

LETTER TO THE EDITOR

Many-body effects in the electronic structure of Sn/Si(111)- α - $\sqrt{3}$

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Abstract

The unoccupied electronic structure of the model interface Sn/Si(111)- α - $\sqrt{3}$ has been measured at room temperature (RT) using angle-resolved inverse photoemission spectroscopy (KRIPES). In addition to a partly occupied surface band crossing the Fermi level, there is a second unoccupied surface state located 1.5 eV above E_F ; the existence of these two surface states is not compatible with the single adatom site used to describe the α - $\sqrt{3}$ reconstruction. These surface states receive a natural explanation, once many-body effects are introduced, in the framework of a dynamical fluctuations model, where two types of adatom site, reminiscent of a possible low-temperature (3×3) phase, coexist at RT.

The ($\sqrt{3} \times \sqrt{3}$)R30° reconstructions induced by 1/3 ML coverage of trivalent or tetravalent atoms adsorbed on the (111) face of group IV semiconductors are old and familiar objects in surface science [1]. At the heart of these $\sqrt{3}$ reconstructions are adatoms at the T₄ site, directly above a second-layer substrate atom, which bind to three atoms in the substrate first layer [2]. This adatom–T₄ model, widely accepted for trivalent adatoms on top of Ge(111) and Si(111), is also believed to be valid for tetravalent adatoms (Sn, Pb) in a $\sqrt{3}$ adlayer structure. However, the recent discovery of a reversible phase transition α - $\sqrt{3} \leftrightarrow (3 \times 3)$ at low temperature in the systems Pb(Sn)/Ge(111) has shown that these systems have not yet delivered all their secrets [3].

Indeed, a number of recent results seem hardly compatible with the ideal T₄ model. The Sn 4d core levels, for example, clearly show two components instead of the single one expected from the unique T₄ site of the ideal structural model [4]. It has also recently been shown for the Sn/Ge(111) interface [5, 6] that the T₄ model is not sufficient to account for an occupied surface state lying deeper than the partly filled surface state which gives α - $\sqrt{3}$ its metallic character. On the basis of the intriguing similarities between the electronic structure of the (3×3) and the $\sqrt{3}$ reconstructions of Sn/Ge(111), some authors [5, 6] have proposed that a

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disordered form of the low-temperature (LT) (3×3) phase may survive at room temperature (RT). In fact, first-principles computer simulations suggest that at RT the Sn atoms fluctuate between two different positions corresponding to the (3×3) reconstruction, which shows a pronounced vertical rippling of the Sn layer, where one Sn atom moved up and two atoms moved down are separated by roughly 0.3 \AA [5, 7].

On the other hand, recent x-ray diffraction data on Sn/Ge(111) do not support this interpretation [8,9], suggesting rather a unique T_4 site for Sn adatoms in the $\sqrt{3}$ reconstruction observed at RT. Other authors have recently stressed the crucial role played by defects in the $(3 \times 3) \leftrightarrow \sqrt{3}$ phase transition [10, 11]. It has been shown that a remnant of the LT (3×3) phase could be stabilized at RT around substitutional Ge adatoms on a significant fraction of the surface [10], in coexistence with an unperturbed $\alpha\text{-}\sqrt{3}$ phase. These defects may severely complicate the interpretation of existing results. There is however a way to reduce the defect-induced perturbation. With that aim, we have investigated the isoelectronic system Sn/Si(111)- $\alpha\text{-}\sqrt{3}$, where it has recently been shown [12] that the defect-induced (3×3) perturbations at RT have a much shorter extent in comparison to those for Sn/Ge(111). In this respect, it is expected that the Sn/Si(111)- $\alpha\text{-}\sqrt{3}$ reconstruction may be a better testing ground for validating one of the two models currently under debate.

Realizing that the surface electronic properties should be very sensitive to the precise structure of these model interfaces, we have investigated the unoccupied electron states of Sn/Si(111)- $\alpha\text{-}\sqrt{3}$ using angle-resolved inverse photoemission spectroscopy (KRIPES). In addition to a ‘metallic’ surface state crossing the Fermi level (E_F), we report for the first time a second empty surface state lying about 1.5 eV above E_F . The existence of these two surface states is not compatible with the ideal T_4 model which would show either a half-occupied metallic band crossing E_F , or an insulating phase if correlation effects are introduced. In contrast, these two surface bands receive a natural explanation, once correlation effects are appropriately taken into account, in the framework of the dynamical fluctuations model as originating from a dynamic (3×3) periodicity.

