Evidence of Sn Adatoms Quantum Tunneling at the α-Sn/Si(111) Surface

Fabio Ronci,* Stefano Colonna, and Antonio Cricenti†
ISM CNR, Via del Fosso del Cavaliere 100, I-00133 Roma, Italy

Guy Le Lay‡
CRMCN-CNRS, Campus de Luminy, Case 913, F-13288 Marseille Cedex 09, France
(Received 26 July 2007; published 19 October 2007)

We present a low-temperature scanning tunneling microscopy study of the α-Sn/Si(111) surface that demonstrates the fluctuating behavior of the Sn adatoms. The dynamical fluctuation model, successfully applied in describing the α-Sn/Ge(111) surface, is proposed for the related α-Sn/Si(111) surface too, although with a much lower transition temperature. In addition, a new phenomenon appears responsible for the unexpected evidence that the average oscillation frequency remains constant at temperatures lower than 15 K, in contradiction to the Arrhenius law. We explain this phenomenon as quantum tunneling of Sn adatoms.

DOI: 10.1103/PhysRevLett.99.166103 PACS numbers: 68.35.Ja, 68.35.Rh, 68.37.Ef

For two decades it has been well established that at the bare Si(001) surface pairs of atoms form buckled dimers whose symmetric appearance in scanning tunneling microscopy (STM) measurements at room temperature (RT) results from their thermally activated flip-flopping motion [1,2]. Similar dynamical effects at metal-covered semiconductor surfaces were also suggested [3,4] and recently directly observed at the α-Sn/Ge(111) surface, i.e., 1/3 monolayer (ML) coverage of Sn on Ge(111), [5]. This surface undergoes an intriguing low-temperature phase transition to a 3×3 superstructure [6], nowadays explained in the framework of the ''dynamical fluctuation'' model [3]. According to this model, at low temperature (i.e., $T < 80$ K) Sn adatoms are frozen in two different vertical (''up'' or ''down'') positions separated by about 0.3 Å giving rise to one of the three possible degenerate 3×3 configurations (i.e., the three different ways of laying the up or down Sn adatoms on the bulk-truncated Ge(111) surface [7,8]). When the temperature is increased, so that the thermal energy becomes comparable to the interconversion energy barrier $E^{\ddagger}$ between these different configurations, the Sn adatoms start fluctuating between up and down positions with a correlated motion that maintains instantaneously the 3×3 structure. Consequently, the apparently flat α-Sn/Ge(111) $\sqrt{3} \times \sqrt{3}$ phase observed at RT with STM—a slow probe which time averages the diverse configurations—is understood as actually consisting of rapidly oscillating Sn adatoms. Because of the similarity of STM images at RT and spectroscopic signatures (even if the two Sn-4d core level components in each case possess interchanged intensities [9,10]), it was suggested [10–12] that the related α-Sn/Si(111) surface would also pertain to a similar model. However, this view has been disputed in a recent paper by Profeta and Tosatti [13] who proposed new theoretical calculations including electron correlation effects resulting, for both α-Sn/Ge(111) and α-Sn/Si(111), in a Mott-Hubbard magnetic insulator (MI) with an undistorted (flat) $\sqrt{3} \times \sqrt{3}$ ground state. These theoretical calculations appear in agreement with the filled state STM images and the symmetrized valence band photoemission spectroscopy results below 20 K reported by Cortes *et al.* [14] for α-Sn/Ge(111). Such experimental facts point to a new low-temperature (LT) transition to a novel $\sqrt{3} \times \sqrt{3}$ phase. They appear also in accord with the results reported by Morikawa *et al.* [15] showing no transition to a 3×3 phase down to 6 K on α-Sn/Si(111). Moreover, for the α-Sn/Si(111) surface, a recent work by Modesti *et al.*, has shown at low temperature a depletion of the electronic density of states at the Fermi level compatible with an insulating Mott-Hubbard ground state [16]. In spite of this, the description of the α-Sn/Si(111) surface remains unclear. In fact, for a flat $\sqrt{3} \times \sqrt{3}$ MI phase a single (spin-orbit splitted) component of the Sn-4d core level is expected instead of the observed two components. Furthermore, such spectra remain essentially unchanged as a function of temperature down to 30 K [16,17] even in their asymmetric line shapes, that are indicative of the metallic character of the surface, despite the proposed metal-insulator phase transition.

