1×10^{-9} torr. LEED was used to determine the sample orientation and surface quality and to verify the presence of a single domain.

Inverse photoemission spectra were recorded along the $[\bar{1}10]$ - $[110]$ azimuth, parallel to the Au chains, and along the $[\bar{1}1\bar{2}]$ - $[11\bar{2}]$ azimuth, perpendicular to the chains. These directions were chosen so that the present study would provide complementary information to that of the previous photoemission study.⁸ Great care was exercised to ensure alignment of the [111] axis of the sample, which differs by 4° from the sample normal due to the vicinal miscut. It was found that the surface quality degraded as either a function of time, or by exposure to the electron beam. The quality of the LEED images was noticeably inferior after the collection of three inverse photoemission spectra. For this reason, the sample was annealed at 650°C for 2 min after the collection of every second inverse spectrum. The pressure during the collection of inverse photoemission data and annealing remained below 3×10^{-10} torr. The spectra presented are representative of the more than 15 samples studied. The shapes of the spectra and the peak positions were found to be reproducible from sample to sample.

RESULTS

The sample flashing process described in the previous section reliably produced a sharp 7×7 pattern, as shown in Fig. 2(a). The splitting of the 1×1 spots, visible at LEED energies around 40 eV, was taken as evidence of an evenly spaced step/terrace structure on the vicinal surface. After Au deposition, the LEED patterns consisted of a well-defined 5×1 pattern, with diffuse half-order streaks [Fig. 2(b)]. The weakness of the half-order intensities has been attributed to a lack of registry between well-ordered neighboring chains.^{6,14}

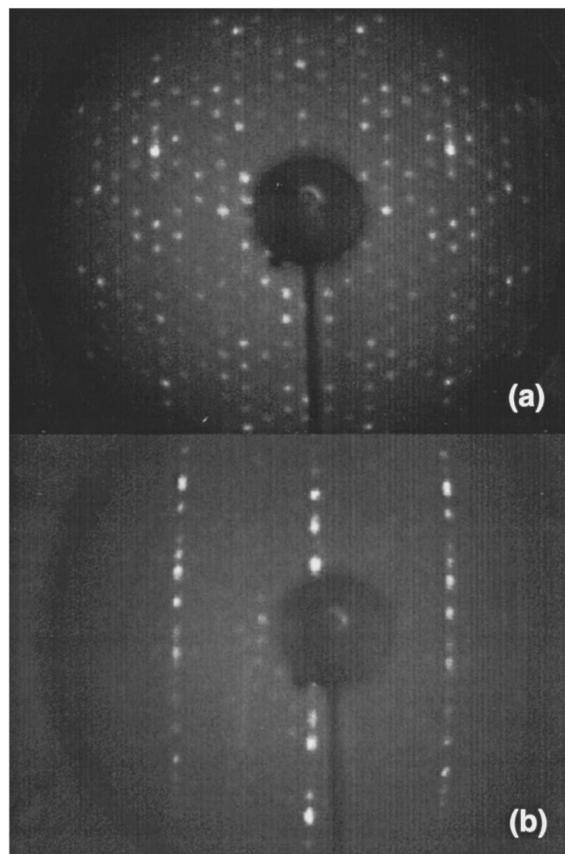


FIG. 2. (a) The top panel shows a typical 7×7 LEED pattern prior to Au deposition. (b) The bottom panel is an example of a single-domain Si(111)-Au(5×2) LEED pattern. The sample is oriented such that the $[11\bar{2}]$ direction is pointing upward. In both cases, the energy of the electrons is 80 eV. The Au chains are horizontal.

