RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 58, NUMBER 20 15 NOVEMBER 1998-II

Direct measurement of field effects on surface diffusion

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(Received 10 August 1998)

We present here a method for quantitatively determining tip effects on surface diffusion during a scanning tunneling microscopy experiment. Using the technique of atom tracking, we measure the bias voltage and tunnel current dependencies of adsorbed Si dimer dynamics on Si(001). Throughout the range of typical tunneling conditions, the activation barrier for diffusion varies by less than 3%. We also find a striking difference between the electric-field effects on dimer diffusion and rotation, indicating the importance of transition states for this system. [S0163-1829(98)52744-0]

A microscopic understanding of electric-field effects on atom and cluster diffusion could provide new ways to tailor evolving morphology during crystal growth, or prevent detrimental electromigration effects. In the past 30 years, numerous studies have been conducted to explore the effect of applied fields, both perpendicular[1] and parallel[2] to a crystal surface. Whereas most of these investigated mesoscopic effects such as mass-transport and step flow in real time, some involved atomic resolution, albeit with a ''cook-and-look'' approach. We find that exceptional spatial and temporal resolution can be achieved simultaneously and directly with atom-tracking scanning tunneling microscopy (STM). In this technique, a conventional STM tip is placed over a diffusing species. Its position is continually maintained either directly atop the object or offset as much as one half of a lattice constant to the side (depending on the user-input set-point slope) by employing *lateral* feedback.[3] The instantaneous apparent X, Y, and Z positions[4,5] of the object are thereby recorded. Because the tip continuously follows the diffusing object of interest, the duty-cycle issues in conventional raster imaging are eliminated. Thousands of consecutive diffusion events can be recorded and analyzed within the context of classical statistics to determine precise surface energetics.[6] Data can be acquired throughout a range of tunneling conditions.

Because of the close proximity of the tip to the sample, and the small lateral area over which the electrons tunnel, surfaces can be subjected to very large electric fields and current densities while imaging with an STM. It is well known that this electric field and/or current can influence the kinetics of adsorbates and defects on the surface[7]—in some systems completely overcoming the intrinsic activation barriers for diffusion or desorption. Therefore, STM measurements of intrinsic activation barriers must be performed carefully to assure that the tunneling process itself has little or no consequence on the acquired results. In this study, we quantify such effects on the diffusion of adsorbed Si dimers over the Si(001) surface. We systematically vary the tip-induced electric field in both magnitude and direction by changing the applied bias voltage and the tip's lateral offset, and directly determine any changes in the activation barrier. For the case of Si dimer diffusion on Si(001), the presence of the STM tip introduces only a small perturbation on the intrinsic diffusion process throughout a reasonable and normal range of tunneling parameters.

We produce clean, well-ordered Si(001) substrates by resistively heating 5×13 mm^2 portions of a 0.5-mm-thick polished wafer to 1250 °C in ultrahigh vacuum (chamber base pressure $<5\times10^{-11}$ torr). Afterwards, the surface consists of Si dimer rows oriented perpendicularly on adjacent terraces, resulting in a dual domain (2×1) symmetry[8] (see Fig. 1). Low coverage (0.01–0.05 monolayer) Si deposition is accomplished by exposing the clean surface (<100 °C) to a hot (1150 °C) Si source for 1–3 s. Under these conditions, adsorbed Si monomers diffuse very rapidly; most combine to form dimers.[9] The sample is then heated to 100 °C on the STM where the data are acquired. Under ~175 °C, dimers diffuse primarily along the direction of the underlying substrate row.[10] In the same temperature range, diffusing dimers are reflected by many types of surface defects. Often, an adsorbed dimer becomes trapped between a pair of defects that constrains its motion to a short one-dimensional region for an extended period of time. Recording the diffusion statistics of these dimers enables us to extract detailed quantitative measurements of the local potential energy landscape over which they travel.[6]

To measure the perpendicular electric-field dependence of dimer kinetics, we acquire statistics using atom-tracking STM in the configuration of Fig. 2(a). With the lateral-feedback set-point slope equal to zero (corrected for incidental sample inclination), the tip's average position is main-

