Insulating Ground State of Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$

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(Received 31 August 2006; published 19 March 2007)

The Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$ surface was so far believed to be metallic according to the electron counting argument. We show, by using tunneling spectroscopy, scanning tunneling microscopy, photoemission, and photoelectron diffraction, that below 70 K this surface has a very low density of states at the Fermi level and is not appreciably distorted. The experimental results are compatible with the insulating Mott-Hubbard ground state predicted by LSDA + U calculations [G. Profeta and E. Tosatti, Phys. Rev. Lett. **98**, 086401 (2007)].

DOI: 10.1103/PhysRevLett.98.126401 PACS numbers: 71.30.+h, 73.20.At, 79.60.Dp

The effect of strong electron-electron interaction in a strictly two-dimensional system can be profitably studied on some semiconductor surfaces that present narrow surface bands, and where consequently the electron kinetic energy may be comparable to the Coulomb energy. One third of a monolayer of group IV adatoms in the T_4 site on Si(111), Ge(111), and SiC(0001), having an odd number of electrons per surface unit cell, forms a narrow surface state band that is half filled, and therefore ideally metallic but prone to structural and electronic instabilities. These instabilities may compete for the stabilization of the surfaces, causing phase transitions, and giving rise to a variety of metallic or insulating ground states [1]. A 3×3 structurally distorted two-dimensional (2D) metal state [2] or a glasslike state [3] are the low temperature phases of Pb/Ge(111); an undistorted ($\sqrt{3} \times \sqrt{3}$)$R30°$ 2D Mott-Hubbard insulator is realized in Si/SiC(0001) [4,5], K/Si(111) : B [6], and also in Sn/Ge(111) [7]; a simultaneously distorted and insulating Mott state has been predicted for C/Si(111) [8].

Here we focus on Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$ ($\sqrt{3}$ in the following). In contrast to the previous cases, scanning tunneling microscopy (STM) data at 6 K indicate an undistorted 2D metallic ground state for this surface [9]. Calculations in the local density approximation (LDA) predict an undistorted metallic state [10]; however, more recent local spin density + U (LSDA + U) calculations by Profeta and Tosatti [11] indicate that the ground state should be a magnetic Mott-Hubbard insulator. The splitting observed in the Sn 4d core levels in this system [12], the x-ray standing wave [13], and the electron standing wave [14] data are instead suggestive of a vertically distorted surface structure. The experimental investigations on the surface electronic structure of Sn/Si(111)-$\sqrt{3}$ by photoemission [12] and inverse photoemission [15] actually indicate a band structure more complex than that predicted for the simple undistorted metallic state [10]; no experimental evidence for an insulating state exists so far for Sn/Si(111).

In this Letter we demonstrate that the ground state of Sn/Si(111)-$\sqrt{3}$ has a deep minimum in the density of states (DOS) at the Fermi level, compatible with the opening of a narrow band gap, while the Sn layer is not appreciably distorted. The properties of the Sn/Si(111) surface at low temperature resemble therefore those of Si/SiC(0001) and of K/Si(111) : B, but the energy gap is much narrower. We used scanning tunneling microscopy (STM) and spectroscopy (STS), angle resolved ultraviolet photoemission spectroscopy (ARUPS), and photoelectron diffraction (PED) at temperatures from 300 K to 5 K to perform a detailed study of the electronic DOS near the Fermi level (E_F) and of the structure of this surface. The experiments were carried out in three different ultrahigh vacuum chambers, one for STM and scanning tunneling spectroscopy (STS) from 300 to 5 K, one equipped with a Scienta SES 2002 electron analyzer for ARUPS from 300 K to 30 K, and the SuperESCA beam line at the Elettra Synchrotron Light Laboratory for the PED measurements at 30 K. The samples were prepared by evaporating 1/3 of a monolayer of Sn on Si(111)-(7×7) surfaces of n-doped (0.01 Ω cm) Si wafers and by annealing the samples at 900 K. The normalized conductance spectra were measured by STS with the lock-in technique by applying a sinusoidal modulation to the sample bias voltage of 40 mV peak to peak at 2.1 kHz.

