Direct Determination of Surface Diffusion by Displacement Distribution Measurement with Scanning Tunneling Microscopy

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A scanning tunneling microscopy (STM) method for studying surface diffusion is developed based on measurements of the displacement distribution of adsorbates by "image-anneal-image" cycles which allow direct observation of the diffusion process while avoiding potential STM tip effects. The method is used to study the anisotropic diffusion of Sb dimers on Si(001). The energy barrier and the prefactor for the faster diffusion *across* the substrate dimer rows are measured. On the other hand, the diffusion observed by the "image-while-hot" method appears nearly isotropic and also much faster. It is shown that this discrepancy is due to the STM tip influence present in the latter method.

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Surface diffusion of adsorbates is an important subject of surface science [1]. Although many methods have been developed to study surface diffusion [2-8], reliable measurements of random-walk diffusion coefficients are still rare, especially for semiconductor surfaces. Field ion microscopy (FIM) has provided the most direct observations of random-walk migration by directly measuring the atomic scale displacements of adsorbates caused by thermal annealing [2,3,9]. Much insight on the basic physics of adsorbate-surface interactions has been gained from these studies [10]. The substrate material suitable for the FIM studies, however, is rather limited because of the stability requirements under the strong electric field needed for imaging.

Scanning tunneling microscopy (STM), because of its ability to image many conducting surfaces with atomic resolution, offers great potential for studying surface diffusion. A method based on average island-density analysis [6] provides a measurement of surface diffusion, but it depends on modeling of the nucleation and growth processes. A more direct method is to image the surface while keeping the sample at a temperature at which adsorbates diffuse with a rate suitable for STM to track [8]. For simplicity this will be called the "image-while-hot" method herein. Because of the strong electric field and the high current density under the STM tip, the presence of the STM tip while diffusion is occurring raises the issue of the influence of the STM tip on diffusion processes [11,12], especially for adsorbates with a large net charge or polarizability.

In this Letter, we report studies of the surface diffusion of Sb dimers on Si(001) with a new STM method. The displacement distribution is directly measured by imaging the same adsorbates before and after thermal annealing at a certain temperature for a certain time period. The STM images are all taken at room temperature (RT) at which Sb dimers are immobile, while thermal diffusion is induced with the STM tip fully retracted. Thus potential STM tip effects on diffusion can be avoided. This method possesses the same advantages of FIM but it allows studies of adsorbate diffusion on a much broader range of surfaces. The diffusion of Sb dimers is found to be anisotropic with the faster direction being *across* the substrate dimer rows. The corresponding energy barrier and prefactor are measured. For comparison, we have also performed an "image-while-hot" experiment and the results are significantly different from the above in both the anisotropy and the magnitude of the diffusion rate. We show that this is due to the STM tip effect present in the image-while-hot method.

The experiment was carried out in an ultrahigh vacuum chamber with a STM and an Sb source. One crucial requirement of this method to study surface diffusion is the ability of the STM to image exactly the same area before and after thermal annealing. This is achievable because of the rigid STM design such that the shift of the tip position relative to the sample during the annealing is nearly all reversed when the sample is cooled to RT. The large scan range of the STM (~ 5 μm) also provides adequate tolerance for the residual shift which is typically below 0.2 μm in both the x and y directions even after annealing at as high as 700 K. The same areas are located using as landmarks the kink features in the substrate steps which stay unchanged for the temperatures of the experiments. The sample temperature during annealing is measured with a W(5% Re)-W(26% Re) thermocouple in direct contact with the sample during annealing and the uncertainty in the temperature measurement is estimated to be ± 10 K including the temperature drift during annealing. The time constants for heating and cooling the sample are several seconds which is much less than the shortest annealing period of 30 s used in the experiment. The Sb is deposited on Si(001) as Sb_4 tetramers because at a source temperature below 700 K Sb evaporates as Sb_4 [13]. This actually provides a convenient means to form Sb dimers on Si(001) as described below.

It has been shown that when Sb_4 is deposited on Si(001) at RT, four types of precursors coexist with the final-state clusters of dissociative chemisorption [14]. The final state consists of two Sb dimers with the dimer bonds perpendicular to the Si dimer bonds in the sub-

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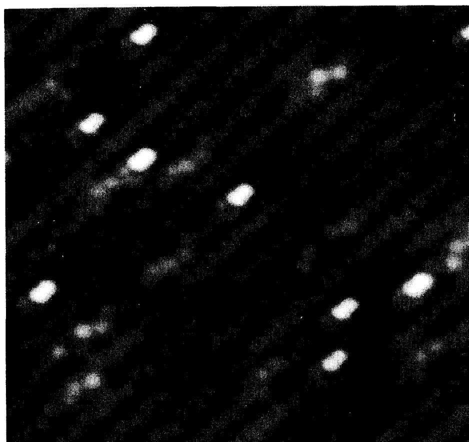

FIG. 1. STM image of individual Sb dimers on Si(001). Two atoms can be seen in each dimer. The sample has been annealed at 573 K for 40 min to disperse the Sb dimers. The image is taken with a tip bias of +1.0 V and a tunneling current of 0.2 nA.

