Time-Dependent Tunneling Spectroscopy for Studying Surface Diffusion Confined in Nanostructures

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By confining a diffusion atom in a nanometer region using surface potential heterogeneity, we have successfully employed a time-dependent tunneling spectroscopy to quantitatively study its random motion. A hopping rate in the range of $1\text{--}10^4$ Hz, ~ 3 orders of magnitude faster than those accessible by the existing diffusion methods based on scanning tunneling microscopy, was demonstrated for single Cu atoms diffusing in the faulted half unit cell of Si(111)-(7 $\times$ 7). Our technique is potentially useful to detect fast diffusion processes such as H quantum diffusion at atomic scale.

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Surface diffusion is an important subject of study in physics, chemistry, biology, and materials science. It plays a vital role in chemical and surface catalytic reactions, self-assembly, crystal growth, and thin film epitaxy [1–5]. Observation and understanding of surface diffusion phenomenon in the past largely depend on the development of techniques [1,4]. Among the techniques, scanning tunneling microscopy (STM) [6] is advantageous in directly providing the atomistic mechanisms of diffusion [3–5,7–10] but is severely limited to slow diffusion rates from 10^{-19} to 10^{-14} cm²/s, as compared to the wide range from 10^{-19} to 10^{-5} cm²/s covered by the collection of different techniques [4]. Thus, processes in quantum diffusion of light atoms and in many other systems of practical interest with fast diffusion rates remain inaccessible by the STM technique.

Limited by the electronic feedback loop response, the diffusion rate that can be probed by the widely used frame-by-frame imaging [11] and atom-tracking [12] methods is in the slow regime. In atom tracking for which no full frame imaging is required, the fastest measurable hopping rate is about 10 Hz. With a state-of-art design [7,9,10], STM imaging can now be performed at a rate of ~ 10 frame/s, again leading to observation of a maximum hopping rate of only ~ 10 Hz (equivalent to $\sim 10^{-14}$ cm²/s for nearest neighbor site hopping). Using a new concept of measuring diffusion by the bypass of the feedback loop, we demonstrate in this Letter a new STM-based method that can expand the range by *at least* 3 orders of magnitude faster, to a hopping rate on the order of $\sim 10^4$ Hz (equivalent to $\sim 10^{-11}$ cm²/s). Further expansion of our method will become possible if faster preamplifier and data acquisition systems are used. This leads to significant overlaps in measurable diffusion rates with other techniques while retaining the atomic resolution. The extension will not only enable STM study of diffusion in the fast regime to facilitate direct comparison with results obtained by other

techniques, but also enable the study of processes such as H quantum diffusion for which cooling never slows it down [1]. As shown by Gomer and his co-workers with field emission microscopy, the H quantum diffusion measured for a large number of systems [13–16] falls in the range of 10^{-13} to 10^{-10} cm²/s, which is beyond the capability of the existing STM modes. The use of the new STM-based method for H quantum diffusion study will definitely shed light onto the understanding of this important process at atomic scale and help to resolve the dispute [16–18] on this topic with more experimental data.

Figure 1 shows the principles of our new STM mode for diffusion measurement. In this mode, the STM feedback loop is temporarily turned off while acquiring a time-dependent tunneling spectrum between a stationary STM tip and a fixed position (e.g., an adsorption site) on the sample surface. By taking advantage of the heterogeneity of the surface potential energy, a diffusing particle confined in a nanometer size region would repeatedly pass through a given site and thus be detected by the tip above it. The time-dependent tunneling current would then be encoded with the information of the residence time of the diffusing particle at the given site. Assuming that at time $t = 0$ the diffusing particle is at a given site, the probability $P(t)$ to find it remaining at this site at time t is given by [4]

FIG. 1. A sketch of operational principle for diffusive hopping measurement using a stationary STM tip.

$$P(t) = \exp(-\Gamma t),$$

where Γ is the hopping rate out of this adsorption site. If now all the events of the diffusing particle detected at the given adsorption site are regarded as a statistical ensemble, we can analyze their residence time and obtain the above probability function to find Γ . To demonstrate this method, we choose to study the single Cu atom diffusion within the faulted half unit cell of Si(111)-(7 × 7) on which a nanometer size confinement naturally exists by the surface reconstruction. Previously, similar analysis of a time-dependent tunneling current was used for the observation of electron driven hopping between two rotation states for C₂H₂ and between two-site displacement for Si [19,20].

