Direct Observation of Sn Adatoms Dynamical Fluctuations at the Sn/Ge(111) Surface

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(Received 29 April 2005; published 4 October 2005)

The well-known low-temperature phase transition $\sqrt{3}\times\sqrt{3}$ to 3×3 for the 1/3 monolayer of Sn adatoms on the Ge(111) surface has been studied by scanning tunneling microscopy. The STM tip was used as a probe to record the tunneling current as a function of time on top of the Sn adatoms. The presence of steps on the current-time curves allowed the detection of fluctuating Sn atoms along the direction vertical to the substrate. We discuss the effect of temperature and surface defects on the frequency of the motion, finding consistency with the dynamical fluctuations model.

DOI: 10.1103/PhysRevLett.95.156101 PACS numbers: 68.35.Ja, 68.35.Rh, 68.37.Ef

The Sn/Ge(111) interface has recently attracted considerable interest due to the very intriguing and still highly debated behavior of the so-called α phase obtained after deposition at room temperature (RT) of 1/3 ML Sn on the clean, $c(2\times 8)$ reconstructed, Ge(111) surface, which, after a short and mild annealing, gives rise to a $\sqrt{3}\times\sqrt{3}R$ (30°) surface reconstruction (in short, $\sqrt{3}$) [1]. Scanning tunneling microscopy (STM) and diffraction studies have shown that the surface structure is characterized by Sn adatoms located in the T_4 sites of the bulk terminated Ge(111) surface [2,3]. Upon cooling, a gradual reversible transition from the $\sqrt{3}$ surface reconstruction toward a symmetry breaking 3×3 new one is observed by STM [4]. While at RT the STM images show all equivalent Sn adatoms ($\sqrt{3}$); at low temperature (LT) the new 3×3 surface cell contains three inequivalent Sn adatoms, two appearing displaced upward and one downward (resulting in a honeycomb pattern) when the empty electronic states are probed. The opposite picture is observed when probing the filled electronic states (resulting in a hexagonal modulation) [4]. A $\sqrt{3}\Leftrightarrow 3\times 3$ phase transition is also observed in the 1/3 ML Pb/Ge(111) interface [5,6] and attributed to a surface charge density wave (CDW) formation [7]. Yet, photoemission measurements on the Sn/Ge(111) α phase have shown no real nesting of the Fermi contour nor gap opening [4]. Beyond this, the most intriguing aspect of the transition is the Sn 4d core level photoelectron spectroscopy results, that clearly show two components with an intensity ratio of 1:2, regardless of the sample temperature and surface reconstruction, be it $\sqrt{3}$ or 3×3. These distinct components are compatible with the LT 3×3 STM images, which distinguish two inequivalent Sn adatoms with a 1:2 ratio. Their persistence indicates that the electronic nature of the Sn adatoms at the surface remains unchanged with temperature, thus conflicting with the RT STM images that suggest a "static" $\sqrt{3}$ reconstruction with all equivalent Sn adatoms [8–13]. Accordingly, the 3×3 reconstruction can be obtained with two different adatoms arrangements in the unit cell: one displaced upwards and two downwards (1U2D) or the opposite (2U1D). Whether the stable 3×3 surface is 1U2D or 2U1D is still under scrutiny [14–18].

Different attempts have been made to provide an alternative model to the surface CDW development so far [8–10,19]; in particular, a dynamical fluctuation model has been proposed [10]. In this model the stable surface is considered to be the 3×3 one in the whole temperature range. At LT the system is frozen in the stable reconstruction, while, above the transition temperature, it starts oscillating with increasing frequency as the temperature is raised. This model settles the apparent contradiction between the STM and photoemission measurements at high temperature. In fact, while a fast-sampling technique like photoemission is capable of distinguishing the fast-oscillating inequivalent Sn adatoms, a standard STM image just shows the average picture, i.e., an apparent $\sqrt{3}$ reconstruction.