In this Letter we report the direct observation of Sn adatoms vertical oscillations at the α-Sn/Si(111) surface. The STM was used to probe the Sn adatoms up-down fluctuations by recording the tunneling current as a function of time on a grid of points over the scanned area of the surface. The Sn adatoms fluctuations, evidenced by the presence of steps in the current vs time traces [5,18], indicate that the dynamical model pertains also to the present system. Yet, these fluctuations persist down to very low temperatures, with essentially constant average frequency in between 15 and 2.3 K. This is an indication that below 15 K quantum tunneling of Sn adatoms takes over thermally activated oscillations precluding the stabilization of a 3×3 configuration.

The experiments were carried out using a low-temperature STM (Omicron LT-STM) system described in Ref. [5]. Silicon substrates were cut from Si(111)

n-type wafers (Siltronix, P or As doped, 4–6 mΩ cm). Clean 7×7 reconstructed surfaces were obtained by annealing at 900 °C and flashing the sample at 1250 °C for a total time of about 60 s. The 7×7 reconstruction was confirmed both by LEED and STM measurements before Sn evaporation. A nominal 1/3 ML Sn deposition was performed at RT, followed by sample annealing at 650 °C for 120 s. The quality of the $(\sqrt{3} \times \sqrt{3})R30°$ reconstruction, was again checked by LEED and STM.

STM measurements were carried out at negative sample bias voltage [19] (filled states) at temperatures ranging from 80 to 2.3 K. We simultaneously acquired current vs time traces (''current traces'' hereafter) and constant current images in order to know the exact location of the surface point on which every current trace was recorded. Such measurements were in fact performed by acquiring spectroscopy $I(V)$ curves with a constant V value on a 80×80 grid over the investigated area. At every single grid point the STM feedback loop was switched off and the tunneling current was recorded acquiring 400 points in 12 ms with a sampling rate of 33.3 kHz. Using such a procedure it is possible to obtain 3600 current traces on every STM image from which we elaborated ''σ-maps'' that report the standard deviation value of every current trace data set, thus providing a useful way for visualizing the position of the fluctuating adatoms on the investigated surface in our detectable frequency window [5].

Figure 1(a) displays an STM constant current image (6×6 nm^2) collected at 4.6 K in which a clear $\sqrt{3} \times \sqrt{3}$ periodicity is observed, confirming the results obtained by Morikawa *et al.* [15] at 6 K. Interestingly, the current traces acquired on the same area show a dynamical oscillation behavior similar to the one detected at the α-Sn/Ge(111) surface at markedly higher temperatures (i.e., $T =$ 80–220 K [5]). Such stepped traces were detected on top of the Sn adatoms all over the surface, as demonstrated by the similarity of the σ-map [shown in Fig. 1(b)] to the STM image [like in the α-Sn/Ge(111) case [20]]. Three stepped current traces collected at points I, II, and III are shown in Fig. 1(c) as an example of the whole set, while a fourth trace without step is reported in order to show that the step amplitude is much larger than the intrinsic measurement noise level. The direct detection of stepped current traces at 4.6 K strengthens the hypothesis that both α-Sn/Ge(111) and α-Sn/Si(111) can be described by the dynamical fluctuation model, as suggested in Ref. [11]. In this framework, for α-Sn/Si(111), the interconversion energy barrier $E^{\ddagger}$ between the three different underlying 3×3 configurations should be much smaller than in α-Sn/Ge(111). The transition to a frozen 3×3 reconstruction should be observable upon decreasing the temperature. We reached a minimum temperature of 2.3 K at which α-Sn/Si(111) still retains, nevertheless, the $\sqrt{3} \times \sqrt{3}$ reconstruction as shown in Fig. 2(a).

