Surface diffusion of Pb single adatoms on the Si(111)-($\sqrt{3}\times\sqrt{3}$)*R*30°-Pb system

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(Received 18 April 2007; published 19 July 2007)

The adsorption and diffusion of additional Pb adatoms on the 1/3 monolayer Si(111)-($\sqrt{3}\times\sqrt{3}$)*R*30°-Pb surface have been investigated by means of variable temperature scanning tunneling microscopy experiments. This surface experiences a reversible phase transition to a (3×3) symmetry at a critical temperature T_c=86 K. Scanning tunneling microscope (STM) images, acquired below and above T_c, have allowed us to identify the nature and adsorption sites of the additional Pb adatoms. A careful analysis of the diffusion, in which the influence of the STM in the measurements has been addresed and discarded, has been performed at temperatures well below room temperature but above T_c. In this way, the activation energy and the preexponential factor for the surface diffusion of single Pb adatoms on the high temperature ($\sqrt{3}\times\sqrt{3}$)*R*30° phase have been obtained. Attention has been paid to the role played by the underlying (3×3) phase at these temperatures.

DOI: 10.1103/PhysRevB.76.035422 PACS number(s): 68.43.Jk, 68.37.Ef, 68.35.Rh, 68.43.Fg

I. INTRODUCTION

Many fundamental processes that take place on solid surfaces, such as, for example, catalytic reactions, thin film growth, or the formation of different surface phases and nanostructures, are strongly influenced by the diffusion of atoms or molecules adsorbed on them.[1–5] In the past few years, scanning tunneling microscopy (STM) has enormously contributed to the understanding, at the atomic scale, of the mechanisms involved in the diffusion process.[6–20]

The Pb/Si(111) system is a very attractive playground for the study of diffusion. On one hand, it has been observed previously by Slezák *et al.*[21] and Custance *et al.*[22] that the interface between the Si(111)-(1×1)-Pb and the Si(111)-($\sqrt{3}\times\sqrt{3}$)*R*30°-Pb [($\sqrt{3}\times\sqrt{3}$) in the following] reconstructions, which coexist on this surface at room temperature (RT), is highly mobile. The borders between both reconstructions present fluctuations, and the rate between the area occupied by the (1×1) and ($\sqrt{3}\times\sqrt{3}$) in a certain region oscillates with time. These fluctuations imply the cooperative motion of a large number of Pb adatoms. Thus, the study of the different paths and activation energies for the diffusion of single Pb adatoms adsorbed on the ($\sqrt{3}\times\sqrt{3}$) surface can represent a first step in the understanding of these oscillations. On the other hand, due to a temperature mediated reversible phase transition, the ($\sqrt{3}\times\sqrt{3}$) surface symmetry existing in this system at RT evolves toward the (3×3) symmetry found at low temperatures (LTs).[23,24] As is well known, the existence of surface phase transitions can affect diffusion, originating anomalous behaviors of it.[25] For example, near a surface phase transition non-Arrhenius temperature dependence has been theoretically predicted[26–28] and experimentally observed.[25,29–31] In particular, in the W(100) surface, which undergoes a reversible phase transition $c(2\times2)\Leftrightarrow(1\times1)$, a strong dip in the diffusion coefficient *D* for H adatoms has been experimentally observed[31,32] close to the transition temperature T_c.

In the present work, we have investigated by means of variable temperature STM the adsorption and diffusion of additional Pb adatoms on the 1/3 monlayer (ML) Pb/Si(111) surface. As is shown here, additional Pb single adatoms diffuse at temperatures above the critical temperature of the ($\sqrt{3}\times\sqrt{3}$)$\Leftrightarrow$$(3\times3)$ phase transition [$T_c\sim86$ K (Ref. 24)]. Therefore, Pb adatom diffusion takes place on the ($\sqrt{3}\times\sqrt{3}$) phase. We have identified the nature and adsorption sites for the additional Pb adatoms. We have carefully examined and discarded possible influences of the STM tip on the dynamics of the diffusion. Moreover, performing the experiments at different temperatures, we have obtained the activation energy and the preexponential factor for the diffusion process. Finally, we have analyzed the role played by the underlying (3×3) LT phase on the adsorption and/or diffusion of extra Pb adatoms.

II. EXPERIMENTAL DETAILS AND ADATOM NATURE

The experiments were carried out in an ultrahigh vacuum system whose base pressure is below 5×10^{-11} Torr. The system is equipped with a homemade ultrastable variable temperature STM which allows imaging at sample temperatures in the range of 40 to 400 K,[18,33] low energy electron diffraction, and Auger electron spectroscopy. It has sample and STM tip transfer and heating capabilities, a STM tip cleaning system by field emission, several interchangeable evaporation cells, a quartz crystal microbalance, and an ion gun for sample cleaning purposes.

