Structural Origin of the Sn 4*d* Core Level Line Shape in Sn/Ge(111)-(3 × 3)

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High-resolution photoemission of the Sn 4*d* core level of Sn/Ge(111)-(3 × 3) resolves three main components in the line shape, which are assigned to each of the three Sn atoms that form the unit cell. The line shape found is in agreement with an initial state picture and supports that the two down atoms are inequivalent. In full agreement with these results, scanning tunnel microscopy images directly show that the two down atoms are at slightly different heights in most of the surface, giving rise to an inequivalent-down-atoms (3 × 3) structure. These results solve a long-standing controversy on the interpretation of the Sn 4*d* core-level line shape and the structure of Sn/Ge(111)-(3 × 3).

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Materials that are characterized by a strong interplay between different degrees of freedom tend to exhibit complex physical phenomena, difficult to understand within conventional notions [1]. A conspicuous example in low-dimensional systems is the (3 × 3) structure formed by 0.33 monolayers (ML) of Sn atoms on a Ge(111) surface [2]. In this structure, one Sn atom per surface unit cell is at a higher level than the other two [3–5]. The electronic and lattice degrees of freedom are coupled, so that the atom displaced upwards receives charge from the two down atoms (one-up, two-down model, 1U2D) [4]. A delicate balance between elastic and electronic energies stabilizes this phase only in the 25–220 K temperature range. Above ~220 K, thermal induced vertical fluctuations destroy the (3 × 3) long-range order [6], and below 25 K, a flat, Mott insulating phase is formed [7].

The 1U2D model for the surface structure is supported by compelling experimental [2–12] and theoretical [3,4,4–16] evidence. However, a controversy lasting almost a full decade affects the interpretation of the Sn 4*d* core-level line shape and contradictory results are obtained from core-level related structural techniques. Early work identified two different Sn 4*d* components [17], which were related later on to the up and down Sn atoms. The lowest binding energy (BE) component was found to be more intense and thus was attributed to the down atoms, which are twice as many as the up atoms [4,18,19]. However, within an initial state photoemission picture, the lowest BE component is expected to originate from up Sn adatoms, which are charge acceptors. The apparent exchange was attributed to unclear site-dependent final-state screening effects [4,18]. Later on, doping experiments [20] showed the filled valence character of the lowest BE component. These two arguments support a unit cell containing two up atoms (the 2U1D model). Finally, core-level photoelectron diffraction (PED) concludes that down adatoms correspond to the lowest BE component [21], while chemically resolved x-ray standing wave experiments support the opposite assignment and find 2U1D fluctuations (at 300 K) [22]. This long-standing debate on the interpretation of the Sn 4*d* line shape reaches far beyond this particular system. Taking into account the known role of electron correlation effects in the Sn/Ge(111) surface [7,23], and the proposed formation of a magnetic ordered ground state in Sn/Si(111) [24,25], the polemic affects both our understanding of shifting mechanisms in surface core levels and the interplay between crystalline structure and charge transfer in complex systems.

This Letter reports on high-resolution photoemission and scanning tunnel microscopy (STM) experiments. The contribution of three kinds of Sn atoms in the unit cell is resolved with both techniques, indicating that the two down Sn atoms are at slightly different heights, forming an inequivalent-down-atoms (IDA)-(3 × 3) structure. The results conclusively solve the contradictions on the interpretation of the Sn 4*d* core-level line shape, and support a model fully consistent with an initial state picture.

The experiments were carried out in two different ultrahigh vacuum chambers for photoemission spectroscopy and STM. STM images were obtained with a low-temperature microscope (Omicron) and analyzed with the WSXM package [26]. Photoemission experiments were performed at the Swiss Light Source (SIS beam line) using a Scienta SES-2002 electron analyzer. The energy resolution was 20 meV. The substrate was *n*-type Ge(111) ($\rho = 0.4\ \Omega\,\mathrm{cm}$). The surface preparation has been described elsewhere [4]. The coverage was calibrated from the Sn 4*d*/Ge 3*d* intensity ratio, surface state intensity, and the evolution of the low-energy electron diffraction (LEED) pattern, in agreement with previous work [18].

