Metallicity of In chains on Si(111)

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The electronic structure of the Si(111)-In(4×1) system, between the Fermi level and the vacuum level, has been studied using inverse photoemission. Single domain 4×1 overlayers were grown on vicinal Si(111) surfaces that were offcut by 3° towards $[\bar{1}\bar{1}2]$. In contrast to an earlier inverse photoemission study of this system, which was performed on a multidomain sample, but in agreement with recent photoemission and STM studies, the overlayer system was found to be metallic. A clear Fermi level crossing was detected near the Brillouin zone boundary at $\bar{X}$. We suggest a possible reinterpretation of the inverse photoemission study that naturally resolves the controversy about the surface metallicity. [S0163-1829(97)00948-X]

INTRODUCTION

Indium displays a rich set of surface reconstructions on Si(111).[1–4] Six different phases have been detected[2] in the relatively narrow coverage range from 0.2 to 1.2 monolayers (ML). While the low coverage phases, $(\sqrt{3} \times \sqrt{3})R30°$ (hereafter $\sqrt{3}$) and $(\sqrt{31} \times \sqrt{31})$, are semiconducting, the three higher coverages phases, $(1 \times 1)R30°$, $(\sqrt{7} \times \sqrt{3})$, and (4×4), that occur around 1 ML are metallic.[2] Between these two groups, situated at ≈0.5 ML,[2,5] is the 4×1 phase.

A thorough survey of these In surface phases[1,6] using inverse photoemission, and several other surface science techniques, found the 4×1 phase to be semiconducting. However, later studies,[7] performed on single domain samples, with photoemission found the phase to be metallic. Furthermore, recent spectroscopic studies of this system,[2] performed with scanning tunneling microscopy (STM), have found the system to be semimetallic. The density of states near the Fermi level was significantly lower than the density of states of the higher coverage phases in the same energy range.

In this study we have reexamined the electronic structure of the 4×1 phase, with inverse photoemission, to try to establish why the previous inverse photoemission study[1,6] found the system to be semiconducting. We will present a simple explanation that, we believe, resolves this paradox.

Another interesting characteristic of the 4×1 phase is that it is quasi-one-dimensional (quasi-1D). STM topographs[2] have revealed the existence of double rows aligned with the step edges on the vicinal surface. The double rows are separated by ≈13.3 Å and within the rows there is a zigzag pattern of topographic maxima suggestive of relatively close packing along the chain.

EXPERIMENT

The inverse photoemission experiments were performed with a high sensitivity band pass photon detector[8] and low-energy electron gun.[9] The detector is a Geiger-Müller tube that utilizes dimethyl ether as the detection gas and a MgF_2 entrance window to produce a bandpass centered on 10.6 eV. The detector bandwidth was estimated to be 0.6 eV full width at half maximum from the Fermi level emission onset of freshly evaporated polycrystalline Au. Although the detector design is not new,[10] we found that it is essential to correctly compensate for detector dead time for it to be prac-

tically useful.[8] The electron gun is mounted on a goniometer that allows it to be rotated about the sample. The momentum resolution of the system is dependent upon both the electron energy and the angle between the electron gun and the sample normal (θ). For the range of energies and angles used in this study, the momentum resolution lies in the range 0.1–0.2 Å^{-1}.

INDIUM CHAINS

Single-domain 4×1 overlayers were grown on vicinal n-type Si(111) wafers, with resistivities of ≈5 Ω cm, miscut by 3±0.5° towards $[\bar{1}\bar{1}2]$. To compensate for the rotation of the sample normal, the sample was mounted in a holder that counterrotated the sample by the vicinal offcut angle. This aligned the Si(111) planes parallel with the front of the sample holder. Clean, well-ordered 7×7 surfaces [Fig. 1(a)] were created by resistively heating the substrates to 1050 °C using dc current which was passed in the "uphill" direction to avoid step bunching.

It has been reported that it is possible to grow single 4×1 domain samples by depositing In on a room temperature, vicinal substrate and then annealing the substrate to ≈450 °C.[1,5,7] Unfortunately, our attempts to reproduce this procedure were unsuccessful. Instead, we found that it was necessary to deposit In on a substrate that was heated to ≈395 °C. However, it is conceivable that in the studies cited above, the surface may have been slightly hotter than room temperature if the In was deposited shortly after the surface had been cleaned.