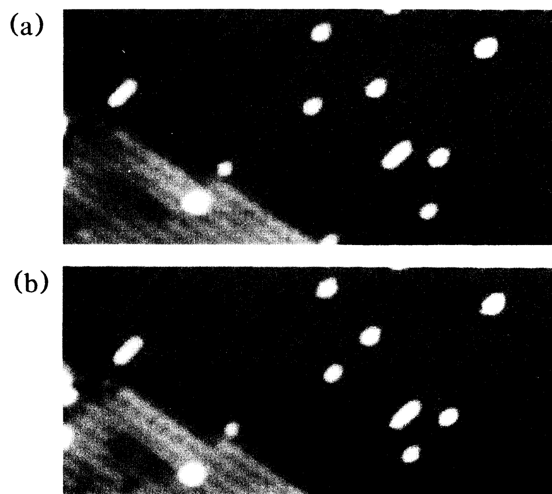

FIG. 2. STM images of the same surface area before (a) and after (b) thermal annealing at 479 K for 2 min, both taken with 1.0 V tip bias and 0.1 nA current. After the anneal several Sb dimers have moved across the substrate dimer rows (stripes in the images). The substrate step at the lower left corner serves as a reference point for determining the displacements. The long spots consist of two neighboring Sb dimers and they are excluded in the displacement measurement.

strate. Moderate annealing at, e.g., 420 K, can convert all the precursors to the final state but the two dimers in each final-state cluster are still mostly located next to each other. With further annealing at higher temperatures, however, they diffuse apart to become isolated dimers as shown in Fig. 1. These dimers are all located on the top [15] of the substrate dimer rows and are immobile at RT for as long as we have tracked them, at least for 2 d. When taking all these images, a low tip bias, e.g., 1.0 V, is used to avoid tip-induced displacements which will be discussed later.

Diffusion of these isolated Sb dimers is studied with the following procedure. After several STM images have been taken of surface areas that include a large number of dispersed Sb dimers, the STM tip is withdrawn from the sample by ~ 100 μm and the sample is annealed at a certain temperature for a certain time period to induce random displacements of the Sb dimers. The sample is quenched to RT at the end of the annealing. The exact same areas are imaged again to determine the displacements of the Sb dimers. In order to avoid either misidentifications or complications of dimer-dimer interactions, a low Sb coverage of 0.02 monolayer is used to obtain a large average separation between Sb dimers. The Sb dimers that happen to be located next to a defect including another Sb dimer are excluded in the displacement measurements. The time period for annealing at each temperature is chosen such that enough displacement is observed for good statistics while not too large as to cause difficulty in identifying the Sb dimers.

Figure 2 is an example of these image-anneal-image sequences. The two images are taken before and after an annealing at 479 K for 2 min during which several Sb dimers have displaced across the substrate dimer rows. Using this method we have measured the displacement distribution induced by annealing at different temperatures and some of the results are listed in Table I. It can be

TABLE I. The displacement distributions caused by annealing at several temperatures. The unit for the displacement across the dimer rows is the separation between the neighboring rows, 7.7 Å, while the unit for displacements along the dimer rows is the separation between neighboring dimers in a dimer row, 3.85 Å. Note the large range of annealing time which in turn provides a large temperature widow for determining the activation energy of diffusion. Because of space limitations, data for only four representative temperatures are shown.

	Across dimer rows					Along dimer rows	
Δ:	0	±1	±2	±3	±4	±1	±2
416 K, 648 min	256±16	95±10	13±4	0	0	0	0
446 K, 20 min	394±20	173±13	21±5	2±1	0	2±1	0
479 K, 2 min	449±21	197±14	20±4	0	0	2±1	2±1
533 K, 0.5 min	59±8	63±8	30±5	14±4	2±1	3±1	2±1

seen that the diffusion is very anisotropic, with the dominant displacement being *across* the substrate dimer rows. The number of Sb dimers that have displaced across the dimer rows are 1–2 orders of magnitude larger than that along the rows. Because the total number of displacement events along the dimer rows is too small for reliable statistics, we will only examine the diffusion of Sb dimers across the substrate dimer rows, effectively treating it as one-dimensional diffusion.