In order to properly investigate the extra Pb adatom diffusion on the ($\sqrt{3}\times\sqrt{3}$) surface, it was necessary to grow as large as possible defect-free domains of this phase. Our sample preparation procedure was the same as the one described in Ref. 24. Briefly, it consisted in depositing at RT $\sim$1 ML Pb on top of a clean Si(111)-(7×7) surface. Subsequently, Pb was desorbed by annealing the sample at $\sim$450 °C (Ref. 34) for several minutes until a final coverage of $\sim$0.6–0.7 ML Pb was obtained. With this preparation procedure the surface, at temperatures slightly below RT, is formed by ($\sqrt{7}\times\sqrt{3}$)-Pb islands coexisting with ($\sqrt{3}\times\sqrt{3}$)-Pb domains.[22,35]

The surface presents, in a natural way, some additional Pb adatoms on it. At very low temperatures, these extra Pbadatoms are usually found near the borders with the ($\sqrt{7}\times\sqrt{3}$)-Pb phase or close to defective regions. In Fig. 1(a), measured at 40 K, it can be observed, near a defective

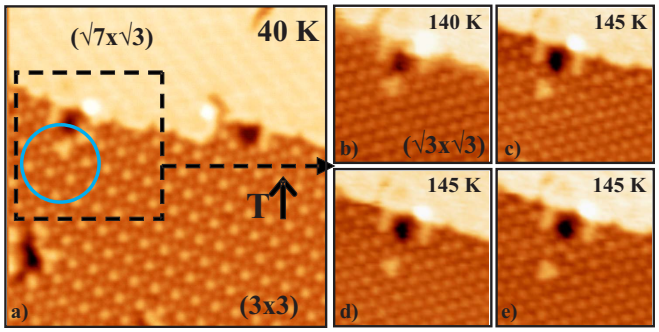

FIG. 1. (Color online) (a) STM image, measured at 40 K, showing an additional Pb adatom (outlined with a circle) which exists in a natural way on the Si(111)-(3×3)-Pb surface. (b) STM image showing the region squared in (a) but at a sample temperature of 140 K. It can be observed that the $(\sqrt{3}\times\sqrt{3})\Leftrightarrow(3\times3)$ phase transition has taken place and that the Pb adatom is still in the same position as in (a). [(c)–(e)] STM images, measured in the same region as in (b) but at 145 K; at this temperature it is possible to observe how the additional Pb adatom starts to diffuse on the $(\sqrt{3}\times\sqrt{3})$ phase. Time elapsed for each image since the acquisition of (a): (b) 6 h, 28 min; (c) 6 h, 55 min; and (d) 7 h, 37 min. Image sizes: (a) 15×15 nm^2 and [(b)–(e)] 6.5×6.5 nm^2. The sample voltage and tunneling current are −1.5 V and 0.2 nA for all images.

region, a triangular bright feature outlined with a circle. We have ascribed this feature to an additional Pb adatom adsorbed on the Si(111)-(3×3)-Pb surface. We have continuously increased the sample temperature while scanning exactly on the same region, and recorded the evolution of the surface by measuring in this way temperature dependent STM movies. In this kind of movies, it can be observed how the (3×3) phase evolves to a $(\sqrt{3}\times\sqrt{3})$ one at $T\sim86$ K.[24] By further increasing the sample temperature, it can be seen that the additional Pb adatom stays immobile until a temperature of ~145 K is reached, and how above this temperature the adatom starts to diffuse on the $(\sqrt{3}\times\sqrt{3})$ reconstruction [see Figs. 1(b)–1(e)]. This temperature is a first indication of the onset of the Pb adatom diffusion on this surface.

In order to confirm the nature of the adatoms (i.e., that the triangular features really correspond to Pb adatoms) and also to have a higher number of them compared to the naturally occurring ones, very small Pb amounts were deposited at low sample temperatures ($T<140$ K). The same Pb evaporation cell employed for the preparation of the Pb/Si(111) substrate was used, which ensures good calibration and cleanness of the Pb deposit. The deposition was made in the ultralow coverage regime, with a coverage of ~0.005 ML Pb. Figure 2 shows the result of two of these low temperature evaporations. In these images, a substantial increase in the number of bright triangular features can be observed, which confirms that they correspond, indeed, to single Pb additional adatoms adsorbed on the $(\sqrt{3}\times\sqrt{3})$ surface.