The experiments were performed in two separate ultrahigh-vacuum chambers equipped respectively with a scanning tunnelling microscope (STM) and with both low-energy electron diffraction (LEED) facilities and the inverse photoemission set-up ($h\nu = 9.5 \text{ eV}$, overall energy resolution $\Delta E \simeq 0.35 \text{ eV}$) [13]. Prior cleaning of the Si(111) substrate (n-type, phosphorus-doped, 0.02 \Omega cm) was done *ex situ* by a wet hydrogenation procedure. Inside the UHV, the (7×7) reconstruction was then formed by high-temperature annealing below $1200 \text{ }^\circ\text{C}$, either by direct Joule heating or by electron bombardment on the back. The preparation procedure of the $\alpha\text{-}\sqrt{3}$ phase was carefully optimized using STM, which allows proper control of the atomic composition within the adatom layer which can vary continuously between the limiting cases of the $\text{Si}_x\text{Sn}_{1-x}$ 2D solid solution, namely $\alpha\text{-}\sqrt{3}$ ($x \approx 0$, corresponding to $\theta_{\text{Sn}} = 1/3$ monolayer (ML)) and $\gamma\text{-}\sqrt{3}$ ($x \approx 0.5$, $\theta_{\text{Sn}} = 1/6$ ML) [14]. After tin deposition on the (7×7) surface, the sample was annealed at around 900 K for about four minutes, stabilizing large, flat areas of nearly perfect $\alpha\text{-}\sqrt{3}$ -reconstructed terraces with a residual substitutional Si-adatom concentration lower than 5% (typically 3%) as estimated by STM.

Figure 1 shows selected KRIPES spectra (photon quantum yield normalized to the transmitted current) representative of the $\alpha\text{-}\sqrt{3}$ phase along the high-symmetry directions $\bar{\Gamma}\bar{K}'$ of the $\sqrt{3}$ surface Brillouin zone (SBZ). Several structures can be seen in the small energy range $[0, 5 \text{ eV}]$ above E_F . The surface origin of the two states which are close to E_F , U'_1 and U'_2 , is readily established by considering their high sensitivity to gas adsorption. Figure 2 shows how both U'_1 and U'_2 become strongly attenuated upon adsorption of $\approx 1 \text{ L}$ ($\text{L} \equiv \text{langmuir}$) of activated hydrogen. The higher-energy states, practically unchanged by the adsorption, are thus assigned instead to bulk states.