Figure 1 shows a series of Sn 4*d* core levels for increasing coverages up to 0.5 ML. In previous studies, the

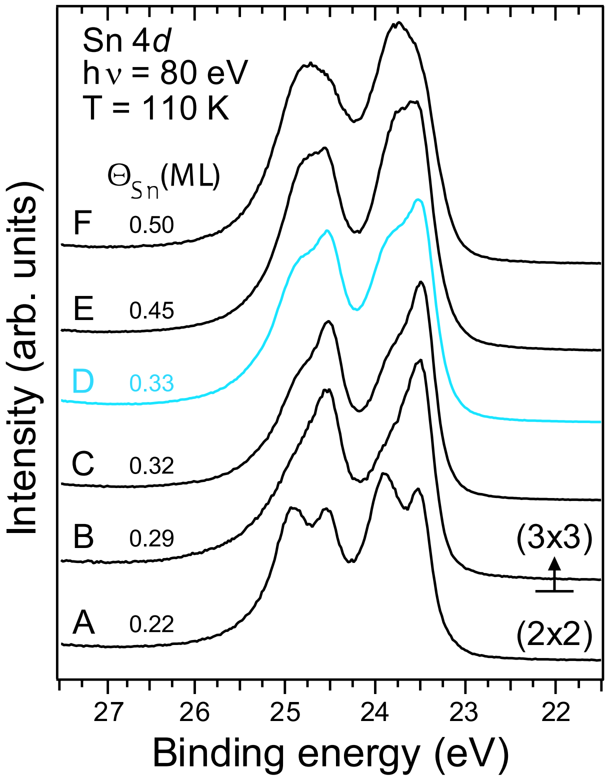

FIG. 1 (color online). Sn 4d core-level spectra (normal emission) for Sn coverages below 0.5 ML. All spectra correspond to a (3 × 3) LEED pattern, with the exception of spectrum A.

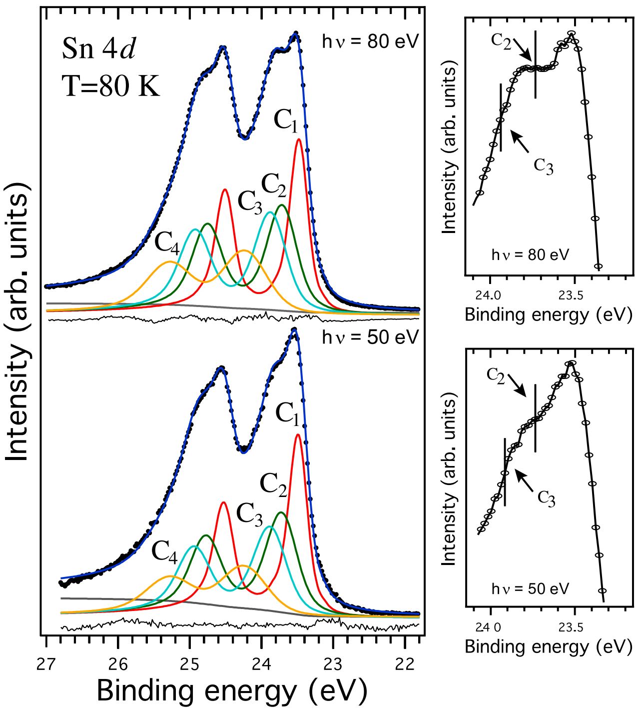

FIG. 2 (color online). Normal emission Sn 4d core-level spectra (circles). Left: solid lines show the four doublets used to deconvolute the spectra and the resulting fit. Right: zooms of the 4$d_{5/2}$ area. Vertical lines indicate the BEs of C_2 and C_3. The continuous line joining the experimental points is a guide to the view.

evolution of the line shape was described assuming the existence of two main components [4,18,19], whose intensities would change with Sn coverage. The first one (at 23.9 eV) is already observed at very low coverages. The second one (at 23.5 eV) grows as the (3 × 3) phase is formed. Our high-resolution data reveal a more complex behavior. As the (3 × 3) domains grow, the peak observed at low coverages at 23.9 eV is damped (see spectrum B for 0.29 ML), indicating that it does not correspond to Sn atoms in the (3 × 3) structure. For coverages in the range 0.29–0.33 ML the characteristic line shape of the (3 × 3) phase shows up, with a main peak at 23.5 eV and a hump at approximately 23.75 eV. This line shape corresponds to a surface covered uniformly by the (3 × 3) structure, as supported by STM images. For coverages exceeding 0.33 ML, another component close to 23.8 eV is detected.