III. RESULTS AND DISCUSSION

A. Adsorption site and diffusion of the additional Pb adatom

Once the additional Pb adatoms on the $(\sqrt{3}\times\sqrt{3})$ surface have been positively identified, in order to be able to investigate their diffusion, it is first necessary to determine which are the adsorption sites in this system. STM data (see Fig. 3) suggest that the additional Pb adatom is adsorbed on T_4 type positions. The observed triangular shape would come from the contribution of the additional Pb adatom together with its three first neighbors, to which the additional Pb adatom is probably bonded. From STM images, it is not possible to know the precise vertical position of the extra adatom, which could be adsorbed slightly above the $(\sqrt{3}\times\sqrt{3})$ Pb adatoms or even at the same height, forming what could be somehow defined as a very local (1×1)-Pb (with Pb adatoms on T_4 sites). This T_4 adsorption site for the additional Pb adatom is observed both at temperatures above the critical temperature of the phase transition (86 K), for which the surface presents a $(\sqrt{3}\times\sqrt{3})$ symmetry, and at temperatures below T_c, for which the substrate symmetry is (3×3) [see Figs. 3(a)–3(f)].

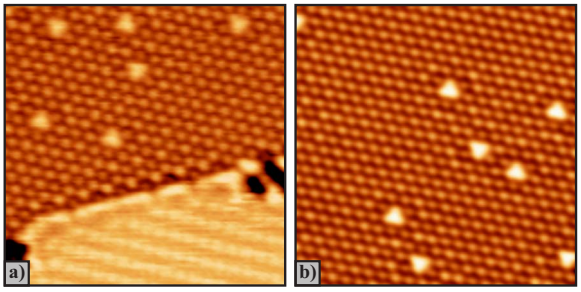

FIG. 2. (Color online) STM images showing the typical morphology of the samples after the LT deposition of ~0.005 ML Pb. Triangular protuberances correspond to additional Pb adatoms adsorbed on the $(\sqrt{3}\times\sqrt{3})$ surface. (a) Image size 13×13 nm^2, $T=145$ K. (b) Image size 14×14 nm^2, $T=140$ K. Sample voltage and tunneling current for both images: −0.5 V and 0.1 nA.

As was mentioned above, these additional Pb adatoms start to diffuse at temperatures ~145 K. Their diffusion was studied by means of STM movies, i.e., large series of successive STM images acquired on the same region of the sample. In order to scan the same region for long enough times, residual thermal drifts were corrected in real time by a procedure described elsewhere.[10] Moreover, to analyze the additional Pb adatom diffusion, we developed a software tool[33] that, once the experimental data were acquired, automatically tracked and recorded the (x,y) position of a certain structure, in the present case the Pb extra adatom, along the different frames of a STM movie. Figure 4 shows an example of one of these STM movies measured at a sample temperature of 150 K. The movie is made up of 631 frames and its total length is 8290 s. Figures 4(a)–4(c) show three of these frames, in which the Pb adatom can be observed in three of the different positions occupied during the whole movie, in particular, (a) the initial, (b) an intermediate, and (c) the final ones. Figure 4(d) illustrates the result obtained after processing the STM movie with the automatic tracking software introduced above. As can be observed, the additional Pb adatom moves randomly, occupying always T_4 sites of the $(\sqrt{3}\times\sqrt{3})$ reconstruction. Therefore, its motion takes place inside the honeycomb lattice formed by these T_4 positions. Moreover, the adatom jump takes place between first neighbors; i.e., the Pb adatom always jumps to one of the