The displacement of Sb dimers across the dimer rows occurs in units of the dimer row spacing $a=7.7$ Å. It can be seen from Table I that displacements of $\pm 1a$ dominate the displacement distribution. Within the experimental uncertainty, the displacement distribution is consistent with that from a random walk with only single-step hops [16], although more data are needed to set a reliable upper limit on the contribution of longer hops.

From the displacement distributions measured above, we calculate the mean square displacement $\langle y^2 \rangle$ using

$$\langle y^2 \rangle = \frac{\sum_i n_i y_i^2}{\sum_i n_i},$$

where n_i is the number of Sb dimers that have been displaced by y_i. In a one-dimensional random walk, the mean square displacement is related to the diffusion coefficient D by [1]

$$\langle y^2 \rangle = 2Dt,$$

where t is the annealing time during which the displacements have occurred. This linear dependence of mean square displacement on time is confirmed within the experimental uncertainty. The diffusion coefficients obtained in this manner are plotted against the annealing temperature as shown in Fig. 3. The fact that the Arrhenius plot follows a linear relation further supports the conclusion that the diffusion is dominated by single-step hops. From the linear fit, the activation energy and the prefactor for the migration of Sb dimers across the surface dimer rows of Si(001) are determined to be 1.2 ± 0.1 eV and $10^{-4 \pm 1}$ cm^2/s, respectively. The large activation energy explains the fact that Sb dimers are practically immobile at RT, while single Sb atoms are found to be very mobile at RT [14]. This is different from diffusion on metal surfaces where the mobilities of single atoms and dimers are less different [17].

It is interesting that Sb dimers diffuse faster *across* the dimer rows while single atoms of both Si and Ge are found to diffuse faster *along* the dimer rows [18]. The mechanism of the anisotropic diffusion of Sb dimers on Si(001) is not known yet. It has been suggested that diffusion of metal dimers on transition metal surfaces occurs in two consecutive atomic hops [17]. In a separate study [19], we have found that an Sb dimer can be rotated to the orthogonal orientation with the dimer bond parallel to substrate dimer bonds, suggesting that both the energy difference between the two orientations and the energy barrier separating them are small. We speculate that the Sb dimers may move on Si(001) through a series of rotations of the dimer bonds.

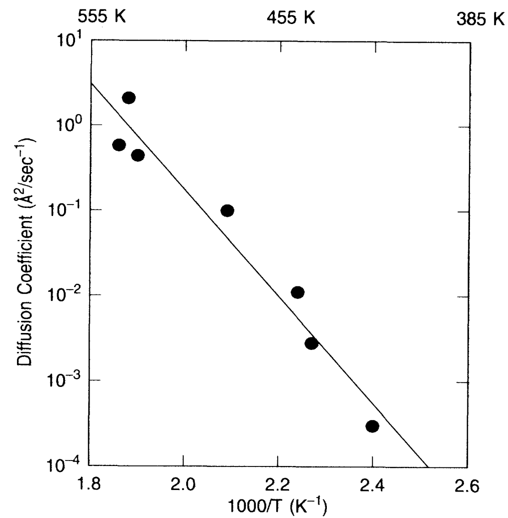

FIG. 3. Diffusion coefficients of Sb dimers across the substrate dimer rows as a function of temperature. From the slope and the intercept of the fit the activation energy and the prefactor are determined to be 1.2 ± 0.1 eV and $10^{-4\pm1}$ cm^2/s, respectively. The error bar for the diffusion coefficients is estimated to be 50% of the measured value.

As a comparison, we have also performed the image-while-hot experiment to observe diffusion at elevated temperatures. The hopping rate is measured by comparing consecutive images to identify the Sb dimers that have moved. We found that the diffusion rate measured in this way is much higher than that obtained from the displacement distribution measurement of image-anneal-image experiments at the same annealing temperature. We estimate that at 479 K, the rate is enhanced by nearly an order of magnitude. Furthermore, contrary to the large anisotropy observed in the image-anneal-image experiments, the diffusion of Sb dimers studied in the image-while-hot mode appears nearly isotropic. These observations indicate that the STM tip could have affected the diffusion of Sb dimers.

