Real-Time Observation of the Dynamics of Single Pb Atoms on Si(111)-(7 × 7) by Scanning Tunneling Microscopy

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The very early stages of Pb deposition on Si(111)-(7 × 7) surfaces have been investigated in real time by scanning tunneling microscopy. The combination of variable temperature scanning with unusual very long periods of imaging time have enabled us to observe that single Pb atoms are highly mobile within each half (7 × 7) unit cell. Individual jumps of single atoms between different half cells have been resolved as well as the formation of atom pairs as a result. An activation energy of 0.64 ± 0.07 eV has been measured for the diffusion of single atoms between different half cells.

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The observation of diffusion of individual atoms adsorbed on a surface was first reported by means of the field ion microscope (FIM). Although first suggested by Müller [1] in 1957, the first quantitative study of individual adatoms by FIM did not appear until 1966 by Ehrlich and Hudda [2]. Since this pioneering work, a great deal of information has been gathered in the last 30 years on the processes of adatom surface diffusion on metal surfaces by using this valuable technique [3]. Nevertheless, the experimental study of diffusion of single adatoms on semiconductor surfaces has not known a comparable development.

Very recently, the application of scanning tunneling microscopy (STM) to this kind of study is starting to fill the information gap. Some experimental difficulties, however, still hamper this development and the number of STM studies on that subject is quite limited. The main problem being the adequacy between scanning speed of STM imaging and the rate of atomic motions produced by diffusion, only some specific systems have been studied [4–9]. The surface diffusion of Pb atoms on Ge(111) substrates is one of the cases that has attracted great interest due to the spectacular results that have been obtained with STM [6].

The different phases of Pb chemisorption on Si(111)-(7 × 7) have been studied using different techniques including STM [10,11]. The main interest has been directed to the analysis of high coverage and high temperature phases, somehow disregarding the very early stages of Pb chemisorption at room temperature (RT).

In this paper we present the first experimental evidence showing the mobility of single Pb adatoms deposited at room temperature on Si(111)-(7 × 7) surfaces. Ultralow coverage deposition combined with variable temperature STM and unusual very long periods of observation time have enabled us to analyze the trapping character of the reconstructed cells for highly mobile Pb adatoms, as well as the first stages of the nucleation of Pb atom pairs.

The experiments were carried out in an ultrahigh vacuum chamber equipped with STM, LEED-AES, sample transfer and heating capabilities, ion sputtering, and a Pb evaporation cell. The base pressure of the system is $\sim 5 \times 10^{-11}$ Torr. Very small amounts of Pb [~0.01 ML (monolayer)] were evaporated at RT on clean reconstructed Si(111)-(7 × 7) at typical rates of 0.05 ML/min ($1\ \text{ML} = 7.84 \times 10^{14}$ Pb atoms/cm^2), as monitored with a quartz crystal thickness monitor.

The STM data presented here are the result of thousands of images. STM images were acquired over surface regions for long periods of time (up to 8 h). In order to ensure that the same surface spot was imaged over such long times, residual thermal drifts were automatically corrected in real time using a novel experimental approach which will be described elsewhere [12]. It basically consists in calculating the 2D correlation function of successive images and modifying the X-Y piezovoltages of the center of the next image accordingly. Moreover, variable temperature measurements were performed in the range of 22 to 68 °C, by heating the whole microscope in order to minimize thermal drifts. The STM was typically operated at 200 pA tunneling current and ±2 V bias.

Figure 1 is a representative example corresponding to RT chemisorption of Pb at very low coverage (0.01 ML). STM images are shown at both polarities in order to make clear the difference between the two Si(111)-(7 × 7) triangular half cells, faulted and unfaulted [13]. The most remarkable feature of these images is the presence of some half cells which present a fuzzy appearance. In these half cells the STM image does not show a well-resolved spot, however, but rather a delocalized region with higher brightness occupying the whole triangular cell. This can be understood as due to the fast movement

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of one Pb adatom between the various adsorption sites offered by the triangular cell of the silicon substrate [14].