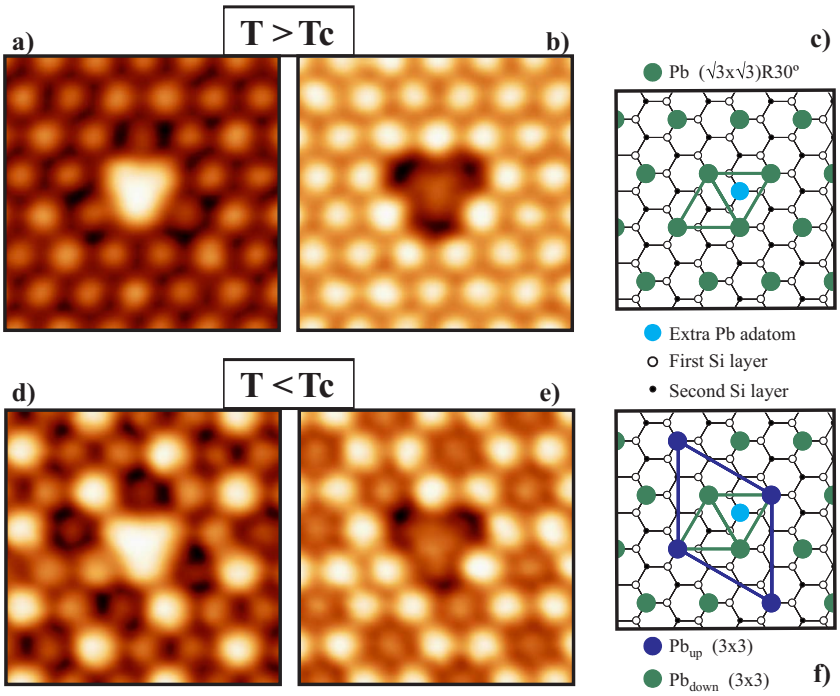

FIG. 3. (Color online) Simultaneously measured STM images suggesting that the additional Pb adatom is adsorbed on a T_4 type site both [(a) and (b)] at $T > T_c$ and [(d) and (e)] at $T < T_c$. [(c) and (f)] Top views of the atomic model of the additional Pb adatom adsorbed on the high and low temperature phases, respectively. Sample voltage of [(a) and (d)] −0.5 V and of [(b) and (e)] +0.5 V. The tunneling current and image size of (a), (b), (d), and (e) are 10 nA and 6.7 $\times$ 6.7 nm^2. The sample temperatures are 100 K for (a) and (b) and 40 K for (d) and (e).

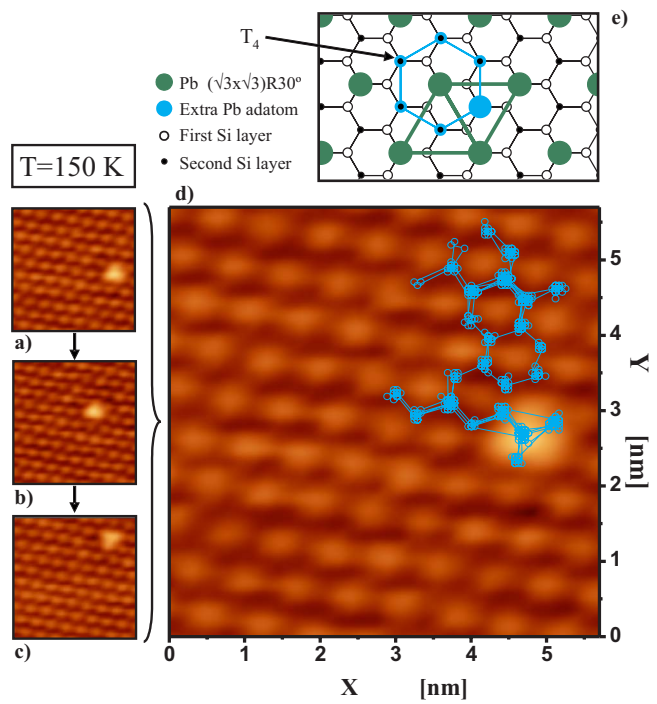

FIG. 4. (Color online) (a)–(c) Frames extracted from a STM movie measured at 150 K. (d) Initial frame of the same STM movie, in which all positions occupied by the extra Pb adatom during the movie are shown by circles linked by lines that connect two consecutive positions. Tunneling conditions: −0.5 V, 0.1 nA. Image size: 5.7 $\times$ 5.7 nm^2. Total movie length: 8290 s, number of frames: 631, and number of jumps: 71. (e) Top view showing a schematic atomic model of the $(\sqrt{3} \times \sqrt{3})$ surface with an additional Pb adatom adsorbed on it and a hexagon of the honeycomb lattice formed by the T_4 sites through which this additional adatom moves.

three T_4 positions which are closer to it (exceptionally apparent double jumps can be observed, but these jumps correspond, indeed, to two individual jumps that take place faster than the time elapsed between two consecutive frames).

B. Analysis of the STM influence

The possibility of a tip-sample interaction that modifies the dynamics of the diffusion was carefully investigated in order to perform the experiments under such tunneling conditions where the diffusion was not influenced by the STM tip. With this purpose, we acquired STM movies at 148 K, in which the hopping rate of the Pb adatoms was measured as a function of the tunneling conditions. It was observed that when high sample voltages were applied, the adatom hopping rate significantly increased. This increase in the hopping rate was even higher at positive sample voltages, increasing by more than 1 order of magnitude at +1.0 V. The influence of the tunneling current was much smaller. It was necessary to reach very high currents (~10 nA) to observe any variation in the hopping rate of the adatoms. Figure 5 summarizes the result of such analysis. As can be observed, depending on the tunneling conditions employed, the motion of the adatom was affected or not due to an interaction with the STM tip. In short, it was observed that for sample voltages between −1.0 and +0.5 V and tunneling currents below 1 nA, the hopping rate was not affected. Thus, working in such a range of tunneling conditions, the Pb adatom diffusion is not modified by the presence of the STM tip. In the present work, a sample bias of −0.5 V and a tunnel current of 0.1 nA were used, which ensure that the dynamics of the diffusion was not influenced by the STM.