Figure 1(a) shows a filled state STM topographic image of the Sn adatoms of the Sn/Si(111)-$\sqrt{3}$ surface taken at 5 K. The dark regions are caused by Sn vacancies or substitutional Si atoms in the Sn layer [16]. These are the dominant surface defects and their total density is about 3%–4%. All the Sn adatoms far from the defects are

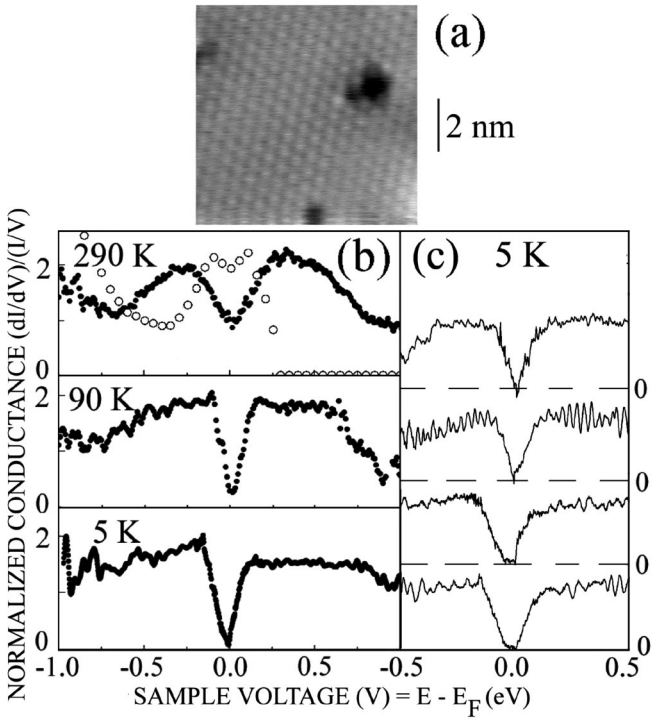

FIG. 1. (a) Filled state STM image of the Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$ at 5 K, sample bias -1.9 V, tunneling current 0.3 nA. (b) ●: average tunneling spectra of the same surface measured far from the defects at different temperatures, ○: calculated normalized conductance from Ref. [18]. (c) Single conductance spectra at 5 K.

equivalent in STM, i.e., the surface remains $\sqrt{3}$ even at 5 K with no trace of (3×3) or other phases, in agreement with the results of Morikawa *et al.* [9].

The normalized differential conductance $(dI/dV)/(I/V)$ measured on the Sn layer far from the defects is shown in Fig. 1(b) at three temperatures. V is the sample bias voltage and I is the tunneling current. These curves mimic the surface DOS [17]. Each curve is the average of several tens of spectra measured with different tips on different samples. The single spectra at a given temperature were consistent [see Fig. 1(c)]. I at the maximum V was set less than 200 pA and it was less than 20 pA for V between -0.2 and 0.2 V in order to minimize "spreading resistance" effects [5], heating effects, or other current-induced modifications. At 290 K the spectrum shows two nearly symmetric broad maxima, respectively, 0.3 eV above and below the Fermi level and is similar to that reported in Ref. [18]. The normalized conductance at the minimum at E_F is about one half of that of the two maxima.

The normalized conductance at E_F drops dramatically upon cooling, down to values below 5% of the maxima between 60 K and 5 K. The dip in the tunneling spectra is V shaped and is about 0.2 eV wide. By linearly extrapolating the slopes of the averaged conductance inside the dip we estimate an upper limit for the energy gap at E_F of 40 meV. The normalized conductance at E_F remains close to zero up to about 60 K and shows a continuous increase above about 70 K (see Fig. 2). In order to prove that the insulator-like minimum observed at low temperature is not an experimental artifact, we measured the tunneling spectra of small metallic defects intentionally induced by the tip on the same surface, of a few monolayer thick Sn layer on the same surface, and of the Si(111) (7×7) in the same experimental conditions and temperatures used for Sn/Si(111)-$\sqrt{3}$. We never observed the conductance dip in these cases.