In Fig. 1(b) we present a low-energy electron diffraction (LEED) image collected from a single-domain 4×1 overlayer that clearly shows the suppression of the two other 4×1 domains that would be expected, from the C_{3v} symmetry of the surface, to contribute to the diffraction pattern on a nonvicinal surface.

In Fig. 2, three normal incidence inverse photoemission spectra are reproduced which probe the $\bar{\Gamma}$ point of the surface reciprocal zone. Curve a was collected from a surface that was predominantly single domain 4×1 [Fig. 1(b)]. As described above, the In had been deposited on a substrate that had been heated to ≈395 °C. We note that this spectrum is remarkably similar to a previously published spectrum that
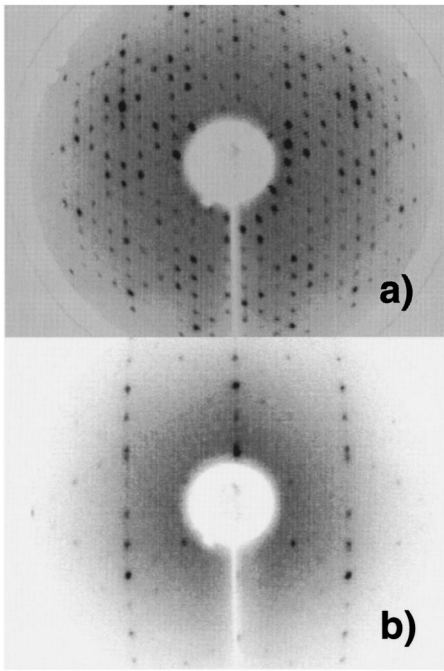
FIG. 1. (a) A Si(111)7×7 LEED pattern collected at 77.6 eV from a vicinal surface prior to the deposition of In. (b) A LEED pattern of a predominantly single-domain Si(111)-In(4×1) sample collected at 79 eV. The [$\bar{1}\bar{1}2$] direction is vertical and the In chains are horizontal.

FIG. 2. Inverse photoemission collected in normal incidence probing the $\overline{\Gamma}$ point of the surface zone. Spectrum (a) was collected from a surface that displayed a strong 4×1 LEED pattern. The surface was created by depositing In on a surface heated to 395 °C. Spectrum (b) was collected from a surface that displayed a three domain 4×1 LEED pattern. The In had been deposited on the Si(111) at room temperature and subsequently annealed. Spectrum (c) was collected from a $\sqrt{3}$ overlayer for comparison. The dots are the unprocessed raw data. The curve is a smooth line fit to the data points.

was collected from the $(1\times1)R30°$ phase.[1] However, the diffraction pattern we obtained from this surface [Fig. 1(b)] is very clearly 4×1. Maybe in both systems the In atoms have similar bonding configurations. Curve c was collected from a surface that possessed a clear $\sqrt{3}$ LEED pattern and curve b was collected from a 4×1 surface that had been produced by room temperature In deposition and subsequent annealing to ≈450 °C for 5 min. This surface produced a three-domain 4×1 LEED pattern. Curve b can clearly be considered to be a linear superposition of curves a and c. It has features that appear in both curves. This suggests that, at least in our case, the annealing process produces a mixture of the two phases. The earlier inverse photoemission study of the 4×1 system[1,6] may also have been performed on surfaces that were not entirely single phase because the inverse photoemission spectra of the annealed 4×1 surface[1] contained an appreciable contribution from the state located 1 eV above the Fermi level. Our diffraction studies lead us to believe that this state (labeled IS in the former study) is characteristic of the $\sqrt{3}$ phase and it is not an intrinsic feature of the 4×1 phase. However, it still remains to explain why the previous inverse photoemission study[1,6] found the 4×1 phase to be semiconducting. We will return to this later.