In this Letter we present an STM study of the $\sqrt{3}\Leftrightarrow 3\times 3$ phase transition at the α-Sn/Ge(111) surface. The STM tip was used as a probe to verify the presence of oscillating Sn adatoms by studying the tunneling current as a function of time. A similar method was successfully applied for the study of the flip-flop motion of the asymmetric dimers at the Si(100) 2×1 surface [20,21]. The observed fluctuations in the tunneling current are interpreted as a confirmation of the dynamical fluctuations model.

The experiments were carried out using a low-temperature STM (Omicron LT-STM) housed in a vacuum chamber having 5×10^{-11} mbar base pressure. Electrochemically etched tungsten tips were used after they were cleaned by field emission discharge against a metal electrode. The Sn (Balzers 99.9995%) source, consisting of a calibrated effusion Knudsen cell, was thoroughly outgassed before use in order to maintain the pressure in the 10^{-10} mbar range during the metal deposition. Germanium substrates were cut from Ge(111) *n*-type wafers (Eagle Picher, 0.327 Ω cm). A clean Ge(111) surface was obtained, after sample degassing at 500 °C overnight keeping the pressure in the 10^{-10} mbar range, with 3–5 cycles of Ar^+ sputtering ($E = 500$ eV, $I = 6$ μA, $t = 10$ min., $T_{\rm sample} = 500$ °C) and annealing ($T =$ 600–700 °C, $t = 5$ min.). The $c(2 \times 8)$ reconstruction was confirmed both by LEED and STM before Sn evaporation. A nominal 1/3 ML Sn deposition was performed at RT, followed by sample annealing at 200 °C. Again, the formation of the α-Sn/Ge(111) phase was checked by LEED and STM.

STM measurements were carried out at temperatures ranging from 80 K to RT. Careful attention was devoted to thermal and piezo drifts by stabilizing the instrument overnight on every temperature change. Tunneling current vs time traces (“current traces” hereafter) were acquired simultaneously to the acquisition of constant current images by interrupting the tip scan on a 80×80 grid over the chosen area. At every single grid point the STM feedback loop was switched off and the tunneling current was recorded during 12 ms with a sampling rate of 33 kHz. Thus, we obtain 6400 current traces on every 10×10 nm^2 STM image, with a distance between adjacent current traces of 0.125 nm, much smaller than the distance between Sn adatoms (0.693 nm). In this way, we can observe steps in the current trace if an adatom underneath the tip moves in the z direction between two stable levels (Fig. 1). Furthermore, it is possible to exactly locate on the images the position of flip-flopping adatoms. We call this instability “flip flop“ to stress that it occurs between two well-defined z levels.

Figure 2(a) shows the STM images obtained on the Sn/Ge(111) α phase at 140 K with positive (empty states) and negative (filled states) sample bias Vs. We found a great number of stepped current traces, two of which are reported as examples in Fig. 2(b). To show where such traces were recorded on the sample surface, we calculated the standard deviation (σ) of all the current traces and reported these values on the z axis of an 80×80 x-y grid. The resulting images (hereafter called “σ maps”), reported in Fig. 2(c), show brighter color for higher values of σ, evidencing where flip flop is occurring. It is worth noting that, for both empty and filled states images, the σ map follows the corresponding STM image, meaning that the current traces have, as expected, a more pronounced square-wave behavior over the adatoms and confirming that the flip-flop motion involves all the adatoms. We checked the reproducibility of the phenomenon by performing the same experiment many times on different sample areas and we repeated the same procedure on the bare Ge(111)$c(2 \times 8)$ substrate, always finding flat current traces. We further calculated the average time duration of high-current (t_H) and low-current (t_L) steps. In Fig. 2(d) we report the histograms obtained by selecting the current traces whose standard deviation value is far above the noise level of a flat one (i.e., $\sigma > 0.1$ nA) and by summing their histograms. Such curves, reporting on the y axis the number (counts) of current readings for every current value (i.e., how many times we find a certain current value in all the selected curves), can be deconvolved with three

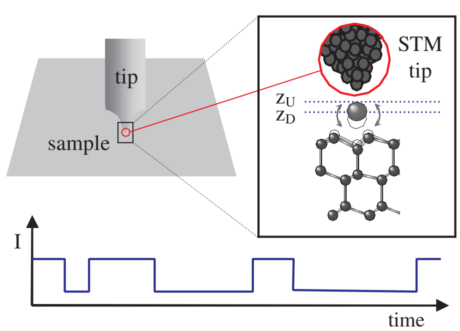

FIG. 1 (color online). Schematics of the measurement.