The tunneling spectra of Fig. 1(b) differ heavily from those expected for an undistorted Sn $\sqrt{3}$ layer with a narrow half-filled surface band centered at E_F originated by the Sn p_z dangling bonds [10]. The calculated normalized conductance [18] [empty circles in Fig. 1(b)] has maxima within 0.1 eV from E_F, where we observe a minimum instead, and vanishes or has a minimum where the experimental data have maxima. The general features of our tunneling spectra are instead in agreement with the photoemission [12] and inverse photoemission data [15] that show broad Sn-induced filled states between E_F and $E_F - 0.8$ eV and empty Sn-induced states between $E_F + 0.2$ eV and $E_F + 1$ eV.

The main result obtained from the tunneling spectra is the opening of a relatively narrow but clear energy gap below about 70 K that represents a deepening of the broad pseudogap seen at higher temperatures. In order to confirm this finding we measured the ARUPS spectra of the Sn/Si(111)-$\sqrt{3}$ surface between 300 K and 30 K with an energy resolution of 30 meV. Figure 3 shows some photoemission spectra of the surface states near E_F at 298 K and 30 K along the ΓM direction of the $\sqrt{3}$ Brillouin zone. The spectra at the same wave vector have been normalized to the same integrated intensity between -0.8 and -1.7 eV.

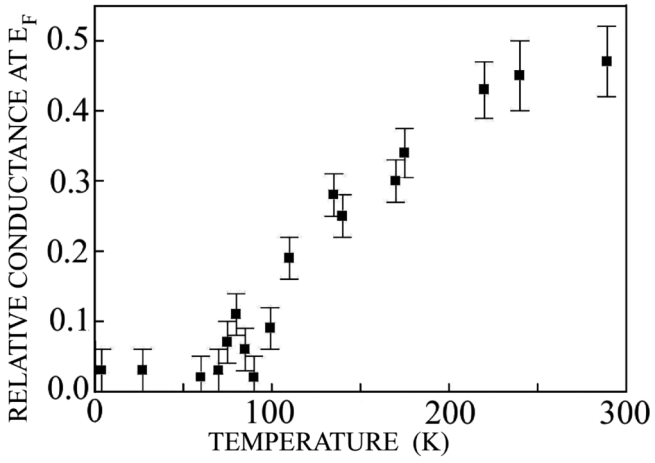

FIG. 2. Temperature dependence of the conductance at the Fermi level. The values have been normalized at the maximum value of the conductance ~0.3 eV above and below E_F.

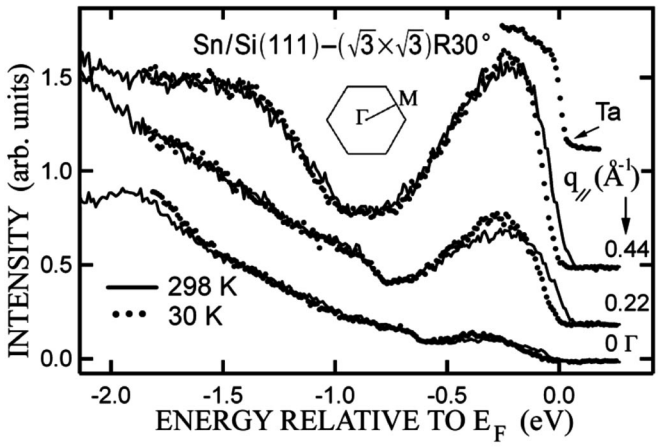

FIG. 3. Photoemission spectra at 298 K and 30 K along the ΓM direction of the surface $\sqrt{3} \times \sqrt{3}$ Brillouin zone for different values of the parallel wave vector. The photon energy is 21.2 eV and the M point is at 0.56 Å^{-1}. Also shown for comparison is the Fermi edge measured on polycrystalline Ta at 30 K.

