Direct Measurement of Diffusion by Hot Tunneling Microscopy: Activation Energy, Anisotropy, and Long Jumps

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We measure the activation energy for surface diffusion of isolated Pb adatoms on Ge(111) by observing individual atomic interchanges using a scanning tunneling microscope. The diffusion occurs mainly along one direction of the $c(2\times8)$ reconstructed surface with Pb adatoms moving between substitutional Ge adatom sites. Only half of the adatom interchanges are to near-neighbor sites, the rest are "long jumps." The scanning process does not affect the diffusion. For temperatures from 24 to 79 °C we find the diffusion obeys an Arrhenius law with an activation energy of 0.54 ± 0.03 eV.

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The diffusion of adatoms on surfaces is of fundamental importance in epitaxial growth and in catalytic reactions. In this Letter, we report the direct atomic-scale observation of adatom diffusion using a scanning tunneling microscope (STM) operating over a range of temperature. Atomic migration frequencies, activation energies, and diffusion constants can be obtained from analysis of the tunneling images. Anisotropic diffusion can be identified on the atomic scale and correlated with specific atomic sites. Additionally, we observe a surprisingly large number of "long jumps" (movements of more than one atomic spacing). We show that elevated-temperature STM is a practical technique to extend diffusion studies to very low migration rates because of the large surface areas and number of atoms which can be imaged.

Fundamental atomic-scale studies of surface diffusion have been made using the field-ion microscope (FIM) [1]. FIM studies are restricted to those materials from which one can make field emission tips, chiefly transition metals, and the small facet sizes at the end of the tips limit the area available for study (typical terrace sizes are less than 60 Å). However, FIM has been the only atomic-resolution technique available for the study of surface diffusion for the last 25 years, and has provided dramatic insights into the diffusion process. A few atomic-scale surface diffusion studies have recently been carried out with the STM [2], but have relied on detailed models for nucleation and growth rather than the direct observation of the motion of individual atoms that we discuss below.

We have previously studied the Pb on Si(111) [3] and the Pb on Ge(111) systems in detail, and found Pb/Ge(111) to be a favorable system for our diffusion studies for several reasons. Pb adatoms on both Si and Ge form a two-dimensional lattice gas at low coverages at room temperature [4]. The Pb adatoms are readily distinguishable from the Si or Ge adatoms in STM images over a range of biases [3]. Bulk Pb and Ge do not intermix, and therefore Pb adatoms remain at the surface. Furthermore, Pb adatoms do not evaporate from the surface for temperatures below 300 °C. Thus this system provides a uniquely direct opportunity to observe the motion of identifiable atoms in large terraces of a reconstructed semiconductor surface. As far as the authors are aware, this is the first direct, atomic-scale measurement of the diffusion of atoms which lie within the plane of the reconstruction, rather than on top of it.

The experiments were performed using a custom-built STM in an ultrahigh vacuum chamber with base pressure 6×10^{-11} torr. Clean reconstructed Ge(111)-$c(2\times8)$ surfaces [5] were produced by successive Ne-ion sputtering and annealing, repeated until very sharp and bright $c(2\times8)$ LEED spots were observed across the entire sample. Subsequent STM imaging showed very clean surfaces with terrace widths of roughly 500 to 1000 Å. After cooling the sample to room temperature, approximately 0.05 monolayer (ML) of Pb was deposited from an effusion cell with system pressure below 5×10^{-10} torr. The sample was then transferred to the STM stage for imaging. Temperatures were varied by passing current through the sample. Pb atoms sparsely occupy adatom sites of the $c(2\times8)$ surface after gentle annealing (to temperatures less than 100 °C) [6]. For the purposes of this diffusion study we consider only those Pb atoms in substitutional Ge-$c(2\times8)$ sites.

The STM was typically operated at 100 pA tunneling current and +2 V bias on the sample. The size of the scanned region was varied between 100 and 390 Å on a side. Before taking images at a new temperature, we waited 30 min to several hours to allow the instrument to stabilize thermally. Sample temperatures corresponding to each current were calibrated after the last STM run by gluing a type-*K* thermocouple with 5-mil-thick wires directly to the center of the sample, using a dot of Torr-Seal for electrical insulation. Again, we waited 30 min to several hours at each heating current until the temperature measurement stabilized. We estimate the uncertainty in our temperature measurement to be ±2 °C [7].