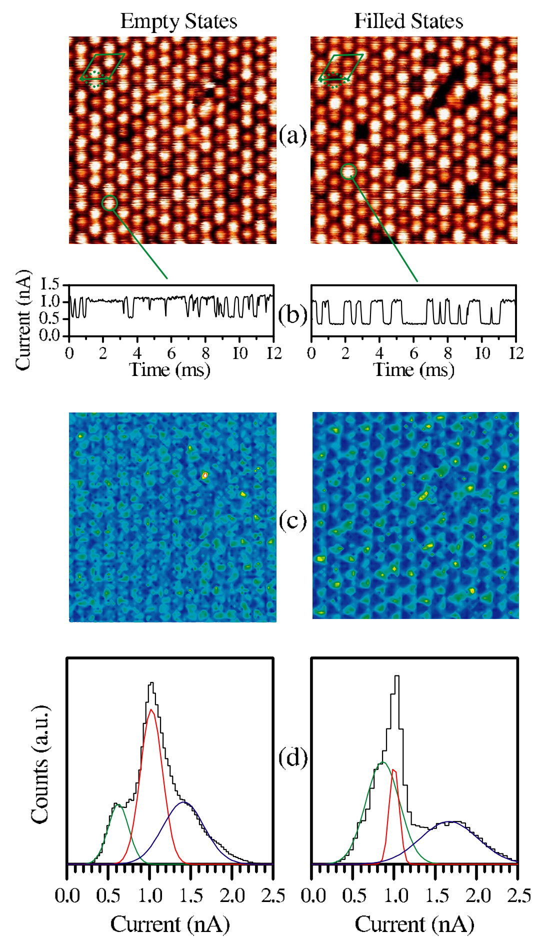

FIG. 2 (color online). Results obtained at 140 K. (a) 10×10 nm^2 STM images. The 3×3 and $\sqrt{3} \times \sqrt{3}$ unit cells are reported as solid and dotted lines. (b) Sample current traces acquired on the indicated locations. (c) σ maps. (d) current histograms. Left panels: $Vs = +1$ V feedback current: 1 nA. Right panels: $Vs = -1$ V, feedback current: 1 nA.

Gaussians representing the three possible current levels: low ($I_L < 1$ nA), feedback set ($I_F = 1$ nA), and high ($I_H > 1$ nA). The intermediate level is due to highly noisy current traces not showing flip-flop steps [22]. The expected inversion of the t_H/t_L ratio for empty (2:1) and filled (1:2) states case (see discussion further on in text), is confirmed by integrating the high- and low-current peaks and comparing their areas, which are proportional to t_H and t_L, respectively. As a further verification, from the simple tunneling current expression $I \propto \exp(-2\kappa d)$ we could estimate [23], from the high- and low-current peaks mean values ($\bar{I}_H$ and $\bar{I}_L$), the adatoms vertical oscillation distance. Considering $\kappa \sim 1$ Å^{-1}, we obtain $\Delta d \sim 0.4$ Å (0.3 Å) for empty (filled) states measurement, in good agreement with the literature (values 0.2–0.5 Å [2,10,14,16,18]).