The low temperature spectra have been corrected for the surface photovoltage effect [19], which in our sample shifts uniformly in energy the valence band features towards higher binding energy values under ultraviolet illumination. The correction was done by measuring the temperature dependent shift of the binding energy of several surface and bulk bands with an error of 15 meV. The photoemission from a Ta foil in contact with the sample and from a thick Sn film on the sample has been used to locate E_F. The broad peak centered 0.3 eV below E_F in the spectra of Fig. 3 is the Sn-induced half-filled surface band. All the photoemission spectra, including those measured along ΓK (not shown), show a substantial decrease of the photoemission intensity between 298 K and 30 K in the high energy side of the Sn-induced band between E_F and about $E_F - 0.15$ eV. This decrease is consistent with that observed in the tunneling spectra near E_F. There is a transfer of photoemission intensity from the region close to E_F to that between -0.25 and -0.4 eV where the intensity increase at 30 K [20]. The width of the high energy cutoff of the Sn peak at 30 K is more than a factor three wider the Fermi edge of a metal (Ta and Sn film) measured in the same conditions. This indicates that the high energy side of the Sn state is not cut by the Fermi level at 30 K and that its shift from the position at 298 K cannot be caused by an error in the determination of E_F at 30 K. It should be noted that there is a weak Sn surface state below E_F also near Γ (see also Ref. [12]), in contrast to the results of LDA calculation which for a $\sqrt{3}$ surface has a Sn surface state below E_F only near the K point [10].

Overall comparison of tunneling, photoemission [12], and inverse photoemission [15] data with the results of the LDA calculations [10] indicates that the structure of the surface is more complex than that of a simple uncorrelated undistorted $\sqrt{3}$ lattice, and/or that either distortions or electron-electron correlation effects, or both, are important. The Sn 4d core level spectrum can be fitted by two doublets [12]. This result could indicate two inequivalent Sn atoms, suggesting that the observed $\sqrt{3}$ structure on Sn/Si(111) could be caused by the disordering of a hypothetical low temperature or metastable (3×3) structure with vertical distortion of the Sn adatoms [12], similarly to the case of the dynamically disordered Sn/Ge(111) $\sqrt{3}$ at high temperature [21]. In such a dynamic structural distortion, a slow technique, such as STM, will measure the average positions, the same for all the Sn adatoms, but a fast structural techniques, such as the photoelectron diffraction, should be able to measure the actual instantaneous position of the inequivalent adatoms, as demonstrated for Sn/Ge(111) [22].

To pursue that, we measured the intensity of the two doublets of the photoemission peaks of the Sn 4d levels of Sn/Si(111)-$\sqrt{3}$ at 30 K as a function of the photon energy (180 eV $\leq h\nu \leq$ 520 eV) and of the emission angle. Following the approach of Ref. [22], we acquired the PED in the energy scan mode both by aligning the electron analyzer with the Sn-Si bond—bond emission (BE) geometry—and with the surface normal—normal emission (NE) geometry. In the first case we have the maximum sensitivity to the bond length between the Sn atom and the nearest neighbor Si atoms, in the second case to the distance between the Sn atom and the underneath Si atom [23]. The PED modulation functions of the two doublets for a particular geometry have maxima and minima at the same wave vector within the experimental error (see Fig. 4), in contrast to the case of Sn/Ge(111)-$\sqrt{3}$ and (3×3), where the Sn layer is rippled and the modulation functions of the two components differ in the NE geometry [22]. This result indicates that in Sn/Si(111)-$\sqrt{3}$ the two core level components are originated by Sn adatoms with the same instantaneous bonding geometry. The multiple scattering analysis [22,24] indicates that the Sn atoms are in the T_4 sites and that all the Sn-Si bond lengths are (2.70 ± 0.03) Å, the bond angles are $52° \pm 3°$, and the distances d between the Sn atoms and the Si atoms directly below is (2.86 ± 0.04) Å for both components. These numbers are equal within the errors to the values obtained by LSDA + U for an undistorted Sn layer [11]. The geometry described above corresponds to the best fit of all the PED data with a reliability factor $R = 0.26$. Other relative minima of R at $d = 3.24$ Å and $d = 2.42$ Å, correspond to $R = 0.44$, i.e., the fit is not reliable. Therefore, our PED data indicate that the vertical distortion of the Sn/Si(111) surface at 30 K is less than 0.06 Å, i.e., about a factor 5 less than that of Sn/Ge(111) or lower. The complex structure of the Sn 4d core levels cannot be attributed to geometrically inequivalent sites, such as that of a buckled layer.