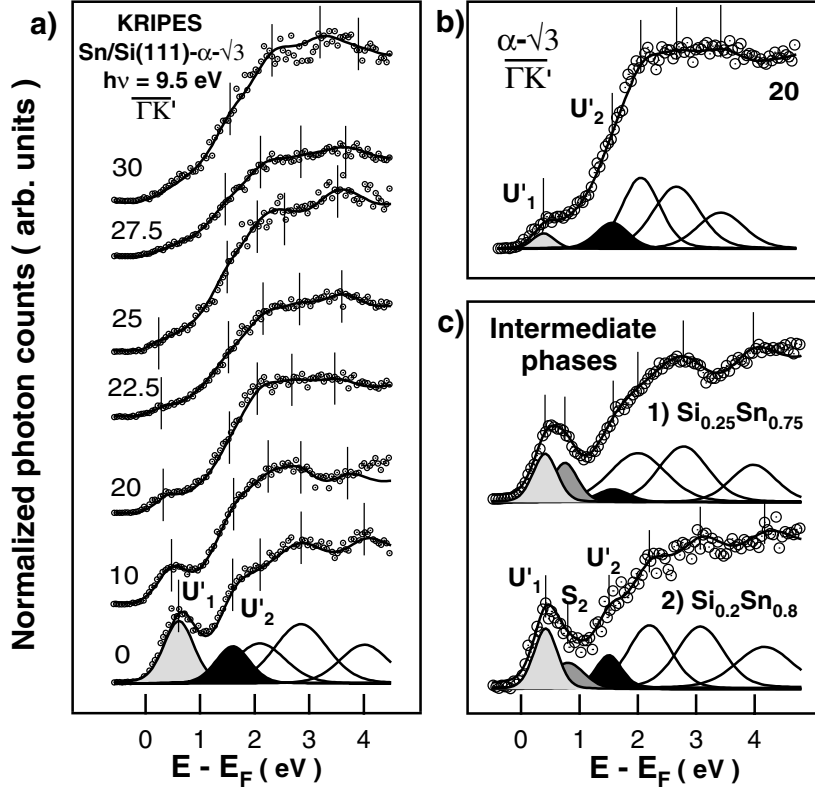


Figure 1. (a), (b) Selected Kripes spectra (photon quantum yield normalized to the transmitted current) representative of the $\alpha\text{-}\sqrt{3}$ phase for various electron incidence angles θ along the high-symmetry direction $\bar{\Gamma}\bar{K}'$ of the $\sqrt{3}$ SBZ. The positions of the various peaks and shoulders, marked by the vertical bars, were determined by adjusting a sum of Gaussian lineshapes and a background baseline to the raw data (the solid line is the envelope of the synthetic spectra obtained from the addition of the Gaussian peaks and the background, and open circles are raw experimental data). Two spectra in (a) and (b) show this decomposition in detail. (c) Normal-incidence Kripes spectra of two intermediate phases with an increasing concentration of substitutional Si adatoms, which are associated with the additional empty surface state S_2 .

In the remainder of this work, we will focus on the two empty surface states U'_1 and U'_2 . The dispersing U'_1 state, the closest to E_F , is located around 0.5 eV above E_F at the centre, $\bar{\Gamma}$, of the SBZ. Figure 3 indicates that U'_1 disperses downwards in the $\bar{\Gamma}\bar{M}'$ direction by up to ≈ 0.37 eV. The dispersion of U'_1 is more pronounced along $\bar{\Gamma}\bar{K}'$, and it is obvious in figure 1 that the intensity of U'_1 decreases with electron incidence angle θ along $\bar{\Gamma}\bar{K}'$, finally vanishing around $\theta = 27^\circ$ near to the \bar{K}' point, indicating a clear Fermi level crossing. The $\text{Sn/Si}(111)\text{-}\alpha\text{-}\sqrt{3}$ reconstruction thus has a metallic character, in accordance with the electron counting rule on a simple adatom T_4 model: three electrons of the single tetravalent tin adatom per $\sqrt{3}$ unit cell are involved in the covalent bonding with three Si atoms of the first substrate layer, while the remaining electron fills the dangling bond. This state which primarily derives from adatom p_z states could readily explain the observation of U'_1 above E_F . The occupied counterpart of U'_1 revealed by direct photoemission has been reported [15]. We note, however, that it is the first time that Fermi level crossing as seen from the unoccupied side of the metallic band is reported in an unambiguous way. Although Fermi level crossing has been claimed earlier [16],

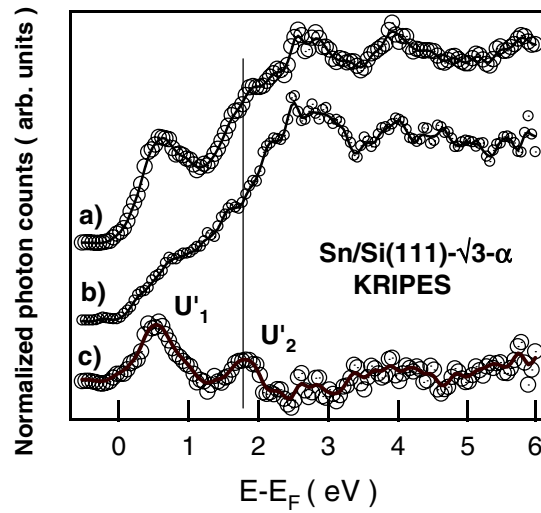


Figure 2. A normal-incidence ($\theta = 0^\circ$) KRIPES spectrum of Sn/Si(111)- $\alpha\text{-}\sqrt{3}$ before (a) and after (b) exposure to roughly 1 L of atomic hydrogen. (c) The KRIPES difference curve for spectra (a) and (b).