In Fig. 3, we show a series of inverse photoemission spectra that were collected from the 4×1 phase in the azimuth that is perpendicular to the In chains ($\overline{\Gamma X'}$, [$\bar{1}\bar{1}2$]). In the top part of the figure, there is a spectrum collected from evaporated polycrystalline Au which provides a convenient Fermi-level reference. Clearly, there is no emission in the Fermi level region at normal incidence ($\theta=0$) or in any other spectrum in this azimuth. The spectra are dominated by an intense, In-induced feature located 2 eV above the Fermi
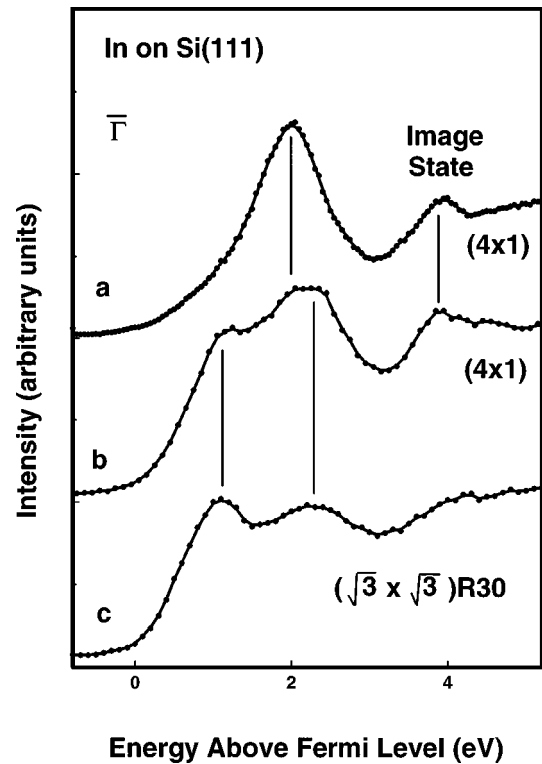
level. Within our experimental uncertainty, the dispersion of this state is completely flat. The less intense feature located ≈4.0 eV above the Fermi level has previously been attributed to the $n=1$ level of a hydrogenic image state series[1,6] and we agree with this assignment. We will describe the momentum-resolved behavior of this interesting state in a later paper. Suffice it to say, at this stage, that it displays one-dimensional character and it appears to be quantum confined to the In chain.

In Fig. 4, we show a series of inverse photoemission spectra that were collected from the 4×1 phase, in the azimuth that is parallel to the In chains ($\overline{\Gamma X}$, [$\bar{1}10$]). The spectra are now strongly dependent upon the incidence angle and consequently also on momentum. Again a Au Fermi level reference is reproduced in the upper part of the figure. Notice that the intense feature that dominates the spectra at normal incidence disperses down towards the Fermi level and back up to approximately the same binding energy near the $\overline{X}$ zone boundary ($\theta\approx35°$). In sharp contrast to the momentum-resolved behavior perpendicular to the In chains, the image state, located ≈4.0 eV above the Fermi level, disperses parabolically (in momentum space) upwards as the electron gun is moved away from the sample normal. The presence of a Fermi level crossing near the zone boundary is also visible in the spectra. At 20° there is no emission intensity at the Fermi
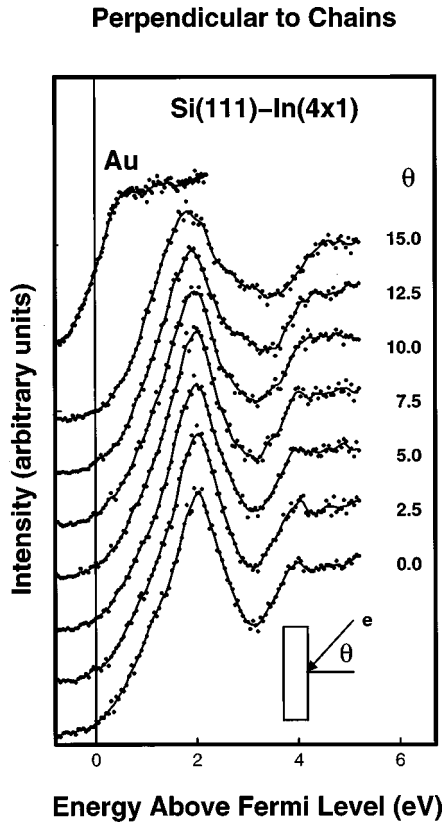
Perpendicular to Chains

Parallel to Chains

FIG. 3. Inverse photoemission spectra collected in the azimuth that is perpendicular to the In chains ($\overline{\Gamma X'}$, [$\overline{1}\,\overline{1}2$]) from predominantly single-domain 4×1 samples. The numbers on the right-hand side of each spectra are the incidence angles, relative to the sample surface normal, in degrees. The spectrum in the upper part of the figure was collected from polycrystalline Au. In the spectra collected from the 4×1 samples, no states cross the Fermi level and the binding energy of the states is almost completely independent of incidence angle and momentum.

level. By 25° a state has emerged that appears to disperse downwards towards the Fermi level. At 35° the state appears to have crossed below the Fermi level. This is convincing evidence that the overlayer system is metallic and that the Fermi level crossing occurs at $\approx 0.6\overline{\Gamma X}$.