C. Variable temperature experiments and discussion

As was mentioned above, Pb adatoms move between the available T_4 type positions of the surface that form a honey-

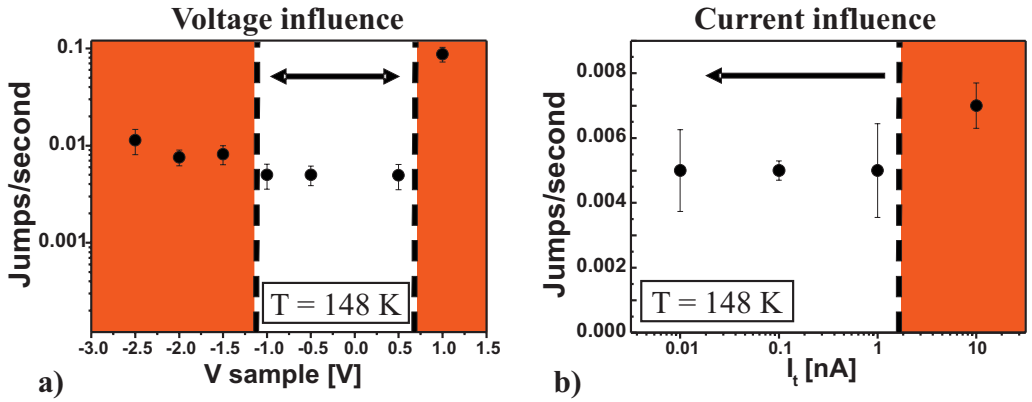

FIG. 5. (Color online) (a) Graph showing the hopping rate of the additional Pb adatom as a function of sample bias for a sample temperature of 148 K and a tunneling current of 0.1 nA. (b) Graph of the hopping rate as a function of the tunneling current for a sample temperature of 148 K and a sample bias of −0.5 V. In both graphs, the arrows indicate the range of tunneling conditions for which the STM does not affect the Pb adatom diffusion.

comb lattice. In the $(\sqrt{3}\times\sqrt{3})$ unit cell, there are two kinds of T_4 sites available, which are, therefore, the two possible adsorption sites of the system. In order to determine if, as could be expected, these two adsorption sites are energetically equivalent, we performed a statistical analysis of the mean residence time distribution probability for each of the two positions. This statistical analysis consisted in obtaining histograms of the time elapsed between two consecutive jumps. If the distributions so obtained fit to a decreasing exponential function of the form $N \propto e^{-\Delta t/\tau}$, where N is the number of events, Δt is the time between jumps, and τ is the mean residence time, then diffusion takes place by means of statistically independent events. From the fit of the experimental data, it is possible to obtain the mean residence time for each of the two T_4 positions. As can be seen in Figs. 6(a) and 6(b), the histograms for both T_4 positions of the unit cell fit perfectly to this decreasing exponential function. Moreover, within our experimental error, both residence mean times are identical. Therefore, both adsorption positions are equivalent and Pb adatom diffusion takes place above a single activation barrier by means of statistically independent jumps.