In order to understand the reason why the 3×3 periodicity was not stabilized even at such a low temperature, we performed a series of measurements varying the temperature from 80 K to 2.3 K. In the dynamical fluctuation model the driving force of the surface instability, leading to the apparent $\sqrt{3} \times \sqrt{3}$ reconstruction, is thermal energy. Thus, the average fluctuation frequency $\bar{f}_{\text{therm.}}$ is expected to follow an Arrhenius-like trend as a function of the sample temperature

$$\bar{f}_{\text{therm.}} = f_0 \exp\left(\frac{E^{\ddagger}}{kT}\right) \tag{1}$$

as demonstrated at the α-Sn/Ge(111) surface [5]. In the present case, stepped current traces were clearly observed only for temperatures below 32 K [21]. A small representative set of current traces collected at the α-Sn/Si(111) surface at different temperatures is reported in Fig. 2(b) [22]. A remarkable decrease of the average fluctuation frequency $\bar{f}$ is observed from 32 ($\sim$900 s^{-1}) to 15 K ($\sim$150 s^{-1}), as expected for a thermally activated process. Surprisingly, by further decreasing the temperature down to 2.3 K, no significant frequency change is observed.

We calculated the average fluctuation frequency $\bar{f}$ for all the measurements in which stepped current traces where

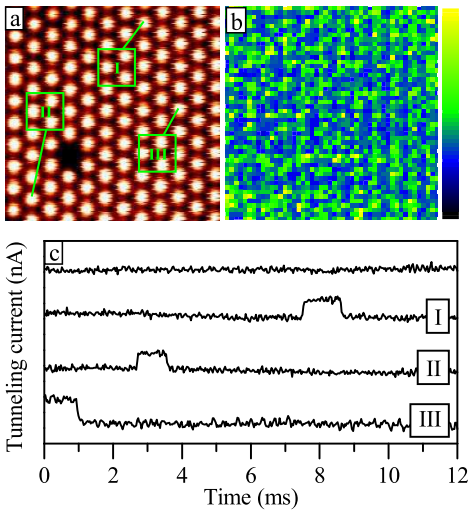

FIG. 1 (color online). (a) 6×6 nm^2 constant current filled states STM image acquired at 4.6 K (gap voltage: -1.0 V, tunneling current: 0.3 nA), (b) σ-map and (c) a collection of stepped current traces detected on the flagged surface spots (a flat trace is reported for comparison purpose).

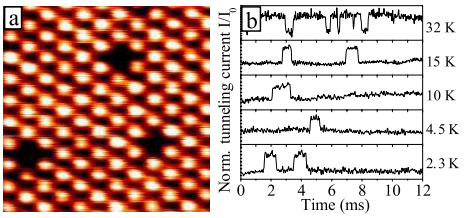

FIG. 2 (color online). (a) 6×6 nm^2 constant current filled states STM image at 2.3 K (gap voltage: -1.0 V, tunneling current: 1.0 nA). (b) current traces collected at different temperatures. All traces are normalized for the feedback current I_0.