Some pairs of Pb atoms occupying the triangular half cells can also be seen on Fig. 1; in that case the STM image shows two well-defined bright spots. Our experiment shows that an atom pair is formed when two single atoms are situated in nearest neighbor cells, as we deduce from the movement of atoms as a function of time. This is shown in the sequence of images of Fig. 2—measured with the sample at 58 °C—where we see the jump of an adatom to one of its three nearest neighbor triangles [Fig. 2(b)] and the formation of a pair in the next jump [Fig. 2(c)]. The resolution of the two atoms after this reaction ensures that the initial situation was that of two single adatoms chemisorbed in two different 7 × 7 half cells.

From this analysis a qualitative picture of the adsorption process is deduced: Pb atoms are adsorbed once they make contact with the Si surface. The atoms are confined at their initial adsorption triangular site. There is a probability that two atoms fall into the same triangular half cell or into nearest neighbor half cells in which case they react to form a pair of adatoms. *Atom clusters of three or four Pb atoms are formed in the same way as atom pairs, as we have observed in our time sequences of images.*

The initial distribution of the Pb cluster size may be computed using a simple model. We assume that each cluster of size n atoms will capture instantaneously all atoms from the incident beam that land on the surface inside its capture area. This capture area consists in s half (7×7) unit cells (hereafter denoted as "sites"). Clusters of size n cannot decay into clusters of smaller size (we have never experimentally observed this kind of decay).

If one notes C_n the average number per site of clusters of size n, and τ the time it takes to deposit (on average) one atom per site from the atomic beam ($\tau \sim$ inverse of the flux), the corresponding evolution equations are

$$\dot{C}_1 = \tau^{-1} - 2s\tau^{-1}C_1 - \sum_{n\geq 2}^{\infty} s\tau^{-1}C_n\,, \qquad (1)$$

$$\dot{C}_n = s\tau^{-1}C_{n-1} - s\tau^{-1}C_n\,, \quad \text{for } n \geq 2\,, \qquad (2)$$

where $\dot{C}_n$ is the time derivative of C_n. The solution of this set of equations is $C_n = (sn\,!)^{-1}(st/\tau)^n \exp(-st/\tau)$, which is equivalent to a Poisson distribution. If one notes θ the coverage (average number of atoms deposited per site), at the end of the deposit we have $C_n = (sn\,!)^{-1}(s\theta)^n \exp(-s\theta)$.

The distribution of the cluster size we expect from the above model for $\theta = 0.25$ [which corresponds approximately to 0.01 ML of Pb for the Si(111) surface] is shown in Fig. 3 for two physically reasonable values of s; that is,

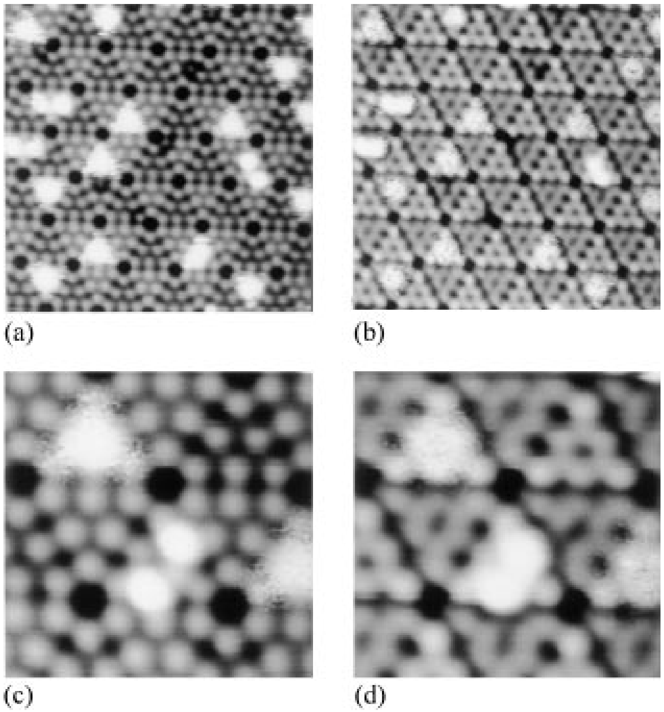

FIG. 1. Filled and empty state STM images of 0.01 ML Pb on Si(111)-(7 × 7) measured at room temperature. The scanning areas are $16.25 \times 16.25\ \text{nm}^2$ [(a) and (b)] and $6.0 \times 6.0\ \text{nm}^2$ [(c) and (d)]. Sample voltages are +2 V [(a) and (c)] and −2 V [(b) and (d)]. Tunnel current is 0.2 nA for all images.