DISCUSSION

The results that we have presented above are consistent with a recent photoemission study of the 4×1 system.[7] In the photoemission study, three In-induced, surface bands ($m_1 - m_3$) were observed to cross the Fermi level along the $\overline{\Gamma X}$ direction. All three bands have binding energy maxima at the zone boundary and approximately parabolic dispersion. The $m_1 - m_3$ bands cross the Fermi level at 0.86, 0.60, and 0.44 $\overline{\Gamma X}$, respectively. It is quite likely that these three bands merge in the inverse photoemission spectra because the instrumental energy resolution (0.6 eV) may be incapable of resolving the individual bands. The energy resolution of the photoemission experiments (0.140 eV) was approximately a factor of 4 better. Also in agreement with the results of our study they found the dispersion of the states perpendicular to the In chains to be relatively flat, confirming the 1D nature of the overlayer system. Furthermore, based upon
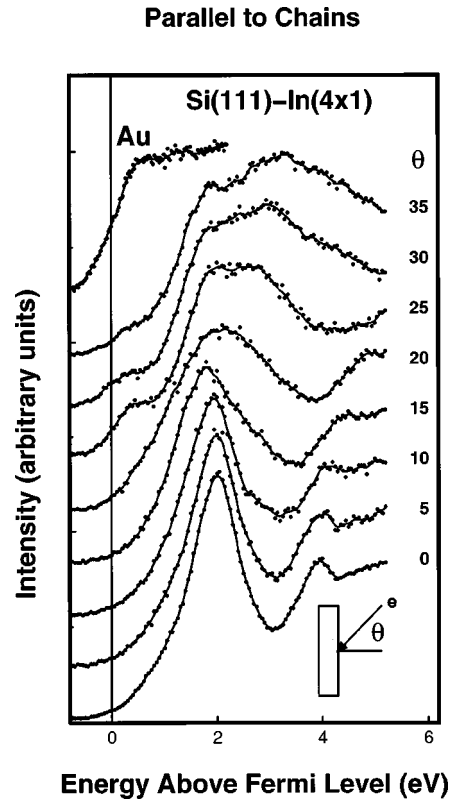
FIG. 4. Inverse photoemission spectra collected in the azimuth that is parallel to the In chains ($\overline{\Gamma X}$, [$\overline{1}$10]) from predominantly single-domain 4×1 samples. In contrast to the previous figure, the binding energy of the states are now strongly dependent on incidence angle and momentum.

a consideration of the $m_1 - m_3$ band dispersion, the authors of the photoemission study[7] suggested that the $m_1 - m_3$ bands may originate from the overlap of In $5p_{x,y}$ orbitals.

Regarding the metallicity of the 4×1 system, it is unlikely that electron counting arguments will provide much insight into the electronic structure of the overlayer until the atomic structure is solved. However, $\frac{1}{3}$ ML of In atoms in the $\sqrt{3}$ structure naturally saturates the Si(111) dangling bonds producing a semiconducting surface. If we consider creating the 4×1 structure from the $\sqrt{3}$ structure, by moving and adding In atoms to this structure, it is difficult to envisage how an autocompensated structure could be created without a considerable amount of In-In rebonding. Although this is no more than a plausibility argument, it does suggest that ordered metallic overlayer structures should not be unexpected for In coverages greater than $\frac{1}{3}$ ML.