The line shape corresponding to a high quality (3 × 3) phase at 0.33 ML exhibits several unique features when observed with high resolution at 80 K (Fig. 2). The most evident is that the low BE side of the peak and the maximum at 23.5 eV are defined by a narrow component (C_1), and that close to the maximum there is an almost flat area around 23.7 eV (for $h\nu = 80$ eV). A fit was made using Gaussian-convoluted Doniach-Šunjić doublets [18] and a Shirley background. The fit was optimized using a Levenberg-Marquardt algorithm. The spin-orbit splitting, branching ratio, and singularity index were kept constant for all the doublets at each photon energy. The quality of the fit was judged from two reliability factors, the normalized χ^2 and the normalized mean of the residuals R [27], and from visual inspection. As the first step, we tried to fit the line shape obtained for $h\nu = 80$ and 50 eV photon energy using three doublets. The starting parameters were taken from previous work [18]. After optimization, the parameters changed only slightly, with the exception of the C_1 Lorentzian width, which had to be reduced from 210 meV to 185 meV, and the relative intensities of the three components, which became 1.14:1:0.8. For these parameters, $\chi^2 = 1.82$ and $R = 0.027$ were reached. Although these are good values, the fit with three doublets had several shortcomings. First, the line shape in the area around the main maximum at 23.5 eV was not perfectly reproduced. Second, the intensity ratio between the components was far from the expected 1:2 surface stoichiometry [28]. Because of these reasons, we decided to perform a new fit, trying to better reproduce the area around 23.5 eV. Four doublets were used instead. A first doublet (C_1) is needed to reproduce the maximum at lowest BE. An additional doublet (C_4) is needed to account for the high BE part of the spectrum. Finally, two additional doublets (C_2 and C_3) are necessary to fit the area around 23.8 eV. C_4 has been previously attributed to surface defects [18]. We found that its intensity is not affected by the surface preparation, but it increases strongly as temperature decreases, which indicates a different origin [29]. Its BE can be accurately determined from this additional information. The other two doublets, C_2 and C_3, are necessary to resolve the spectral features close to 23.8 eV, and their change with photon energy crucially facilitates the task of obtaining its BE and intensity. For instance, the flat line shape observed for 80 eV close to the maximum at 23.5 eV and the slope change for 50 eV (see right panels of Fig. 2) cannot be reproduced using a single doublet. The location of C_2 is determined by the flat shape observed at 80 eV, while the slope break seen at 50 eV fixes the position of C_3. As a first step to obtain a unique fit, only the low BE region and the first maximum at 23.5 eV were considered. The line shape in this BE range reflects mainly component C_1, whose Lorentzian width (LW) is smaller than the value required for the other doublets (C_2, C_3, and C_4) [30]. After a full optimization, we obtained $\chi^2 = 1.09$ and $R = 0.019$, which are better than for a three component fit [32]. All fit parameters are listed in Table I.

The three components C_1, C_2, and C_3 obtained can be naturally attributed to the three Sn atoms present in the (3×3) unit cell. We assign C_1 to the single up atom, and C_2 and C_3 to each of the two down atoms. This assignment is supported by several features. First, the relative intensities of the three components are now very close to each other for both photon energies. Second, C_2 and C_3 have similar widths but are distinctly broader than C_1. Finally, C_1 is significantly more separated in BE from C_2 and C_3, which have closer BEs. This assignment is consistent with an initial state picture, because the Sn atom at the up position is the charge acceptor, so its component should exhibit the lowest BE. The fact that the two components C_2 and C_3 appear at different BEs reflects a different charge state. The simplest explanation is that the two down atoms are not at the same height, forming an IDA-(3×3) structure. Since the BE difference between C_2 and C_3 is smaller than for C_1, we expect that the corresponding height difference is also smaller.

We have performed STM experiments at 77 K to explore the structural origin of the IDA-(3×3) detected in the Sn 4*d* core level. Figures 3(a) and 3(b) show a representative area of the surface for filled (empty) states. Each up atom, which is imaged as a brighter (darker) spot, is surrounded by six down atoms, observed as darker (brighter) protrusions in a filled (empty) states image. A visual inspection reveals that some protrusions corresponding to down atoms are brighter (darker) than others. A zoom of the filled state image highlighting this fact is displayed in Fig. 3(a). This finding has been analyzed quantitatively by performing a height analysis within ~500 unit cells. Six representative height profiles are shown in Fig. 3(c) for both filled and empty states. Two different heights are observed for the two down atoms. Experimental STM parameters like voltage, tunneling current, or sweep direction do not modify the height difference between down atoms, which is reproducibly observed for several different samples and tips. An IDA-(3×3) structure is observed in ~80% of all down atoms at 77 K. The height of up atoms in the IDA-(3×3) structure is very well defined. On the contrary, the height distribution of down atoms is broader at 77 K [29]. This feature certainly contributes to the larger Gaussian width of components C_2 and C_3, with respect to C_1, although photoemission experiments at lower temperatures indicate that there is a significant vibrational contribution. We conclude that STM images and a systematic height analysis reveal two kinds of down atoms, a result that fully backs up the two inequivalent components in Sn 4*d* core-level spectra assignment to the down atoms and the IDA-(3×3) structure.