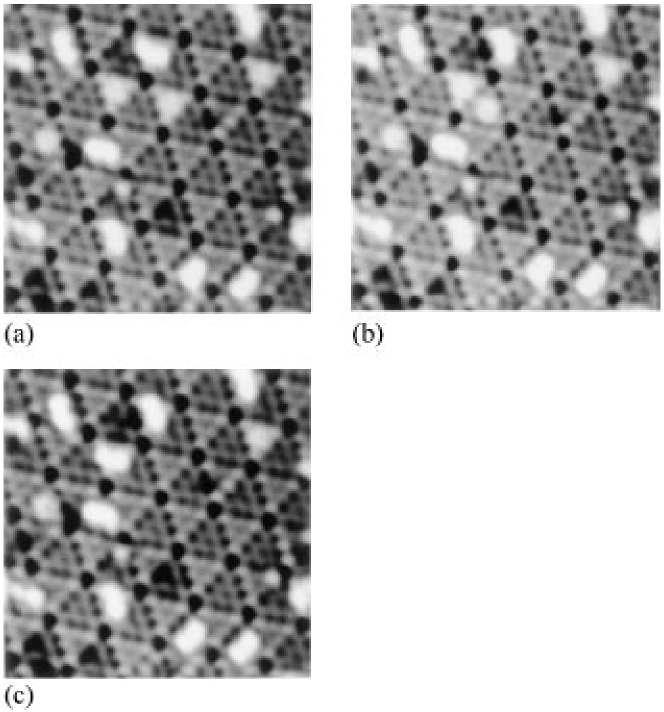

FIG. 2. Successive frames extracted from an STM movie measured at 58 °C, showing the jump of a single Pb atom (b) and the formation of a pair (c). The time between frames is 25 sec. The scanning area is $14.75 \times 14.75\ \text{nm}^2$. Sample voltage: −2 V. Tunnel current: 0.2 nA.

$s = 1$ (capture by direct impingement only) and $s = 4$ (capture also by atom jumps on the cluster site from the three nearest neighbor sites). Also shown is the size distribution of the clusters that we have experimentally obtained by averaging images from several deposits with θ close to 0.25 (θ and C_n are computed directly on the images). The model with $s = 4$ gives a much better account of the experimental results than the model with $s = 1$. Physically it means that atoms on neighboring sites have a strong tendency to agglomerate, and thus some kind of effective attractive interaction exists between atoms on nearest neighbor half (7×7) cells.

After the adsorption process, since we image the same region during a long time, we are able to count the number of jumps per atom and per unit time (or jump frequency per atom, ν) performed by a single Pb adatom between different half cells. We have measured this quantity as a function of the sample temperature in order to deduce the activation barrier represented by the triangular border of a half cell, as for a thermally activated motion, $\nu = \nu_{\mathrm{eff}} \exp(-E_d/kT)$, where ν_{eff} is the attempt frequency.

From the Arrhenius plot (see Fig. 4) we obtain an activation barrier $E_d = 0.64 \pm 0.07$ eV with a prefactor $\nu_{\mathrm{eff}} = 10^{6\pm1}\,\mathrm{s}^{-1}$. The activation energy is lower than the energy per Pb-Si covalent bond, 0.88 eV [15], obtained from desorption experiments at higher coverage. This is somehow an expected result since at our low coverage Pb atoms are not in substitutional places and move relatively free within the half cell. On the other hand, the experimental value for ν_{eff} is orders of magnitude lower than the value of 10^{11}–$10^{12}\,\mathrm{s}^{-1}$ expected for the bare attempt frequency associated with individual single hops. Similar low values have also been obtained for the diffusion of Pb single atoms on Ge(111) surfaces [6]. In that case, Kaxiras and Erlebacher [16] showed that a complicated cooperative motion of a large number of atoms could account for the lowering of the attempt frequency.