observed. The results are reported in Fig. 3 as an Arrhenius plot (ln $\bar{f}$ vs $1/T$, panels a and b) and as a function of temperature ($\bar{f}$ vs T, panel c), where the error bars represent the standard deviation. For comparison, we report in the same figure the results obtained at the α-Sn/Ge(111) surface together with the best linear fit (dashed blue line) from whose slope we obtained $E^{\ddagger}_{\mathrm{Sn/Ge}} = 13 \pm 7$ meV [5]. The interconversion energy barrier value for the α-Sn/Si(111) surface can be estimated by comparing the different temperatures at which the same frequency is detected. For instance, the dotted lines in Fig. 3(c) show that the same frequency value of $\sim 900\ \mathrm{s}^{-1}$ is obtained at 32 and 160 K for α-Sn/Si(111) and α-Sn/Ge(111), respectively. Assuming the same f_0 value for both systems we get from Eq. (1) $\frac{E^{\ddagger}_{\mathrm{Sn/Si}}}{T_{\mathrm{Sn/Si}}} = \frac{E^{\ddagger}_{\mathrm{Sn/Ge}}}{T_{\mathrm{Sn/Ge}}}$, thus obtaining an estimated value of $E^{\ddagger}_{\mathrm{Sn/Si}} = 2.6 \pm 1.4$ meV (solid red line). Figure 3(c) clearly shows that, given the detectable fluctuation frequency range, stepped current traces are observable, in the case of the α-Sn/Si(111) system, at lower temperatures and in a much narrower temperature range with respect to α-Sn/Ge(111). Furthermore, according to this model, the α-Sn/Si(111) surface should freeze to a 3×3 configuration at temperatures lower than about 15 K. At variance, we found no transition and the persistence of almost constant frequency fluctuations, suggesting a residual form of instability which prevents the stabilization of a 3×3 reconstruction. A similar phenomenon was observed at LT at the Si(001) surface and attributed to the injected electrons in STM [23] or LEED [24] experiments. Alternatively, a constant jump rate as a function of temperature can be ascribed to quantum tunneling phenomena, as reported for LT surface diffusion of atomic or molecular species like H [25,26], Cr [27] or CO [28]. In the first case, however, a strong influence of the tunneling current value on the observed fluctuation frequency is expected [23]. Conversely, our data were acquired using different tunneling current values and no frequency change was observed within the experimental error. Consequently, we reevaluated the idea of Sn adatoms quantum tunneling, already discarded by Morikawa *et al.* [15] who considered Sn a too heavy element for tunneling to occur. As a matter of fact, below 20 K, the de Broglie wavelength of a Sn adatom becomes longer than 0.5 Å, a value already larger than the displacement between the up and down positions ($d =$ 0.2–0.4 Å), making quantum phenomena very likely to occur. In more details, a couple of up and down Sn adatoms swapping their positions can be described by a double harmonic oscillator. In the quantum analog, its tunneling swapping frequency ($f_{\mathrm{tunn.}}$) is given, in the fundamental eigenstate, by [29]:

$$f_{\mathrm{tunn.}} = \sqrt{\frac{8E^{\ddagger}\omega}{\hbar\pi}} \exp\left(-\frac{2E^{\ddagger}}{\hbar\omega}\right) \qquad (2)$$

with $\omega = \sqrt{\frac{2E^{\ddagger}}{\mu d^2}}$, in which $\mu = \frac{M_{\mathrm{Sn}}}{2}$ is the reduced mass of the two Sn adatoms and d is the barrier width (in the present case, the height difference between the up and down positions). The quite low estimated value of $E^{\ddagger}_{\mathrm{Sn/Si}}(2.6 \pm 1.4$ meV) and the very small width of d (0.2–0.4 Å) result—in an oversimplified view, i.e., not considering that the first layers of the Si substrate are involved in the fluctuations, the presence of surface defects and the effect of domain boundaries—in a $f_{\mathrm{tunn.}}$ value, whose order of magnitude is $10^{11}\ \mathrm{s}^{-1}$. Yet, we emphasize that this very high value relative to the vertical swapping of a single couple of adatoms (i.e., of an hypothetical *isolated* unit cell), is drastically reduced when considering the correlated up/down motion of all the Sn atoms of the same surface domain [3,30]. In Fig. 4, we plot the calculated frequency $f_{\mathrm{tunn.}}$ as a function of the domain size for both α-Sn/Si(111) (assuming $d = 0.26$ Å [31] and $E^{\ddagger} = 2.6 \pm 1.4$ meV) and α-Sn/Ge(111) (assuming $d = 0.23$ Å [32] and $E^{\ddagger} = 13 \pm 7$ meV [5]). The calculation was performed considering in Eq. (2) the reduced mass μ of n

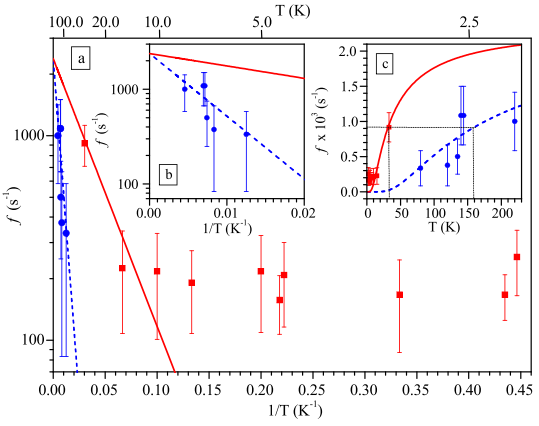

FIG. 3 (color online). (a) Arrhenius plot (ln vs $1/T$) of the average fluctuation frequency (red squares) detected at different temperatures and the calculated slope for $E^{\ddagger} = 3$ meV (red solid line). For comparison, the average fluctuation frequencies detected at the α-Sn/Ge(111) surface (blue circles, [5]) are reported together with the slope for $E^{\ddagger} = 13$ meV (blue dashed line). (b) zoom of previous graph for low $1/T$ values. (c) vs. T plot (same data).