A clear picture on the structural origin of the different components observed in the Sn 4*d* core level and on the nature of the (3×3) structure emerges from these data. The three components found directly reflect that one Sn atom shows a larger vertical displacement than the other two, which are at slightly different, lower heights. The Sn 4*d* line shape is straightforwardly understood within an initial state picture. The new analysis explains the inconsistencies in the results of different experimental techniques. First, the deconvolution found explains doping experiments within an initial state picture and within the 1U2D structural model, because in the new assignment the charge acceptor component appears at lowest BE [20,33]. Second, the contradictory results of structural techniques relying on the core-level deconvolution [21,22] are also explained, taking into account that there are three independent components of close intensity in the line shape, instead of only two, and that they probably survive at room temperature and above. Although the height difference between the two down atoms in the IDA-(3×3) structure is significant, it is always much smaller than the up-down total corrugation, so that a 1U2D description is correct. This is also in agreement with recent Fermi surface studies supporting the 1U2D model [12]. In fact, the observation of this small height difference is only possible in images taken with an excellent vertical and lateral resolution. This explains why a (3×3) structure with equivalent

TABLE I. Parameters used in the deconvolution shown in Fig. 2. The branching ratio and the singularity index are 1.34 ± 0.05 (1.46 ± 0.05) and 0.073 (0.085) for $h\nu = 80(50)$ eV, respectively. The spin-orbit splitting is -1.05 eV.

Component	GW (meV)	LW (meV)	BE (eV)	Area ratio
C_1	210 ± 6%	140 ± 7%	23.50 ± 0.02	1.00 (1.00)
C_2	350 ± 8%	220 ± 5%	23.73 ± 0.04	0.98 (0.96)
C_3	390 ± 8%	220 ± 5%	23.89 ± 0.04	0.95 (0.84)
C_4	590 ± 5%	220 ± 5%	24.24 ± 0.08	0.75 (0.60)

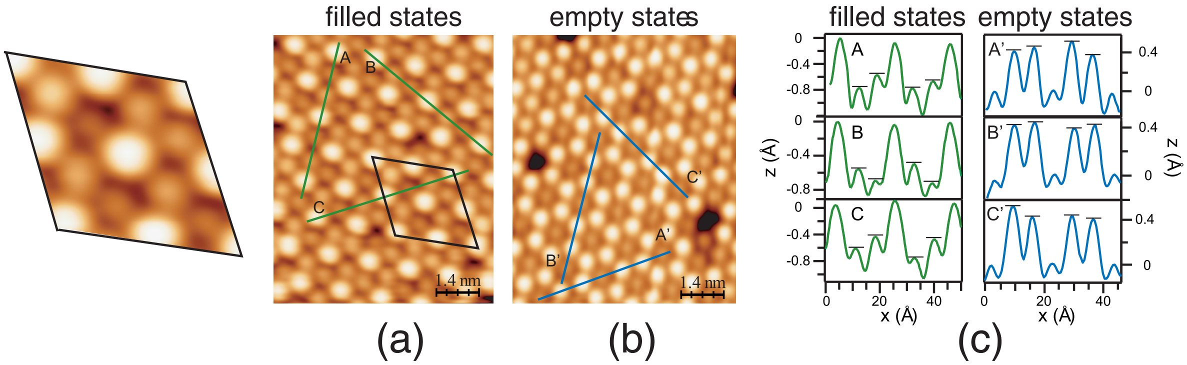

FIG. 3 (color online). Filled [(a), $V = -1.0$ V, $I = 1.0$ nA] and empty [(b), $V = -1.0$ V, $I = 2.0$ nA] states' STM images for the (3×3) phase at 77 K. Note the different heights of the down atoms in the zoom from (a) shown on the left. (c) Height profiles corresponding to the highlighted directions from (a) and (b). The height of the down atoms is marked with horizontal lines for the upper (lower) down atom. The directions are selected so that no nearest neighbor is a defect.

down atoms is usually observed. Nevertheless, asymmetric down atoms are seen in previous STM work [34,35].

In summary, we find a new structure for the (3×3) phase with two inequivalent down atoms, conforming to an IDA structure. The new deconvolution found is relevant for all the structural analysis based in the Sn core-level line shape and also to understand the behavior of the related interfaces Sn, Pb/Si, Ge(111). All this evidence solves a long-standing controversy and provides a solid model to understand the properties of the low-temperature Mott insulating phase.

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