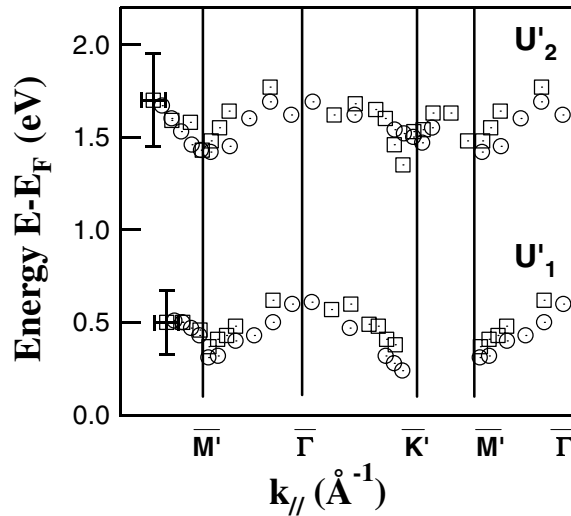


Figure 3. Experimental band dispersions $E(k_{\parallel})$ of the U'_1 and U'_2 surface states of Sn/Si(111)- $\alpha\text{-}\sqrt{3}$.

a significant emission near E_F remains visible at the \bar{K}' point, and Fermi level crossing is not obvious from the published data alone⁴.

The other surface state U'_2 , which appears as a marked shoulder around 1.6 eV, can be unambiguously followed throughout the whole SBZ (figures 1(a) and 1(b) and figure 3).

⁴ This is most probably related to the fact that the authors of reference [16] did not investigate the true $\alpha\text{-}\sqrt{3}$ phase, since we have found that the empty states are sensitive to the actual surface composition of the 2D solid solution $\text{Si}_x\text{Sn}_{1-x}/\text{Si}(111)$. This would also explain the differences in relative intensity of the surface-derived features when their spectra are compared to the present results.

Figure 1(c) also shows two spectra characteristic of two intermediate phases $\text{Si}_x\text{Sn}_{1-x}$ with an increasing number of substitutional Si adatoms. The growth of an additional surface state S_2 which occurs at the expense of U'_1 shows that S_2 is intrinsic to the Si adatoms⁵. This is in strong contrast with the decrease of the U'_2 intensity which unambiguously proves that U'_2 cannot be attributed to Si substitutional defects or their nearest-neighbour Sn adatoms but is really an intrinsic feature of the true α -phase. One could try to explain U'_2 by introducing electron correlation effects in the T_4 model. It is well known, however, that these effects for a half-occupied band and a sufficiently high intra-site Coulomb interaction (see below) create a Mott–Hubbard insulating surface. We conclude that the adatom– T_4 model does not account for the electronic properties observed in the $\text{Sn}/\text{Si}(111)\text{-}\alpha\text{-}\sqrt{3}$ reconstruction. Another structural model is necessary to explain the existence of the two dispersive surface states. Fluctuations in the tin-adatom array have been suggested by the occurrence of two components in the Sn 4d core-level spectra [4] of $\text{Sn}/\text{Si}(111)\text{-}\alpha\text{-}\sqrt{3}$ at RT. The same kind of fluctuation has also been reported [17] for the isoelectronic system $\text{Sn}/\text{Ge}(111)\text{-}\alpha\text{-}\sqrt{3}$, which has recently been shown to undergo a reversible $\sqrt{3} \leftrightarrow (3 \times 3)$ transition at low temperature [3, 18]. Although different interpretations of the real nature of the low-temperature (3×3) phase of $\text{Sn}/\text{Ge}(111)$ still appear under debate, recent structural studies, both experimental [9, 19] and theoretical [7], do agree that the LT phase presents two structurally different Sn adatoms. Of the three adatoms of the (3×3) unit cell, one appears significantly displaced outwards by more than 0.25 Å with respect to the other two. In their dynamical fluctuations model, Avila *et al* have proposed that these two kinds of site still exist at RT, and that adatoms fluctuate between the two positions [5]. The time-averaged dynamical fluctuation of the overlayer at RT gives STM pictures with uniform $\sqrt{3}$ structure. The dynamical fluctuations model readily explains the two components of the Sn 4d core level detected at RT, and also accounts for the striking similarity between the electronic structures of the RT and LT phases as revealed by direct photoemission [5, 6]. In the valence band, the persistence at RT of two kinds of Sn adatom having different s– p_z hybridization states also explains the observation of an additional, deeper surface state not crossing E_F [5, 6].