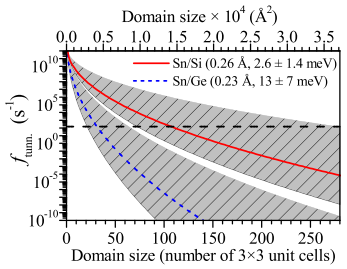

FIG. 4 (color online). Tunneling swapping frequency as a function of the domain size for both α-Sn/Si(111) and α-Sn/Ge(111). The shaded areas represent the error margins calculated from the standard deviation of the $E^{\ddagger}$ values.

couples of swapping adatoms (i.e., n unit cells) $\mu = \frac{(nM_{Sn})^2}{2nM_{Sn}} = \frac{n}{2}M_{Sn}$. The average frequency (150 s^{-1}) detected in the range 15–2.3 K for α-Sn/Si(111) would be obtained with a domain size of about 70–280 unit cells, corresponding to an area of (1.0–3.7) $\times 10^4$ Å^2, a value of the same order of magnitude as the average 3×3 domain size for α-Sn/Ge(111) (ranging from 1×10^4 Å^2 [7] to 4×10^4 Å^2 [33]). Besides, knowing the average 3×3 domain size at the α-Sn/Ge(111) surface, one can derive that the $f_{tunn.}$ value at such a surface is orders of magnitude lower than in the α-Sn/Si(111) case, suggesting that this phenomenon should not be observed at the α-Sn/Ge(111) surface, in agreement with the evidence that the frozen 3×3 reconstruction is observed in this case. In summary, the α-Sn/Si(111) surface has been studied by STM showing Sn adatoms fluctuations similar to the ones reported for the α-Sn/Ge(111) surface [5]. The detection of stepped current traces indicates that the two surfaces can be described in the same framework, i.e., the dynamical fluctuation model. However, at variance with the Ge case, no transition to a 3×3 reconstruction was observable, even when decreasing the temperature down to 2.3 K. Furthermore, the Sn adatoms fluctuations survive at very low temperatures with a constant average frequency in the range 2.3–15.0 K, indicating a residual form of instability which prevents the transition to the 3×3 reconstruction. This low-temperature instability is associated to quantum tunneling of the Sn adatoms.

We would like to warmly thank M. Fanfoni and P. Perfetti for fruitful discussion as well as G. De Santis and M. Rinaldi for their expert technical support.

*ronci@ism.cnr.it
†Also at Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235-1807, USA.
‡Also at UFR Sciences de la Matière, Université de Provence, Marseille, France.