Examples of the spectra collected perpendicular to the chains are included in Fig. 3. There are three distinct features, two of which overlap near the zone center. The feature seen at ≈ 2.7 eV above the Fermi level at normal incidence is believed to consist of two states: one that exhibits no detectable dispersion, and one that disperses away from the Fermi level reaching 3.5 eV at 15° off normal. The third feature occurs at 4.5 eV above the Fermi level at normal incidence, and disperses sharply upward, reaching 5.5 eV at 10° . In addition to these three features, there is an additional, less obvious, feature that appears less than 1 eV above the Fermi level, although the exact energy position is difficult to determine as it only appears as a shoulder on the much stronger 2.7 eV peak. This shoulder is visible at virtually every angle along both azimuths studied. At no point is there any evidence of a state crossing the Fermi level. Possible origins of the observed features will be discussed in the following section.

Spectra collected along the chains are shown in Fig. 4. The states seen in this direction are very similar to those seen perpendicular to the chains. Two states appear to overlap near the zone center, one with negligible dispersion and the other dispersing upwards with increasing angles. A third feature is visible at 4.5 eV at normal incidence, which disperses

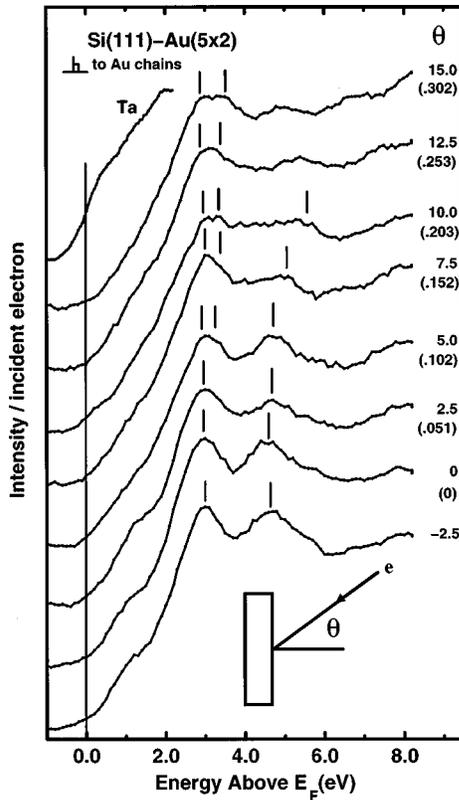


FIG. 3. Inverse photoemission spectra collected with the projection of the electron wave vector onto the surface lying perpendicular to the Au chains. The positive numbers on the right are angles, in degrees, toward $[11\bar{2}]$. Negative angles are toward $[\bar{1}12]$. The numbers in parentheses are the components of the electron wave vector parallel to the surface in \AA^{-1} calculated at $E_F + 2.7$ eV. The zone boundary is reached at a wave vector of 0.142\AA^{-1} . The top spectrum shows the position of the Fermi level on sputtered polycrystalline tantalum in electrical contact with the sample. Tick marks are provided as a guide to the eye.

sharply upward with increasing angles. The shoulder around 1 eV is again seen, and there is no evidence of states crossing the Fermi level.

DISCUSSION

It is informative to first compare the normal incidence spectra of the Si(111)-Au(5×2) and clean Si(111)-(7×7) surfaces as shown in Fig. 5. The state labeled U_1 appears at the same energy and, when the spectra are normalized to the incident electron flux, with the same intensity on both the clean and Au reconstructed surfaces. On the clean 7×7 surface, this state has been shown to be spatially localized on the Si adatom¹⁵ and it is thought to be a surface state that is derived from the interaction of Si adatoms, which sit in the T_4 sites, with the dangling bond orbitals of the substrate.¹⁶⁻¹⁹

Furthermore, the U_1 state on the 5×2 surface is strongly attenuated after approximately one day in ultrahigh vacuum, where the predominant residual gas is hydrogen. The other features remain unaffected. The sensitivity of U_1 to contamination is similar to that of the adatom state on the 7×7 surface.¹⁷