Si(111)-In(4×1) is a member of a class of quasi-1D systems that possess chainlike overlayer structures on Si(111) that includes Si(111)-Au(5×2) (Ref. 11) and Si(111)-X(3×1) where X={Li,Na,K,Cs,Ag}.[12,13] These systems exhibit a wide range of electronic properties. For example, the Si(111)-Na(3×1) overlayer system is insulating with a relatively large band gap of 1 eV.[14] In contrast, the system that we have studied in this paper is metallic. Apart from the fact that these systems present a challenge to our understanding of surface electronic structure, they may also be systems in which, because of the reduced dimensionality, electron correlation effects are important. It would be very interesting,
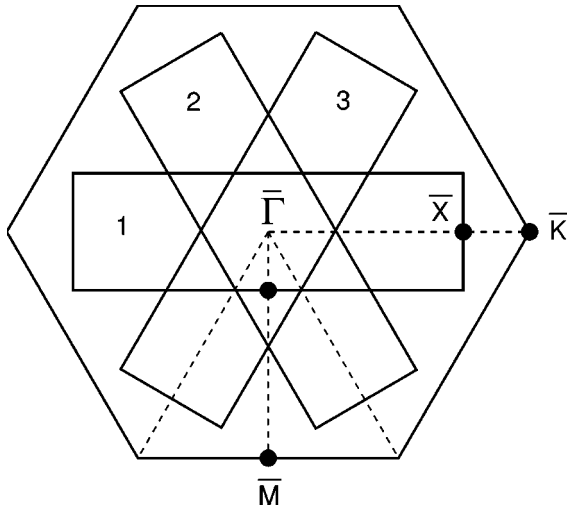
FIG. 5. The Wigner-Seitz reciprocal cell of the 1×1 hexagonal net is shown together with the Wigner-Seitz reciprocal cells of the 4×1 rectangular net in the three possible orientations that appear on the nonvicinal Si(111) surface. The three domains are numbered and referred to in the text.

for example, to find a semiconducting or insulating quasi-1D overlayer system that should, based on electron counting considerations,[15] be metallic. Unfortunately, the 4×1 system does not display this signature of a highly correlated system.

The information contained in Fig. 4 can also be used to explain why the previous inverse photoemission study of this system[1,6] was at variance with the STM (Ref. 2) and photoemission[7] studies. First, based on the results that are presented above, we would not expect to observe a Fermi level crossing at normal incidence ($\overline{\Gamma}$). This is entirely consistent with the earlier inverse photoemission results.[1,6] Second, the earlier inverse photoemission studies[1,6] were performed on samples that contained three 4×1 domains. Spectra collected along (Fig. 5) the $\overline{\Gamma M}$ direction of the 1×1 hexagonal surface net (the $[\overline{1}\,\overline{1}2]$ direction in real space) will probe the $\overline{\Gamma X'}$ direction of the rectangular 4×1 surface net in domain 1, a line 30° from the $\overline{\Gamma X}$ direction in domain 2 and a line 30° from the $\overline{\Gamma X}$ direction in domain 3. In the simplest case, the contribution from domains 2 and 3 to the inverse photoemission spectra will be equivalent. We suggest that the earlier study did not detect a Fermi level crossing simply because the dispersion of the In-induced unoccupied states along the In chains was not studied. To do this, it is necessary to map along the $\overline{\Gamma K}$ direction of the 1×1 hexagonal net. Although the other two domains will, once again, contribute to the inverse photoemission spectrum, it should be possible to detect the Fermi level crossing if the picture that we have developed here is correct. We believe this explanation resolves the controversy regarding the metallicity of this system.

Finally, we note that recent high resolution photoemission studies of bulk quasi-1D systems[16–18] have observed vanishing emission intensity at the Fermi level. This may be a consequence of the fact that quasiparticles do not form in these systems and that Fermi liquid theory[19,20] does not provide an accurate picture of the electronic system.[17,18] Our inverse photoemission studies of the quasi-1D 4×1 system were simply not performed at high enough resolution to determine whether the Fermi level emission is unconventional. However, it should be possible to do this with photoemission where it is now routinely possible to achieve an energy resolution of less than 40 meV.

CONCLUSIONS

We have studied the unoccupied electronic structure of the Si(111)-In(4×1) system with inverse photoemission using single domain samples. In agreement with recent photoemission[7] and STM (Ref. 2) studies, we found the overlayer system to be quasi-1D and metallic. A clear Fermi level crossing was detected along the $\overline{\Gamma X}$ direction of the reciprocal zone.

ACKNOWLEDGMENTS

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