[1] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).
[2] T. Mitsui and K. Takayanagi, Phys. Rev. B **62**, R16 251 (2000).
[3] J. Avila *et al.*, Phys. Rev. Lett. **82**, 442 (1999).
[4] H. Aizawa, M. Tsukada, N. Sato, and S. Hasegawa, Surf. Sci. **429**, L509 (1999).
[5] F. Ronci, S. Colonna, S. D. Thorpe, A. Cricenti, and G. Le Lay, Phys. Rev. Lett. **95**, 156101 (2005).
[6] J. M. Carpinelli, H. H. Weitering, E. W. Plummer, and R. Stumpf, Nature (London) **381**, 398 (1996).
[7] A. V. Melechko, J. Braun, H. H. Weitering, and E. W. Plummer, Phys. Rev. B **61**, 2235 (2000).
[8] D. Farìas *et al.*, Phys. Rev. Lett. **91**, 016103 (2003).
[9] R. I. G. Uhrberg and T. Balasubramanian, Phys. Rev. Lett. **81**, 2108 (1998).
[10] R. I. G. Uhrberg *et al.*, Phys. Rev. B **62**, 8082 (2000).
[11] M. E. Davila, J. Avila, M. C. Asensio, and G. Le Lay, Surf. Rev. Lett. **10**, 981 (2003).
[12] M. E. Davila, J. Avila, M. C. Asensio, and G. Le Lay, Phys. Rev. B **70**, 241308(R) (2004).
[13] G. Profeta and E. Tosatti, Phys. Rev. Lett. **98**, 086401 (2007).
[14] R. Cortes *et al.*, Phys. Rev. Lett. **96**, 126103 (2006).
[15] H. Morikawa, I. Matsuda, and S. Hasegawa, Phys. Rev. B **65**, 201308(R) (2002).
[16] S. Modesti *et al.*, Phys. Rev. Lett. **98**, 126401 (2007).
[17] L. Ottaviano, G. Profeta, L. Petaccia, S. Santucci, and M. Pedio, Surf. Sci. **501**, L171 (2002).
[18] K. Hata, Y. Sainoo, and H. Shigekawa, Phys. Rev. Lett. **86**, 3084 (2001).
[19] At low temperatures ($T < 20$ K) in many cases it was not possible to perform measurements at positive sample bias voltage (empty states) for values lower than about 2 V, probably because of a poor electrical contact between the sample and the holder resulting in a rectifying Schottky barrier. For this reason we only consider filled states measurements whose quality remains unaltered by the presence of such a barrier.
[20] The average fluctuation frequency of such stepped current traces $\bar{f} = 150 \pm 50$ s^{-1} is very close to the lower limit of our frequency window. For this reason some current traces collected on the Sn adatoms have a flat profile and, as a consequence, the σ-map is not as well defined as in the case on α-Sn/Ge(111) [5].
[21] Stepped current traces were detected at higher temperatures (i.e., up to 67 K) on adatoms near surface defects. For this reason, we chose to consider for the average frequency calculation only the stepped current traces collected on adatoms far away from such defects.
[22] Considering the complementary shape of the Sn-4d core level peaks of α-Sn/Ge(111) and α-Sn/Si(111) [9,10], a corresponding complementarity was expected for the current traces. In the α-Sn/Ge(111) case we noticed [5] that the ratio of the average time duration of the high-current level (t_H) and low-current level (t_L) in the stepped traces acquired at negative sample bias was $t_H : t_L = 1{:}2$. Consequently, an inverse $t_H : t_L = 2{:}1$ ratio was expected for the corresponding α-Sn/Si(111) traces. As a matter of fact, we get this ratio only in the current traces acquired at 32 K, whereas a different ratio is found for the traces collected in the 15–2.3 K range.
[23] H. Kaway and O. Narikiyo, J. Phys. Soc. Jpn. **73**, 417 (2004).
[24] T. Shirasawa, S. Mizuno, and H. Tochihara, Phys. Rev. Lett. **94**, 195502 (2005).
[25] L. J. Lauhon and W. Ho, Phys. Rev. Lett. **85**, 4566 (2000).
[26] C. Z. Zheng, C. K. Yeung, M. M. T. Loy, and Xudong Xiao, Phys. Rev. Lett. **97**, 166101 (2006).
[27] P. Ohresser *et al.*, Phys. Rev. Lett. **95**, 195901 (2005).
[28] J. Heinrich, C. P. Lutz, J. A. Gupta, and D. M. Eiglerm, Science **298**, 1381 (2002).
[29] E. Merzbacher, *Quantum Mechanics* (J. Wiley, New York, 1970).
[30] R. Pérez, J. Ortega, and F. Flores, Phys. Rev. Lett. **86**, 4891 (2001).
[31] A. A. Escuadro, D. M. Goodner, J. S. Okasinski, and M. J. Bedzyk, Phys. Rev. B **70**, 235416 (2004).
[32] T. L. Lee, S. Warren, B. C. C. Cowie, and J. Zegenhagen, Phys. Rev. Lett. **96**, 046103 (2006).
[33] D. Farìas *et al.*, Appl. Surf. Sci. **237**, 86 (2004).