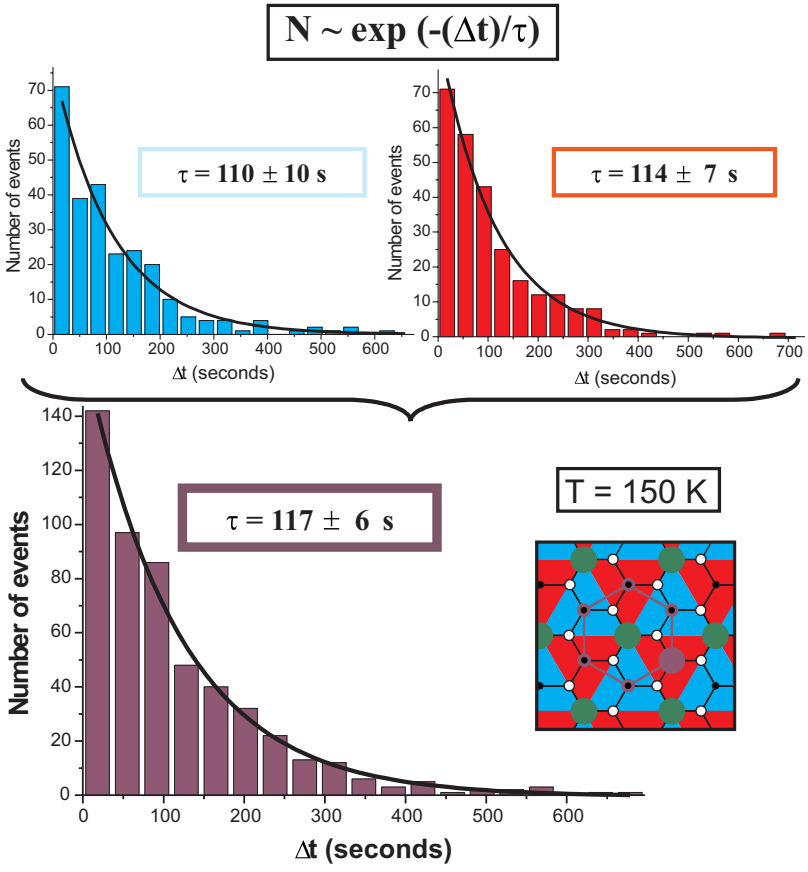

FIG. 6. (Color online) The upper part shows two histograms, obtained from a STM movie acquired at 150 K, of the time elapsed between consecutive jumps considering the two possible T_4 adsorption sites of the $(\sqrt{3}\times\sqrt{3})$ unit cell (see inset in the lower part with a schematic view). As the mean residence time obtained for both T_4 sites is identical, both sites are equivalent. In the lower part, a histogram considering a unique adsorption site is shown. All distributions fit perfectly to a decreasing exponential function, which indicates that diffusion takes place by means of statistically independent events.

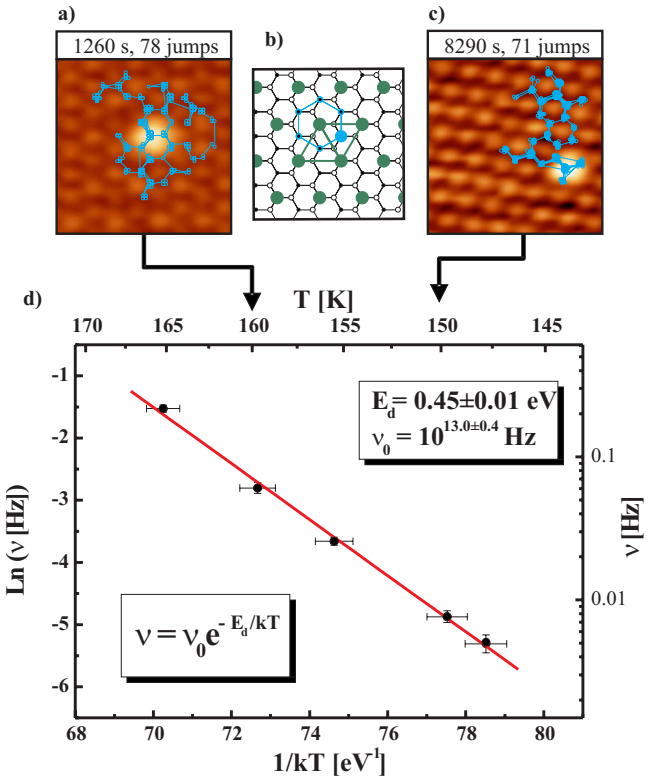

FIG. 7. (Color online) (a) and (c) Initial frames of two STM movies, in which all the positions occupied by an extra Pb adatom during the movies are shown by circles linked by lines that connect two consecutive positions. It can be observed how the mobility is much higher (a) at 160 K than (c) at 150 K. (b) Schematic view showing one possible diffusion path (between T_4 sites) for the additional Pb adatom on the $(\sqrt{3}\times\sqrt{3})$ surface. (d) Arrhenius plot of the Pb adatom hopping rate ν. The activation energy E_d and the preexponetial factor ν_0 were obtained from the best fit to the Arrhenius expression (represented by the solid line).