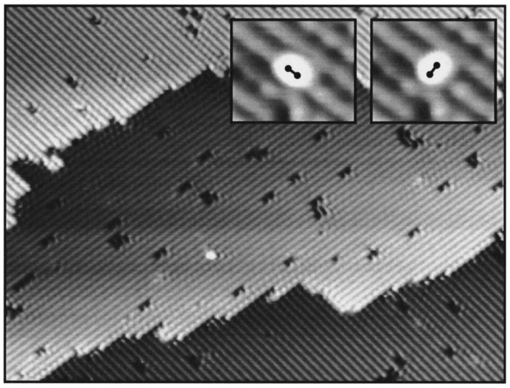

FIG. 1. Filled state STM image of ~100 °C Si(001) showing substrate dimer rows. The insets show room-temperature views of the adsorbed dimer's two possible rotational orientations with ball and stick models.

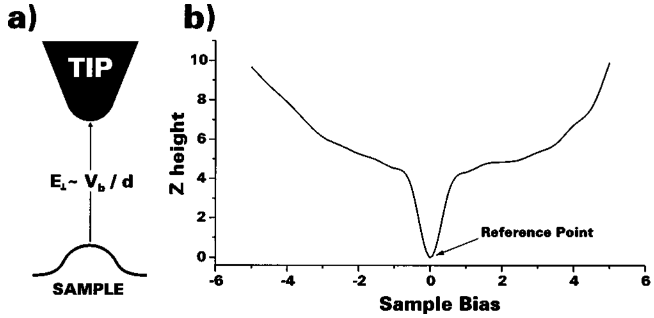

FIG. 2. (a) Effective geometry of the tunnel junction during measurements of the perpendicular field dependence on dimer rotation and translation. (b) V-Z scan result used to estimate tip-sample separation for converting bias voltage into electric-field strength.

tained directly atop the apparent apex of the diffusing dimer. In this geometry, the dimer experiences an electric field perpendicular to the surface with magnitude approximated by the applied bias voltage V divided by the tip-sample separation distance d. We calibrate this distance by performing a V-Z scan with our STM. That is, we determine the relative change in the vertical position of the tip required to maintain a constant tunnel current (0.06 nA) as a function of bias. Typical results are shown in Fig. 2(b). We define the tip-sample distance to be 0 Å at 0 V bias and use this point as an absolute reference.

We previously measured the adsorbed dimers' rotation activation barrier as a function of an applied electric field.[5] An adsorbed dimer can sit in one of two orthogonal orientations on the surface and can rotate between them even at room temperature. A dimer in both orientations is shown in the insets of Fig. 1. In this work, we measure the diffusion rate of the dimers as a function of applied field and extract the activation barrier from rate$=\nu\exp(-E_a/kT)$, in which the prefactor ν has been previously determined.[4] A negative field is defined as one in which the sample is biased negatively with respect to the tip. The results for activation barrier vs field, for both rotation and diffusion, are displayed in Fig. 3. The measured activation barriers are the difference in free energy between the transition states and the stable binding states. Each data point comes from 300–500 consecutive diffusion events recorded at different sample bias conditions between -4 and $+4$ V. Statistical ($\sqrt{N}$) error bars on each data point are about ± 2 meV. The diffusion barrier responds linearly with varying electric field. This is in direct contrast to the rotation barrier, which approximately goes as the electric field squared. We find that the transition rates can be affected by as much as a factor of 3 over the plotted range, but because the transition rate varies as the exponential of activation energy, the actual change in energetics is a small percentage of the barrier (3% for diffusion, 6% for rotation). Additionally, we determine there is no effect on measured barriers when the tunnel current is varied by two orders of magnitude at constant field, indicating the absence of electron stimulated processes contributing to the change in kinetic rates. These results establish that the technique of STM contributes minimal artifact when investigating Si dimer dynamics on Si(001), and especially for the case of dimer diffusion allows one to interpolate the zero-field limit result.