Figure 1 shows four STM images taken at 48 °C at 2- and 4-min intervals. Note that these images are sections of much larger 260-Å scans used for analysis. It is important to analyze large images to minimize the number of atoms which move off the edges of the field of view and to guarantee that subsequent scans contain distinctive

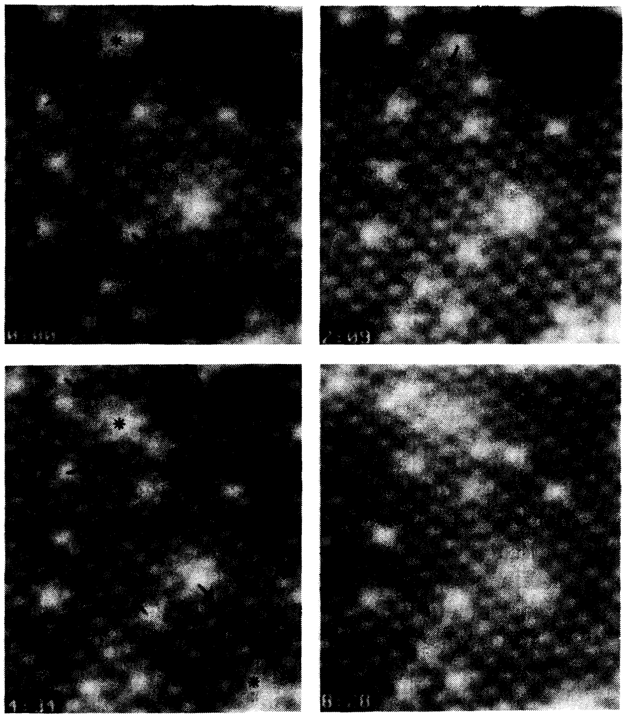

FIG. 1. Four successive 90×100 Å STM images of Pb adatoms in substitutional sites of a Ge(111)-$c(2\times8)$ reconstructed surface. Elapsed time in [minutes:seconds] is indicated at the bottom of each image. The black arrows indicate the direction and length of eight single interchanges. Four atoms which do not appear at the same position of near-neighbor positions in the subsequent frame are marked with black stars. These are discussed in the text as long jumps.

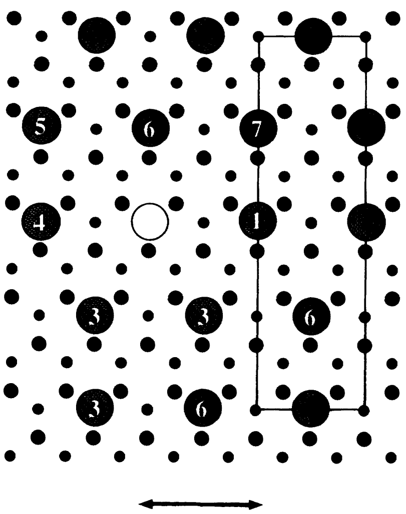

FIG. 2. Schematic diagram of the Ge(111)-$c(2\times8)$ surface. Small circles represent top-layer bulk Ge atoms; large circles are Ge adatoms (shaded) and Pb adatoms (open). Seven near neighbors are identified. We find that the diffusion by single interchanges occurs primarily along the indicated direction.

common features (e.g., a number of Pb atoms which have not moved). For the images used in our analysis, we typically have 30 to 100 Pb adatoms per image, constituting about 6% of the total adatoms in the $c(2\times8)$ reconstruction. The Pb adatoms are clearly visible as white spots, and occupy substitutional adatom sites in the Ge(111)-$c(2\times8)$ reconstructed layer (presented schematically in Fig. 2). The interval between scans is selected so that only a few atoms move between successive images. It is varied from 30 s to 15 min. At room temperature an average of only 4% of the Pb adatoms in the field of view moved between scans, and at the highest temperature studied (79 °C) about 17% of them moved. By comparing the adatom positions in each image, we determine which atoms have moved. 171 images containing 1001 interchanges from a total of 9901 atoms were analyzed. In Fig. 1, we observe eight single (near-neighbor) interchanges. For these eight interchanges we have placed a black arrow showing the position of the adatom in the next image. We also identify four long jumps with black stars. In our analysis, a long jump is counted when an atom is present in one image and is not present either at its old site or at a neighboring one in the next image. Only departures (atoms which move away from sites they previously occupied) are counted, not arrivals (atoms which move into sites they did not previously occupy). Since each individual migration event consists of both an arrival and a departure, this avoids double counting. By analyzing a large number of images, we can measure the diffusion of the adatoms one atomic motion at a time.