However, there are significant differences between the motion of Pb atoms on the $c(2 \times 8)$ Ge(111) and on the (7×7) Si(111) surfaces. In the former case the motion of a Pb adatom takes place between well-defined equilibrium (substitutional) positions. On the 7×7 Si surface, however, the Pb jumps between different half cells. The relatively fast motion of the Pb atom within each half cell indicates that it oscillates between different equilibrium states in a small energy range. It is likely that only a few of them will be such that the atom can actually go through the diffusion path. In other words, the atom could expend most of the time in *states that* do not correspond to the starting point of the diffusion path towards an adjacent half cell. This would lead to a lowering of the effective attempt frequency [17].

Finally, we have ruled out the possibility of tip-induced effects in the jump rate following a procedure proposed by Mo [7]. It consists in recording images of the same area at successive times. Between each acquisition sequence, the tip is withdrawn by ~3000 Å, so that it could not influence the thermal diffusion anymore. This experiment has been performed at RT only, probing the same area every 2 h or more. The decrease of the density of single atoms (and the concomitant changes in the density of larger clusters) is consistent (*within the experimental error bars*) with the results of the continuous observation, which demonstrates that very small influence (if any) can be attributed to the scanning process of the tip on the dynamics of single Pb atoms.

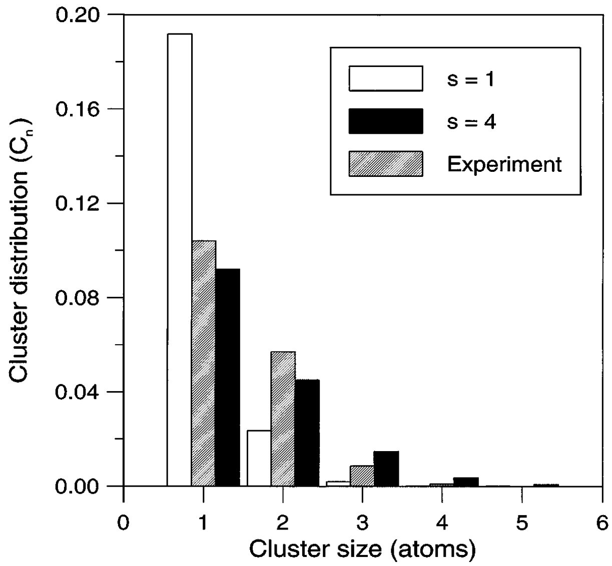

FIG. 3. Initial cluster size distributions of Pb on Si(111)-(7 × 7) at 0.01 ML.

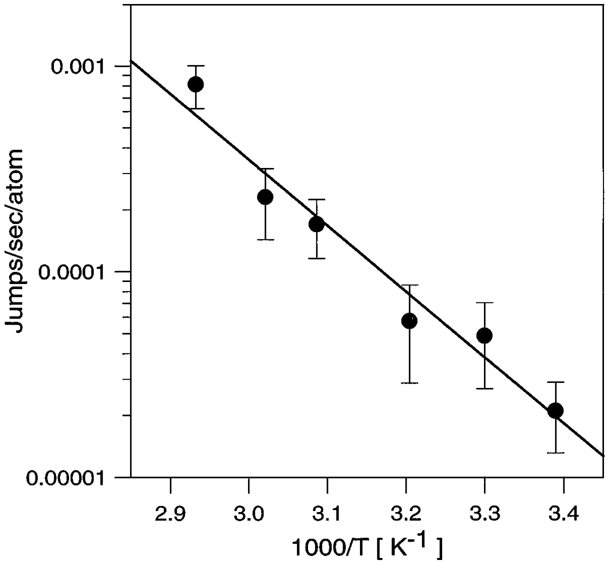

FIG. 4. Arrhenius plot for the diffusion of single Pb atoms between different half cells of the Si(111)-(7 × 7) surface measured from 22 to 68 °C.

In summary, we have investigated in real time the dynamics of single Pb atoms on Si(111)-(7 × 7) by STM. We have observed that Pb atoms are highly mobile inside each half (7 × 7) unit cell. Individual jumps of single atoms between nearest neighbor half cells have been detected, and an activation energy of 0.64 ± 0.07 eV for this process has been measured. The extremely low value of the prefactor deduced from the present study suggests that the mechanism of adatom diffusion on highly reconstructed semiconductor surfaces may be a complex dynamical process and should stimulate future theoretical work.

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