Although the observation of a complete transition to a possible LT (3×3) phase has not been reported yet for the $\text{Sn}/\text{Si}(111)$ system, it is reasonable to expect strong similarities with the isoelectronic $\text{Sn}/\text{Ge}(111)$ system [12, 20–22]. We have substantiated this point of view by means of first-principles calculations. We have thus used a local orbital self-consistent DFT-LDA method on a (3×3) unit cell [23]. As in the case of the $\text{Sn}/\text{Ge}(111)$ interface [7], we have considered a relaxed surface where, in the (3×3) unit cell, one Sn atom is displaced upwards and the other two adatoms are displaced downwards w.r.t. the ideal position of the $\sqrt{3}$ geometry, with a total distortion of ~ 0.3 Å. The calculated DFT-LDA bands, shown as broken lines in figure 4, are readily understood in terms of the reconstructed geometry. The lower surface band, which accommodates two electrons, is mainly localized on the upper Sn adatom and has more s character. The other two surface bands, located around E_F , mainly derive from the two dangling bonds of the recessed adatoms. The more pronounced p_z character of these dangling bonds tends to shift their levels towards higher energies. The presence of two equivalent adatoms within the (3×3) unit cell induces the overlap of the two LDA surface bands and the system is metallic. This is in accordance with the electron counting rule since these two bands, which can accommodate four electrons, are filled with a single electron. However, we will show that this one-electron picture has to be extended by inclusion of many-body effects in order to describe the experimental surface electronic structure in a proper way.

Owing to their relatively small bandwidths $W \leq 0.35$ eV, correlation effects on the surface bands are thought to be important [18, 24]. Correlation effects have thus been explicitly

⁵ The area ratio $I(S_2)/I(U'_1)$ has been used here to titrate the Si-adatom concentration (see reference [14]).

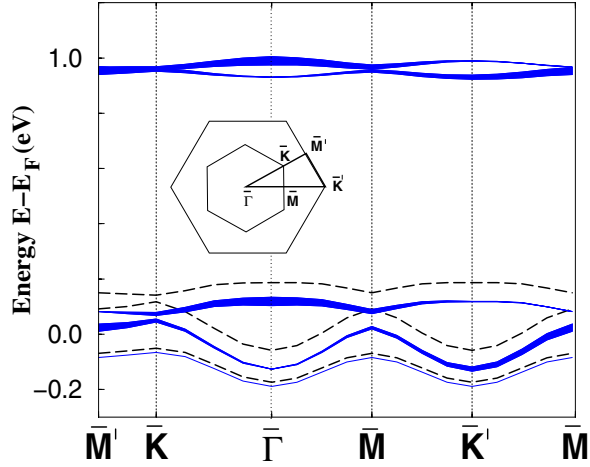


Figure 4. Theoretical DFT-LDA (dashed lines) and many-body (full lines) surface bands on a (3×3) surface Brillouin zone (SBZ) with three adatoms per cell and two structurally different Sn adatom sites (see the text). E_F refers to the correlated bands. A $(\sqrt{3} \times \sqrt{3})R30^\circ$ SBZ is also used as an extended zone (primed letters). The normalized k -dependent values of the (inverse) photoemission matrix elements for selected bands appear in the extended zone scheme as a varying thickness. The inset shows a schematic view of the various surface Brillouin zones of interest, (3×3) (small hexagon, non-primed letters) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ (large hexagon, primed letters).