In order to determine if the diffusion process was thermally activated and to obtain its activation energy as well as the preexponential factor, the experiments where performed at different sample temperatures. Figures 7(a)–7(c) show all the positions occupied by two different Pb adatoms at (a) 160 K and (c) 150 K. In these figures, it can again be observed how Pb adatoms move inside the honeycomb lattice formed by the T_4 sites. This was the situation observed in the whole temperature range used in our investigation (145–165 K). Moreover, when the sample temperature was raised, an increase in the Pb adatom jump frequency was detected, which confirms that it is a thermally activated motion. To quantitatively analyze this motion and thus obtain the activation energy as well as the preexponential factor, we acquired a high number of STM movies, from which we obtained the jump frequency as a function of temperature. From the fit of the experimental data to an Arrhenius expression of the form $\nu=\nu_0 e^{-E_d/kT}$, an activation energy $E_d=0.45\pm0.01$ eV and a preexponetial factor $\nu_0=10^{13.0\pm0.4}$ Hz were obtained.

From our experimental results, two conclusions can be extracted. First, the value obtained for the activation energy ($E_d=0.45$ eV) implies that Pb adatoms should present a very high mobility at RT, which is compatible with the hypothesis that the existing fluctuations between the (1×1) and $(\sqrt{3}\times\sqrt{3})$ phases at this temperature are due to the cooperative motion of a high number of Pb adatoms on the $(\sqrt{3}\times\sqrt{3})$ phase. Second, as can be seen in Fig. 7(d), in the temperature range between 145 and 165 K, experimental data perfectly fit to an Arrhenius behavior and no anomalous dip of the hopping rate can be observed. Moreover, the value $\nu_0=10^{13.0}$ Hz obtained for the preexponential factor is within the range of what is usually considered as normal in simple surface diffusion of single adatoms.[36] Thus, apparently, the underlying (3×3) LT phase is not affecting the dynamics of the diffusion. This is not so surprising, bearing in mind the temperature range studied. The diffusion coefficient can behave in an anomalous way due to the divergence of friction at temperatures close to the critical temperature of the transition.[26,31] In our experiments, the temperatures for which the frequency of the adatom jumps is compatible with STM measurements are, to some extent, distant from the critical temperature of the phase transition ($T_{\min}/T_c<0.6$) as to be able to cause any appreciable effect on the mobility of single Pb adatoms. However, as we showed in a very recent publication,[37] the presence of the additional Pb adatoms induces a local modification of the substrate which can be understood in terms of the underlying (3×3) LT phase. Moreover, when a second Pb additional adatom is present in the region modified by the first adatom, an adatom-adatom interaction mediated by the substrate takes place. Therefore, although we did not detect any anomaly in the behavior of the diffusion for single Pb adatoms in the temperature range studied, even at these temperatures the existence of a surface phase transition affects the adsorption of a single Pb adatom and has a strong influence when the adatoms are not completely isolated.

IV. SUMMARY AND CONCLUSIONS

The adsorption and diffusion of additional Pb adatoms on the Pb/Si(111)-$(\sqrt{3}\times\sqrt{3})$ system have been studied. STM data suggest that these additional adatoms are adsorbed on T_4 type sites. By acquiring STM movies in real time, the diffusion of these Pb single adatoms has been analyzed, observing that it takes place inside the honeycomb lattice formed by the T_4 sites. The measurement of the hopping rate in a temperature range from 145 to 165 K has allowed us to obtain the energy of the diffusion barrier, $E_d=0.45$ eV, and the preexponetial factor $\nu_0=10^{13.0}$ Hz. The relatively low value of the activation energy indicates that these Pb adatoms should be highly mobile at RT. Moreover, although the additional Pb adatoms locally modify the substrate due to the existence of a surface phase transition at lower temperatures, no anomalies in the value of the hopping rate of single Pb adatoms have been detected for this temperature range.

ACKNOWLEDGMENT

Financial support from Spain's MEC under Grant No. MAT2004-03129 is gratefully acknowledged.