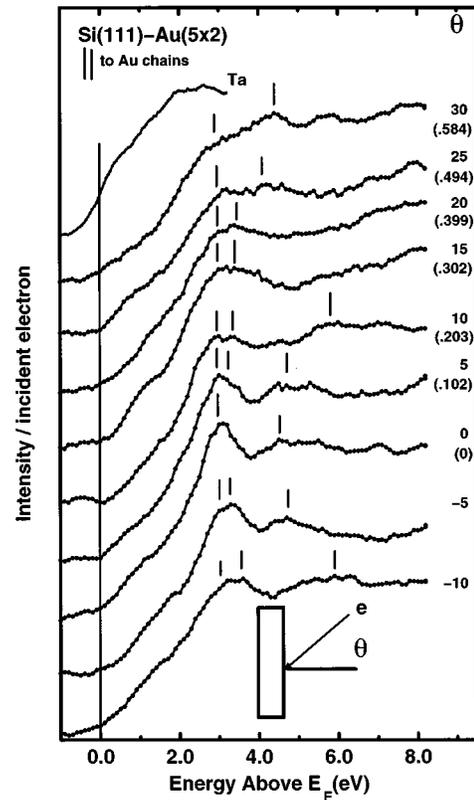


FIG. 4. Inverse photoemission spectra collected with the projection of the electron wave vector onto the surface lying parallel to the Au chains. The positive numbers on the right are angles, in degrees, toward $[1\bar{1}0]$. Negative angles are toward $[\bar{1}10]$. The numbers in parentheses are the components of the electron wave vector parallel to the surface in \AA^{-1} calculated at $E_F + 2.7$ eV. The zone boundary is reached at a wave vector of 0.409\AA^{-1} . The top spectrum shows the position of the Fermi level on sputtered polycrystalline tantalum in electrical contact with the sample. Tick marks are provided as a guide to the eye.

The binding energy of the U_1 state and the time dependence of the state intensity implies the presence of Si adatoms in the 5×2 structure. If this suggestion is correct then the fact that the U_1 state has the same intensity in both systems suggests that the Si adatom density is comparable. On average, each 5×2 unit cell would require ≈ 2.4 Si adatoms to have the same number as the 7×7 structure (12 in the 7×7 cell). Although not all of the structures that have been proposed so far include Si adatoms, there is a model that does⁷ and the Si adatom density is comparable to the density we extract from our spectra. Marks and Plass⁷ propose a structure that requires one Si adatom per unit cell and suggests that additional adatoms may be present.

The remaining features of Fig. 5 bear a strong resemblance to the features seen on Si(111)-Au($\sqrt{3} \times \sqrt{3}$) $R30^\circ$. The states labeled A and B have been previously identified as bulk transitions.²⁰ The bulk transition B looks sharper on the Si(111)-Au($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ surface than on the clean 7×7 surface, as it does here. This sharpening has been previously attributed to a reduction in umklapp scattering by surface reciprocal lattice vectors compared to the clean surface.²⁰ The state labeled U_2 appears very similar to a state that

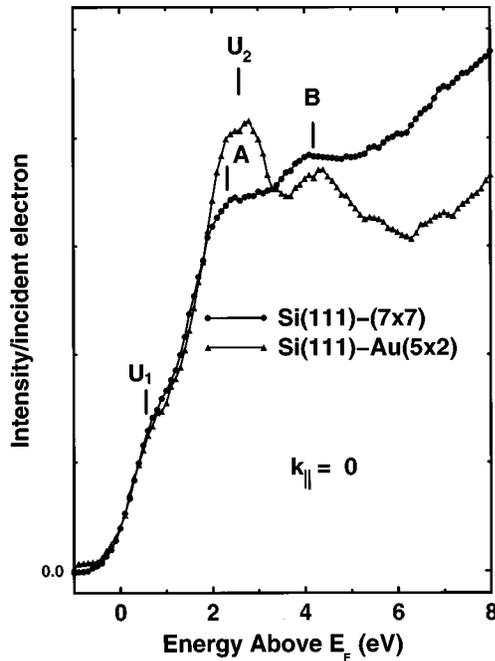


FIG. 5. Comparison of clean Si(111)-(7×7) and Si(111)-Au(5×2) spectra at normal incidence. Feature U_1 is thought to arise from Si adatoms. Note that the normalized intensity of U_1 is the same for both the Si(111)-(7×7) and the Si(111)-Au(5×2) systems, indicating a comparable surface adatom density.