At a given temperature, we find that the number of Pb adatoms which move per image follows the binomial distribution. This is consistent with our assumption that each adatom moves independently. To analyze the diffusion, we record the number of movements m_i that occur among a field of a_i Pb adatoms in the ith time interval t_i. Since both t_i and a_i vary, the average atomic movement rate R and deviation σ at a particular temperature are given by $R=\sum m_i/\sum t_i a_i$ and $\sigma=(\sum m_i)^{1/2}/\sum t_i a_i$. If the motion is thermally activated, then R varies with absolute temperature T as $R=\nu\exp(-E_D/kT)$, where ν is an effective attempt frequency and E_D is the activation energy. To check this prediction, we plot $\log R$ vs $1000/T$ in Fig. 3. Note that a straight line fits the data quite well, and yields $E_D=0.54\pm0.03$ eV and $\nu\approx7\times10^5\ \mathrm{s}^{-1}$. The ratio of single interchanges to long jumps remains constant over our temperature range; we examined $\log R$ vs $1000/T$ of the single interchanges only, and found the same value of E_D (with a larger uncertainty). Either the single interchanges and the long jumps occur by the same process or they occur by processes with very similar activation energies, and we consider the data together.

One might not be surprised to find anisotropic diffusion in a case like ours, where the surface reconstruction breaks the symmetry of the bulk. We have therefore ex-

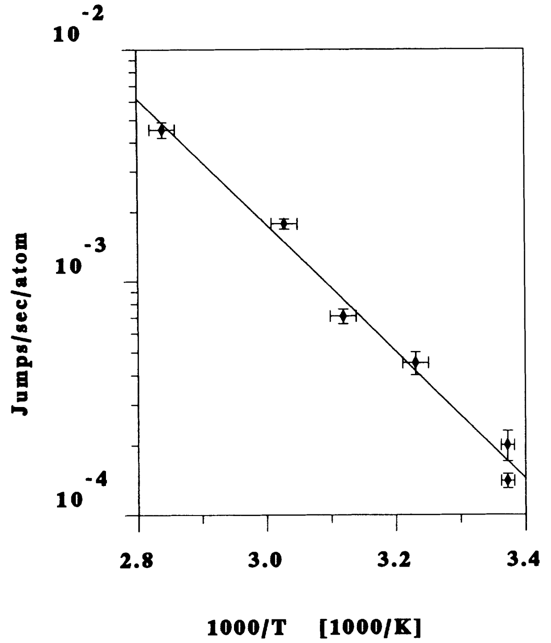

FIG. 3. Arrhenius plot of the observed movement rate for Pb adatoms at temperatures from 24 to 79 °C. Vertical error bars come from the expression for σ in the text; horizontal error bars reflect ±2 °C.

amined the relative frequency of interchanges with the seven near neighbors shown in Fig. 2. Compiling 285 single interchanges and referring to Fig. 2, we find that 56% are to position 1 or 4, 31% to position 2 or 3, 7% to position 5 or 7, and 6% to position 6. Thus diffusion perpendicular to the direction indicated in Fig. 2 is constrained; the ratio between the diffusion coefficient for single interchanges along the indicated direction and that perpendicular to it was found by a Monte Carlo simulation to be 2.6 [8]. [Note that the existence of three differently oriented $c(2\times8)$ domains on the surface will generally mask the role of this anisotropic diffusion in macroscopic measurements.] We observe no correlation between the diffusion and the direction of the current (up to 31 mA) flowing through the sample.

Because of the anisotropy we observe on the microscopic scale, it is not clear what exactly a scalar diffusion coefficient means for this system. However, since the anisotropy could be detected by a macroscopic measurement only under very unusual circumstances, we calculate the diffusion constant here so that these results may be more easily compared to other work. Also, since a macroscopic measurement would include the effect of both the single interchanges and the long jumps, but we do not know the length distribution of the long jumps, we use the total movement rate and the single interchange distance to obtain a minimum value for the two-dimensional diffusion constant. Using the result for an isotropic random walk, we expect the diffusion coefficient D for n dimensions is $D=\lambda^2 R/2n=D_0\exp(-E_D/kT)$, where λ is the distance moved. We take $\lambda=8\times10^{-8}$ cm to calculate the minimum value for the two-dimensional ($n=2$) diffusion constant $D_0\approx1\times10^{-9}$ cm^2/s.

One possible mechanism for the motion is that neighboring adatoms swap in the plane, perhaps in a concerted exchange mechanism related to that suggested for bulk Si by Pandey [9]. Perusal of Fig. 2 shows that there is more room for swaps to occur with sites 1 through 4 than with sites 5 through 7. This might produce both the anisotropy we observe in the single interchanges and the relatively low activation energy. In addition, it is clear that the exchanging atoms must move in concert. Thus it is not surprising that the effective attempt frequency we observe is orders of magnitude smaller than the attempt frequency that would be expected for a one-atom process (usually taken to be about the Debye frequency, $\approx 10^{13}\ \mathrm{s}^{-1}$).