taken into account by solving a generalized Hubbard Hamiltonian for our (3×3) model through the local self-energy approach [25]. An effective intra-site Coulomb interaction $U_{eff} = 1.4 \pm 0.2$ eV was first estimated by restricted LDA calculations where the filling factors of the surface bands were varied and the effect of these changes on the surface band levels evaluated [5, 25]. U_{eff} is an average value representing both raised- and lowered-adatom dangling bonds. The full lines of figure 4 show that the empty correlated bands near E_F are substantially modified with respect to the one-electron LDA bands. In fact, most of the many-body effects mainly concern the unoccupied states. The most important effect of correlation is the splitting of the two LDA surface bands around E_F into two discontinued groups of two correlated bands. Although this kind of band-gap opening evokes a Mott–Hubbard transition [26], it is important to realize that the lower group of bands, with a dispersion similar to the initial LDA bands, is still crossing the Fermi level. Indeed, starting from the upper two LDA bands which could accommodate four electrons (per unit cell), the two correlated bands near E_F can now accommodate three electrons [25], and are actually filled by a single electron. Most of these bands crossing E_F to which we can ascribe U'_1 will thus appear in the empty states. In this quarter-filling system with one electron every second orbital, the condition for strong correlation $U \gg W$ is not sufficient to induce a Mott–Hubbard transition due to the availability of unoccupied sites. In order for a metal–insulator transition to appear, another condition involving the nearest-neighbour, inter-site Coulomb interaction $J \gg W$ should be fulfilled, which is obviously not the case for the present system where we found $J_{eff} \simeq 0.25$ eV. This is at variance with the results obtained on a ‘flat’ $\sqrt{3} \times \sqrt{3}$ reconstruction with a single adatom site, where the same kind of analysis leads to the formation of a Mott–Hubbard insulating system [27].

The upper group of multi-electron bands has appeared ≈ 1.0 eV above E_F with a smaller bandwidth than the lower group, and a total weight of only one electron per unit cell [25]. The value of 1.0 eV is similar to, although a little smaller than, the effective intra-site Coulomb

energy U_{eff} . It is also in good agreement with the experimental mean separation between U'_1 and U'_2 which equals 1.1 eV. The upper correlated bands nicely explain the U'_2 structure detected in inverse photoemission. The dispersion of U'_2 follows that of U'_1 , albeit with a reduced bandwidth, in accordance with the behaviour of the upper and lower groups of correlated bands. In the difference curve of figure 2, it is also apparent that the intensity of U'_2 is roughly half that of U'_1 . Although possibly fortuitous⁶, this value is in good agreement with the predicted weight ratio of one half between the empty part of the correlated upper and lower bands. The difference between the bandwidths (particularly for U'_2) measured in experiment and calculated in theory can be ascribed in part to the limited accuracy of the measurements and to limitations in the approximations involved in the calculations. Moreover, the centre of gravity of the narrow bands sensitively depends on the adatom positions, and the dynamical fluctuations of the adatoms should therefore broaden the energy spectrum. On the other hand, the detailed dispersion of the observed surface bands, described in a $(\sqrt{3} \times \sqrt{3})$ SBZ, compares favourably with the dispersion of the theoretical surface bands calculated in a (3×3) SBZ. For this purpose, the LDA surface bands near E_F have been used to optimize a simple tight-binding (TB) model. In the framework of this simple TB model, it is easy to evaluate the matrix elements involved in direct and inverse photoemission along the various symmetry lines of the (3×3) SBZ. The thickness of the solid lines representing the correlated bands in figure 4 corresponds to the calculated matrix elements in an extended zone scheme. From figure 4, it is apparent that the portions of the (3×3) bands with high matrix elements broadly reproduce the observed dispersion of U'_1 and U'_2 in the $(\sqrt{3} \times \sqrt{3})$ SBZ.

In conclusion, inverse photoemission has revealed two (partly) unoccupied surface states U'_1 and U'_2 in the model interface Sn/Si(111)- α - $\sqrt{3}$. The presence of two empty surface states is not compatible with a 'flat' $\sqrt{3} \times \sqrt{3}$ reconstruction having a single adatom site. Rather, U'_1 and U'_2 receive a natural explanation in the framework of a dynamical fluctuations model, where two kinds of Sn adatom site reminiscent of a low-temperature (3×3) phase do persist at room temperature. Correlated surface bands incorporating many-body effects in a non-restricted way provide a complete description of the experimental surface bands, providing therefore a clear confirmation of the validity of the dynamical fluctuations model for describing this prototypical system at room temperature.

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⁶ The difference curve has been calculated from an angle-resolved KRIPES spectrum at the centre of the SBZ. Furthermore, matrix element effects have not been considered.

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