We further performed a series of measurements as a function of temperature to estimate the interconversion energy barrier ($E^\ddagger$) between the two more stable surface configurations. Data acquisition was performed in the 80–300 K temperature range on filled states images and σ maps. Figure 3 shows a selection of current traces obtained at different temperatures [Fig. 3(a)] and the histograms reporting the frequency of the observed number of steps [Fig. 3(b)]. As expected, the number of steps increases with temperature. The value of the frequency f is obtained by averaging the number of steps in the current traces and dividing this number by the duration (12 ms) of the measurement. From the slope of the Arrhenius plot (Fig. 4) reporting the mean value of the histograms, with the relative standard deviation value, versus $1/T$, we derive an estimate of the energy barrier $E^\ddagger$ [24]; we get $E^\ddagger = 13 \pm 7$ meV, corresponding to a transition temperature $T_t \sim 150 \pm 80$ K. The typical value reported for T_t is 220 K [4,5], but 70 K for a defect-free surface [25], which corresponds to $E^\ddagger = 19$ meV and 6 meV, respectively. The $E^\ddagger$ and T_t values we find (despite the large error bars, most probably due to big variations of the defect density values throughout the experiments) are in the expected range, further confirming the validity of the reported data.

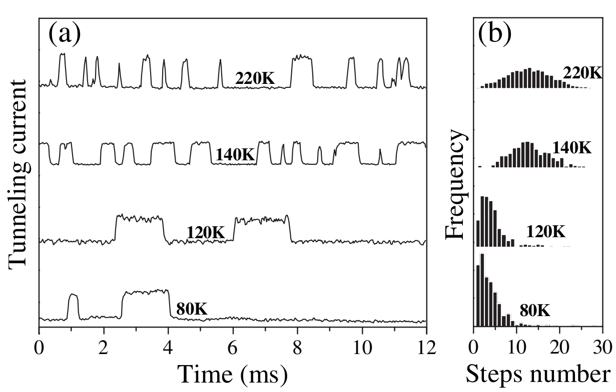

FIG. 3. (a) A selection of current traces taken at different temperatures; (b) histograms reporting the frequency of the observed number of steps. Such histograms were obtained by summing the histograms of all the collected current traces with $\sigma > 0.1$ and normalizing their area with respect to the number of traces.

A hypothetical defect-free α-Sn/Ge(111) surface is actually better described as 3-degenerate different surfaces. In fact, regardless of the 3×3 structure (1U2D or 2U1D), one can build up three different (but energetically equivalent) surfaces, depending on the relative location of U and D adatoms in the unit cell. According to this picture, the STM images would show a 3×3 reconstruction at LT (i.e., when the system is frozen in one of the 3 configurations) with empty (filled) states located on 2/3 (1/3) of the adatoms, as evidenced by the complementarity of the empty and filled states STM images. Increasing the temperature, as kT approaches the value of the energy barrier between the 3 degenerate configurations, the system would start jumping from one to another [26], resulting in a collective Sn adatoms vertical motion with current traces showing $t_H/t_L = 2{:}1$ (1:2) for empty (filled) states measurements, because the system has 1/3 probability of being in one of the three configurations. Hence, the STM image would now show the average picture, i.e., a $\sqrt{3}$ reconstruction, and the transition observed by STM would occur in a quite short temperature range.

In the presence of defects the picture is much more complicated. First of all, the surface divides in different 3×3 domains depending on density and relative position of the defects [25,27]. Furthermore, in each individual domain one of the three possible configurations will be energetically more stable than the other two, even because defects tend to move on a 3×3 sublattice [28]. As the temperature is raised beyond a transition value T^*, the system will start oscillating as in the previous "ideal" example but now, as the three configurations are energetically different, the system will spend more time on the more stable one. In such a situation, the resulting STM images would show a 3×3 reconstruction even if the surface is oscillating because, on average, the system spends more time in one configuration out of three. This is clearly evidenced by considering that the stepped current trace acquired at 80 K [see Fig. 3(a)] was recorded on an area whose STM images (not reported) showed a 3×3 reconstruction. Furthermore, in this case, the transition