Long jumps are observed to have roughly the same activation energy as the single interchanges, and yet are apparently not a series of independent single interchanges. Assuming that the motions are infrequent and independent, and given the single interchange rate $R_{\rm single}$, we expect $a_i t_i^2 R_{\rm single}^2$ cases per time interval where the same atom makes two independent single interchanges in one observation period. We find that up to about 4% of the total Pb movements are two-spacing migrations which can be explained as two independent single interchanges within the observation time. If we correct for these expected double interchanges, we then still find that 47% of the total motions are longer than could be predicted by a model of independent single interchanges. It seems that there are at least two possibilities for the mechanism of the long jumps. The first is that they take place by some process unrelated to the process of the single interchanges which happens to have an activation energy very close to that of the single interchanges. The second is that the long jumps also take place by a concerted exchange mechanism, perhaps involving a larger number of atoms and more complicated pathways.

Long jumps have been predicted by molecular-dynamics simulations of an atom on a metal surface [10], but have not been observed experimentally in such systems [11]. It is interesting that we can observe them in the rather different system of diffusion within a reconstructed semiconductor surface. This suggests long jumps may be a fundamental aspect of surface diffusion in many systems. We plan to study the long jumps further at lower densities of Pb adatoms to learn more about their length distribution. Theoretical studies of the energy of different diffusion paths would also help elucidate the mechanism of the long jumps.

We have carefully examined the influence of the scanning process on the adatom movement rate. First, at each temperature we made a few images at intervals 2–5 times as long as the rest in that data set. By analyzing the dependence of movement rate on imaging frequency, we can measure the number of interchanges induced by scanning. We find 0.01 ±0.015 interchange/adatom for each image scanned. Second, we take the fact that the movement rate increases as a function of the temperature according to the Arrhenius relation as a strong indication that the scanning process has a negligible effect. Therefore we conclude that the scanning process does not alter the measured activation energy.

In summary, we have used the tunneling microscope to quantitatively study diffusion within the reconstruction on a semiconductor surface on the atomic scale. We measured the activation energy for surface diffusion of individual Pb adatoms in substitutional sites of the Ge(111)-$c(2\times8)$ reconstruction from 24 to 79 °C. A large proportion of long jumps was observed. For single interchanges, we find that the diffusion is anisotropic within a single $c(2\times8)$ domain. A mechanism for the single interchanges is proposed; further study will be required to explain the long jumps. We conclude that variable-temperature atomic-resolution STM can be a powerful technique for the measurement of adatom diffusion.

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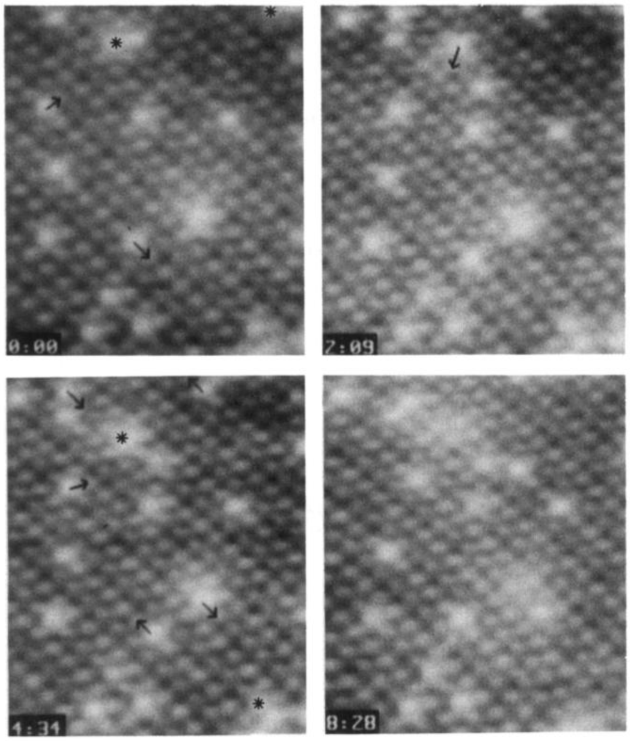

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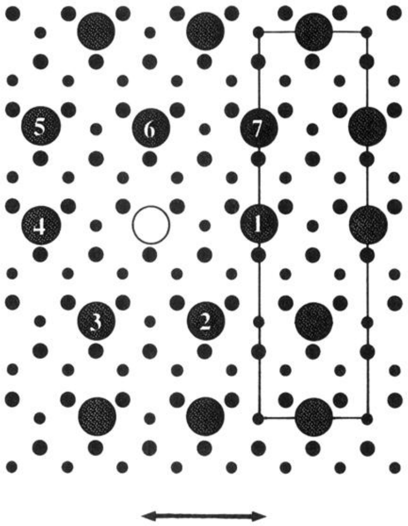

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