arises from Si-Au bonding on Si(111)-Au($\sqrt{3} \times \sqrt{3}$)R30°. ²⁰

If the U_1 band on the 5×2 surface does arise from Si adatoms, then this has important implications for the way we think about the electronic structure of this system. On the Si(7×7) surface both the unoccupied U_1 band and the occupied S_1 band have been shown to be adatom derived. Both *ab initio* density functional theory calculations ¹⁶ and studies of the surface using scanning tunneling microscopy spectroscopy ¹⁵ have made this association. Consequently, the occupied surface band that has been studied with photoemission ⁸ may not arise from the overlap of the Au wave functions. The Au atoms may actually inhibit the overlap of Si adatoms in the direction perpendicular to the Au chains, and this may have the effect of reducing the bandwidth of the adatom-induced bands. So the quasi-one-dimensional behavior that has been observed may only indirectly be a result of the presence of the Au chains.

Photoemission studies of the 7×7 system ²¹ have identified a relatively flat surface band that is believed to extend above the Fermi level. This metallic state is responsible for pinning the Fermi level ≈ 0.7 eV above the bulk valence-band maximum. ¹⁹ The dispersion of this band is not unlike the dispersion observed so far on 5×2. Furthermore, inverse photoemission studies of the 7×7 system have failed to see this metallic state emerge as a peak above the Fermi level, although metallic tails are observed. ¹⁷ This is completely analogous with the behavior we observe on the 5×2 system.

Therefore, the picture we are developing here, that the near Fermi-level states are adatom derived, seems consistent with existing studies of the 7×7 system. ^{16,17,15}

However, we still have one major problem to resolve. Why does the surface band on the 5×2 system possess a well-defined Fermi edge? Does this mean that the system is not truly one dimensional? The lack of dispersion of the occupied surface band perpendicular to the chains clearly indicates that the system is one dimensional. We believe the answer to this paradox will be resolved with high-resolution photoemission studies of the Fermi-level region. We note that an early study of the bulk quasi-one-dimensional material $K_{0.3}MoO_3$ found evidence for a well-defined Fermi edge. ²² However, more recent studies, performed at considerably higher-energy resolution (< 20 meV compared with 150 meV) conclusively demonstrated that the system had vanishing emission intensity at the Fermi level. ¹ The photoemission study of the 5×2 system was performed with an energy resolution of 125 meV. ⁸ This is insufficient to unambiguously determine whether there is a well-defined Fermi edge or not. High-resolution photoemission studies of this interesting system are in order.

CONCLUSION

The unoccupied states of the Si(111)-Au(5×2) system have been studied with inverse photoemission. It was found that the inverse photoemission spectra possessed a feature with a binding energy, intensity, and sensitivity to contamination that are similar to the adatom-induced feature on the Si(111)-(7×7) surface. We have explored the possibility that this feature (U_1), and also the uppermost occupied surface band (S_1), arise from the overlap of the Si adatoms with dangling-bond orbitals of the substrate. In this scenario, the one-dimensional behavior that has been observed in a previous photoemission study, ⁸ would arise from the anisotropic distribution of adatoms on the surface and not from the chainlike distribution of Au atoms. In fact, it is possible that the Au chains may inhibit the formation of a Si adatom band perpendicular to the Au chains.

We have also argued, using the historical precedent of the $K_{0.3}MoO_3$ system, that it is too early to conclusively state that there is a well-defined Fermi edge for the Au(5×2) system. The photoemission studies have to be performed at significantly higher-energy resolution. Since the adatoms interact strongly with the substrate, ¹⁸ it will be interesting to see whether the valence band emission possesses one- or two-dimensional character.

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