The opening of an energy gap at E_F at low temperature, the absence of appreciable vertical distortion of the Sn overlayer, and the presence of filled Sn states at Γ are all

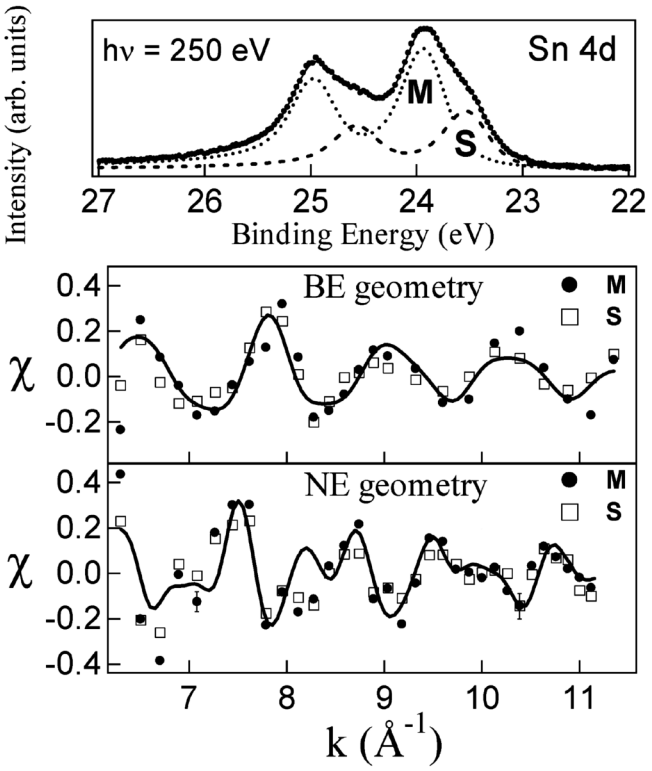

FIG. 4. Top panel: Sn 4*d* core level spectrum at 30 K and its fitting with two doublets, *M* main and *S* secondary. Lower panels: PED modulation functions χ of the two doublets measured along the Sn-Si bond direction (BE) and along normal to the surface (NE). The solid lines are the simulated χ for the bonding geometry described in the text. Error bars are shown for two points.

consistent with the antiferromagnetic Mott-Hubbard ground state predicted by Profeta and Tosatti [11]. While in Sn/Ge(111)-$\sqrt{3}$ this kind of state evolves in a distorted (3×3) structure above 30 K [7], in Sn/Si(111)-$\sqrt{3}$ it seems to become an undistorted bad metal above 70 K. The observation of the filled Sn states at Γ is in agreement with the backfolding caused by the magnetic ordering in the Mott-Hubbard state described in Ref. [11].

In conclusion, the tunneling, photoemission, and PED data presented here, and the LDA + *U* calculations of [11] agree about the insulating Mott-Hubbard nature of the ground state of Sn/Si(111)-$\sqrt{3}$. Unlike Si/SiC(0001) here the gap is relatively small, which should make this system an interesting playground for the rich physics of 2D triangular Mott insulators [25].

Intense consultation with E. Tosatti, discussions with A. Cricenti and S. Colonna, and financial support from MIUR under Grants No. FIRB RBNE019NKS and No. PRIN 2001021133 are gratefully acknowledged.

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