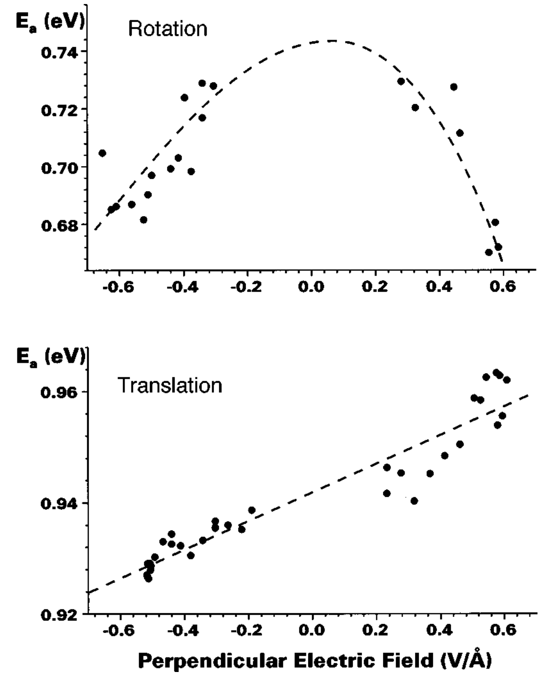

FIG. 3. (Top) Activation barrier for dimer rotation determined as a function of electric field perpendicular to the surface. (Bottom) Activation barrier for dimer hopping as a function of perpendicular electric field.

That the rotation and diffusion barriers have such remarkably different responses to an applied field attest to their contrary transition state electronic structures. An electric field can influence the measured barrier by changing either the initial stable binding state energy, the transition state energy, or both; it is the free energy *difference* between these two that defines the activation barrier. Because the stable binding states (initial states) are the same for both rotation and diffusion events, the observed field dependence functional forms must be largely influenced by their transition states' response. The symmetric field dependence of the rotation barrier reflects the polarizability of the rotational transition state, whereas the diffusion barrier's linear field dependence indicates that the charge of the dimer throughout the diffusion event is important. Coupling these results with field-dependent first-principles calculations will help to elucidate the details of the transition paths.

In order to investigate the field-induced lateral force on a diffusing dimer, we acquired atom-tracking data at various biases with the average position of the tip displaced by about 2 Å (~1/2 a lattice constant) along the direction of the diffusion channel. In this configuration, a parallel component to the tip-induced electric field should result, removing the translational symmetry on the surface—a hop in the direction towards the tunneling atom of the tip is not necessarily the same as a hop away from the tunneling atom of the tip. In these measurements, however, we find that there is no consistent systematic dependence of the preferred diffusion direction on tip displacement. Although in any given trial we measure a diffusion bias of at most 2 meV per site due to the offset tip (relative to the energetics derived when the tip sat directly atop the same dimer), it is observed for diffusion *either* towards or away from the tip. This is likely because of a competing and potentially counteracting effect. We conjecture that the tip morphology within 10–20 Å of the tunneling atom can result in a significant lateral gradient of perpendicular electric fields at the adsorbate position. Using the results from Fig. 3 and a reasonable guess at a possible tip shape envelope, one sees that this effect can easily appear to be several meV/site in either direction. However, as the tip shape is unknown and, more importantly uncontrollable, it is impossible to characterize the field distribution in the tunnel junction with sufficient accuracy, and derive the real interaction energy between the dimer and the parallel electric field. Nonetheless, we do identify a slight but measurable lateral interaction between the tip and the diffusing species, albeit qualitative, and believe that the ability to carefully characterize the tip shape will enable a quantitative understanding of the adsorbate manipulation process.

We have shown how the technique of atom tracking can be used to quantify the tip-induced components to surface diffusion, as studied with STM. In this paper, we present the electric-field dependence of adsorbed Si dimer diffusion on Si(001). We find that the electric field has very little influence on the diffusion kinetics, affecting the diffusion activation barrier by $<3\%$. Because the linear field dependence of the diffusion barrier is so remarkably different from the quadratic dependence of the rotation barrier, we conclude that the electronic structure of the transition state is predominantly responsible for the change in energetics. We also determined that a laterally offset tip has a very small effect on the observed dynamics, the details of which are most likely due to the unknown mesoscopic tip-shape envelope.

This work was performed at Sandia National Laboratory and was supported by DOE/BES Materials Sciences. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

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