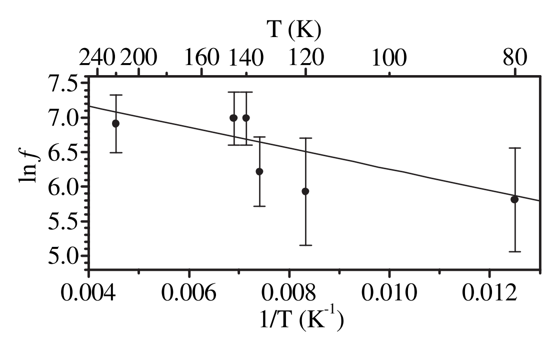

FIG. 4. Arrhenius plot of the flip-flop frequency versus $1/T$.

observed by STM would occur in a much larger temperature range. Comparing our results with molecular dynamics simulations performed on an ideal α-Sn/Ge(111) surface one notices that the flip-flop frequencies are completely different. Theoretical calculations give a typical configuration switch time of $\sim$10 ps at 170 K [26], while we estimate that the detectable frequency range in our measurements is restricted to a 100 Hz–5 kHz range [29]. These contrasting frequency ranges may be explained by considering, first of all, that such calculations were performed on a single unit cell and an exponential frequency decrease is expected as the number of cell is increased [30]. Furthermore, it is very important to take into account the presence of defects on real surfaces. As explained above, they make one configuration more stable than the other two, increasing the value of $E^{\ddagger}$ and, as a consequence, decreasing f. Another possible reason is that the tip itself could affect the measurement. We argue that this possibility, already discussed by Hata *et al.* [21] in the case of the flipping dimers on the Si(100) 2×1 surface, is of minor importance because we could find no relevant influence of the tip-sample interaction (i.e., gap voltage and feedback current values) on the measurements. However, we expect that, if present, this influence would be independent of temperature.

In conclusion, we have directly observed the adatom dynamical oscillations at the α-Sn/Ge(111) surface by using the STM tip to follow the tunneling current fluctuations as a function of time. By performing a study as a function of temperature, we could verify the expected dependency of the oscillation frequency on temperature and estimate the energy barrier for such fluctuations. These results are consistent with the dynamical fluctuation model.

We would like to warmly acknowledge F. Flores and coworkers for their fruitful discussions and M. Capozi for his fundamental technical support and suggestions.

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[22] Actually, a contribution to the central peak comes from a part of the stepped curves that have one of the two current levels around the current feedback value (1.0 nA), like the curves in Fig. 2(b). In fact, before every current trace acquisition, the tip is kept at a certain distance so that the tunneling current equals the feedback current level (in our case 1.0 nA). But, as the surface underneath the tip is oscillating, such a distance may vary depending on the instantaneous vertical position of the adatom underneath the tip. As a consequence, the current levels may vary too.
[23] This calculation is not rigorous because STM probes surface local density of states and not surface topography. Since we obtained values similar to the literature we are confident that the recorded stepped traces are not instrumental artifacts.
[24] To obtain the real frequency, one should multiply the so-obtained value by $3/2$, but this correction has no influence on the slope of the Arrhenius plot and, consequently, on the estimated value of $E^{\ddagger}$. In fact, lets consider, e.g., the tip over a Sn adatom of a 1U2D 3×3 surface while the system is switching from a configuration to another. In all the 3×3 configurations the adatom has a $1/3$ $(2/3)$ probability of being displaced upwards (downwards). If it is initially upwards (U), it can only go downwards (D), but if it is D it has 50% probability of going U and 50% probability of remaining in the D position even if the system has switched to a different configuration. In other words, we can only detect the U-to-D and the D-to-U transitions, but not the D-to-D, missing $1/3$ of the switches. Alternately, for a 2U1D 3×3 surface the U-to-U switches are missed.
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[29] Given the noise level we estimate that, to detect a single current step in a current trace, a minimum of 5 points at one current level and 5 points at another one are necessary. Hence, the maximum detectable frequency is $\sim$5 kHz, whereas the minimum, $\sim$100 kHz, is found by the inverse of the single current trace acquisition time (12 ms).
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