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[1] E. G. Seebauer and C. E. Allen, Prog. Surf. Sci. **49**, 265 (1995).
[2] T. R. Linderoth, S. Horch, E. Lægsgaard, I. Stensgaard, and F. Besenbacher, Phys. Rev. Lett. **78**, 4978 (1997).
[3] H. Brune, Surf. Sci. Rep. **31**, 121 (1998).
[4] J. V. Barth, Surf. Sci. Rep. **40**, 75 (2001).
[5] T. T. Tsong, Prog. Surf. Sci. **67**, 235 (2001).
[6] E. Ganz, S. K. Theiss, I. S. Hwang, and J. Golovchenko, Phys. Rev. Lett. **68**, 1567 (1992).
[7] Y. W. Mo, Phys. Rev. Lett. **71**, 2923 (1993).
[8] I. S. Hwang, S. K. Theiss, and J. Golovchenko, Science **265**, 490 (1994).
[9] C. Pearson, B. Borovsky, M. Krueger, R. Curtis, and E. Ganz, Phys. Rev. Lett. **74**, 2710 (1995).
[10] J. M. Gómez-Rodríguez, J. J. Sáenz, A. M. Baró, J. Y. Veuillen, and R. C. Cinti, Phys. Rev. Lett. **76**, 799 (1996).
[11] B. S. Swartzentruber, Phys. Rev. Lett. **76**, 459 (1996).
[12] B. C. Stipe, M. A. Rezaei, and W. Ho, Phys. Rev. Lett. **79**, 4397 (1997).
[13] R. L. Lo, I. S. Hwang, M. S. Ho, and T. T. Tsong, Phys. Rev. Lett. **80**, 5584 (1998).
[14] T. Hitosugi, Y. Suwa, S. Matsuura, S. Heike, T. Onogi, S. Watanabe, T. Hasegawa, K. Kitazawa, and T. Hashizume, Phys. Rev. Lett. **83**, 4116 (1999).
[15] T. Sato, S. Kitamura, and M. Iwatsuki, J. Vac. Sci. Technol. A **18**, 960 (2000).
[16] O. Custance, I. Brihuega, J. M. Gómez-Rodríguez, and A. M. Baró, Surf. Sci. **482-485**, 1406 (2001).
[17] V. Cherepanov and B. Voigtländer, Appl. Phys. Lett. **81**, 4745 (2002).
[18] O. Custance, S. Brochard, I. Brihuega, E. Artacho, J. M. Soler, A. M. Baró, and J. M. Gómez-Rodríguez, Phys. Rev. B **67**, 235410 (2003).
[19] I. Brihuega, O. Custance, and J. M. Gómez-Rodríguez, Phys. Rev. B **70**, 165410 (2004).
[20] I. Ošt'ádal, P. Kocan, P. Sobotik, and J. Pudl, Phys. Rev. Lett. **95**, 146101 (2005).
[21] J. Slezák, P. Mutombo, and V. Cháb, Surf. Sci. **454-456**, 584 (2000).
[22] O. Custance, I. Brihuega, J. Y. Veuillen, J. M. Gómez-Rodríguez, and A. M. Baró, Surf. Sci. **482-485**, 878 (2001).
[23] O. Custance, J. M. Gómez-Rodríguez, A. M. Baró, L. Jure, P. Mallet, and J. Y. Veuillen, Surf. Sci. **482-485**, 1399 (2001).
[24] I. Brihuega, O. Custance, R. Pérez, and J. M. Gómez-Rodríguez, Phys. Rev. Lett. **94**, 046101 (2005).
[25] R. Gomer, Rep. Prog. Phys. **53**, 917 (1990).
[26] T. Ala-Nissila, W. K. Han, and S. C. Ying, Phys. Rev. Lett. **68**, 1866 (1992).
[27] I. Vattulainen, J. Merikoski, T. Ala-Nissila, and S. C. Ying, Phys. Rev. Lett. **79**, 257 (1997).
[28] M. R. Baldan, E. Granato, and S. C. Ying, Phys. Rev. B **62**, 2146 (2000).
[29] A. G. Naumovets, V. V. Poplavsky, and Y. S. Vedula, Surf. Sci. **200**, 321 (1998).
[30] S. C. Wong and R. Gomer, J. Chem. Phys. **83**, 4193 (1985).
[31] L. Cai, M. S. Altman, E. Granato, T. Ala-Nissila, S. C. Ying, and X. D. Xiao, Phys. Rev. Lett. **88**, 226105 (2002).
[32] L. Cai, C. Z. Zheng, K. L. Man, M. S. Altman, E. Granato, T. Ala-Nissila, S. C. Ying, and X. D. Xiao, Phys. Rev. B **68**, 075422 (2003).
[33] All the STM data were acquired and processed with WSXM, free software downloadable from http://www.nanotec.es, see I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A. M. Baró, Rev. Sci. Instrum. **78**, 013705 (2007).
[34] E. Ganz, I. S. Hwang, F. Xiong, K. Theiss, and J. Golovchenko, Surf. Sci. **257**, 259 (1991).
[35] S. Brochard, E. Artacho, O. Custance, I. Brihuega, A. M. Baró, J. M. Soler, and J. M. Gómez-Rodríguez, Phys. Rev. B **66**, 205403 (2002).
[36] G. L. Kellog, Surf. Sci. Rep. **21**, 88 (1994).
[37] I. Brihuega, A. Cano, M. M. Ugeda, J. J. Sáenz, A. P. Levanyuk, and J. M. Gómez-Rodríguez, Phys. Rev. Lett. **98**, 156102 (2007).