The strong interaction between the STM tip and Sb dimers is directly confirmed by the fact that even at RT the STM tip can induce displacements of Sb dimers if a high bias voltage, e.g., 3.5 V, both polarities, is used. Figure 4 shows an example of the STM tip-induced movements of Sb dimers at RT. We believe that this is caused by the field-induced diffusion due to the polarizability of Sb atoms [19]. It is likely that at a higher temperature at which the thermal energy is almost sufficient to cause diffusion of the Sb dimers, the STM tip could greatly enhance the diffusion rate even if a low tip bias, e.g., 1.0 V, is used. As shown in Fig. 4, with a high bias, the STM tip can move Sb dimers at RT either along or across the

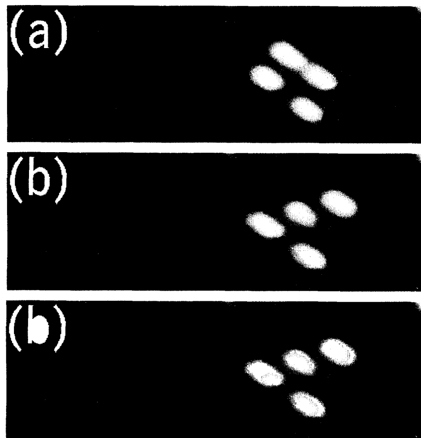

FIG. 4. The STM tip-induced displacements of Sb dimers on Si(001). The images shown are all taken with 1.0 V tip bias and 0.1 nA current which do not cause any motions. Sandwiched between these images, scans with 3.5 V tip bias are taken to induce the movements.

substrate dimer rows, further suggesting that the nearly isotropic diffusion observed in the image-while-hot mode is caused by the STM tip, whereas in the image-anneal-image method the tip is fully retracted during annealing, and imaging is performed at RT with a low bias so that the electric field is not strong enough to move the Sb dimers.

In summary, we have developed a STM method for studying surface diffusion based on measurements of the displacement distribution of adsorbates in an image-anneal-image mode. This method offers the same advantages of the FIM method, yet it allows studies of surface diffusion on a much broader range of substrate materials. The ability of the STM to image large areas also provides a practical convenience because a large number of displacement events can be observed in a single cycle. Using this method, Sb dimers are found to diffuse faster *across* the substrate dimer rows of Si(001). The activation energy and the prefactor for the Sb dimers to diffuse across the Si dimer rows are measured to be 1.2 ± 0.1 eV and $10^{-4 \pm 1}$ cm^2/s, respectively. We demonstrate that the STM tip can exert significant influence on diffusion of Sb dimers on Si(001) in image-while-hot experiments. While the importance of the STM tip effect varies from system to system, its influence on quantitative studies of kinetic processes using the image-while-hot method could be important for many systems. Comparison between the image-anneal-image and image-while-hot methods provides a direct means to check for potential STM tip influences.

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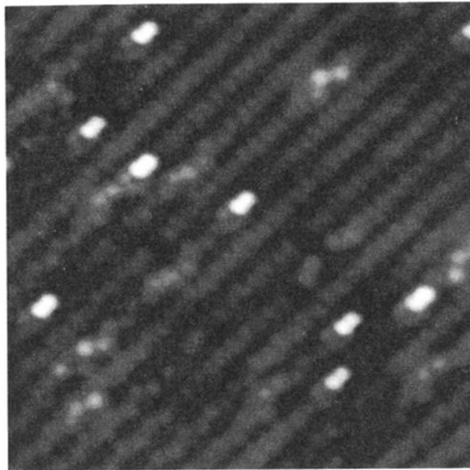

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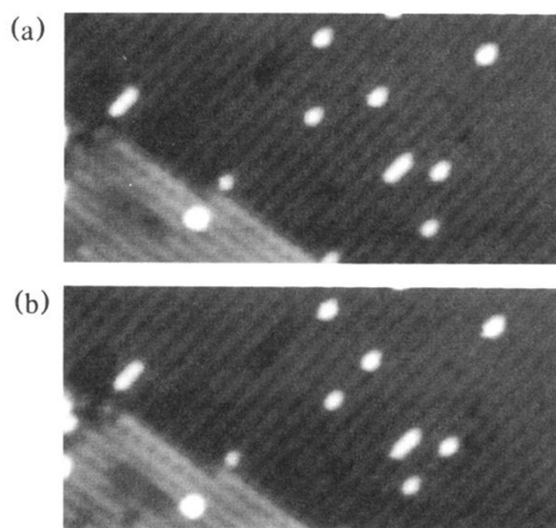

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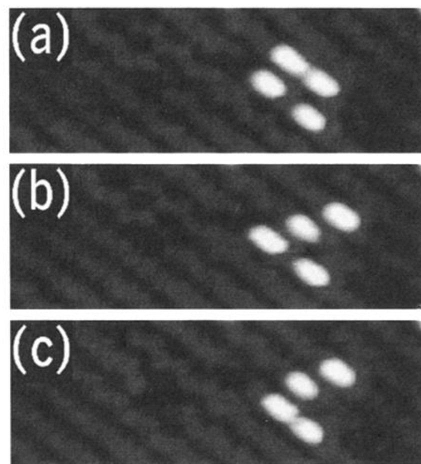

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