The experiment was carried out on an Omicron variable temperature scanning tunneling microscope operated in ultrahigh vacuum (base pressure $\sim 7 \times 10^{-11}$ torr). The STM tips were chemically etched tungsten tips, which, prior to their first use, were cleaned by Ar⁺ sputtering. The Si(111) wafer was *n* type with a resistivity of 7 Ω cm. After a thorough degassing at 600 K for several hours, the clean Si(111)-(7 × 7) surface was prepared by flashing it to ~ 1500 K for a number of times under a vacuum of $< 2 \times 10^{-9}$ torr. A small amount of Au, Ag, or Cu, ~ 0.002 monolayer, was then deposited on the clean Si(111)-(7 × 7) surfaces at room temperature. During the STM measurement, the sample temperature was controlled by a combination of cooling and heating. To have good statistics, a large number of events (~ 200 –700) are recorded and analyzed at a given temperature. To minimize the STM tip effect, we operate the STM at 50 pA with various bias voltages, which guarantees a tip-surface distance to be ~ 1.0 nm as judged from the tunneling current versus the tip-surface distance curve.

In Fig. 2 we show the room temperature (RT) STM images of Au, Ag, and Cu atoms on Si(111)-(7 × 7). As usual, the Si adatoms of the substrate appear bright and the corner holes appear dark under negative bias voltage. Quite unexpectedly, when there is just one single Au, Ag, or Cu atom occupying the faulted half unit cell, the STM images show up as six bright (brighter than Si adatoms) spots that form a triangle. Previously, these triangular patterns were often assigned as clusters formed by three or six atoms [21,22]; our STM images taken at low temperature (LT) [Fig. 2(d)] clearly show that only a single bright spot remains in the faulted half unit cell after cooling to 77 K. This change in STM images between RT and LT is found reversible, indicating that the six bright spots at RT is a result of frequent hopping of an atom among different adsorption sites. The conclusion that the RT triangular pattern is formed by a single Ag atom on Si(111)-(7 × 7) was previously reached by correlating the triangular patterns and the calibrated deposition [23,24].

Using the proposed method, we can quantitatively measure the Cu atom hopping rate out of the corner or the center Si-adatom sites [25]. In Fig. 3(a), we display two

FIG. 2 (color). Typical STM images of (a) Au, (b) Ag, and (c) Cu atoms on Si(111)-(7 × 7) at room temperature. The triangular patterns in each faulted half unit cell are caused by single metallic atoms. (d) The structure of (c) after *in situ* cooling to 77 K, with the triangular patterns becoming single bright spots. The images are taken at -2.0 V and 0.05 nA. The circles and crosses in (c) show the positions at the corner and the center Si-adatom sites, respectively. For reference, the Ag spot in (b) is about 0.5 Å higher than the Si adatoms.

typical time-dependent tunneling spectra: one above the center and the other above the corner Si-adatom sites at 208 K. The high current value is caused by a diffusing Cu atom residing at the site underneath the STM tip, and the low current value corresponds to the Si(111)-(7 × 7) bare substrate at the respective sites. The randomly appearing events of a Cu atom at the adsorption sites are clearly shown by clean-cut high tunneling current (150 pA) pulses in the spectra. In Fig. 3(b), we plot the number of resident events that have a residence time longer than a given duration as a function of time. They follow exponential decay curves well. As shown above, the inverse of the decay time constant from these plots is simply the hopping rate out of a given site. In Fig. 4, we depict the hopping rate over 4 orders of magnitude for a number of temperatures in an Arrhenius plot for both the corner and the center Si-adatom sites. While the hopping rate for a given atom can be determined better than 20%, repeating measurements on different Cu atoms give a reproducibility within 50%. The hopping rate data can be fitted by $\Gamma = \Gamma_0 \exp(-E_a/kT)$ quite well. The deduced diffusion activation energies for the center and corner sites are, respectively, $E_a = 0.36 \pm 0.02$ and 0.40 ± 0.02 eV with an identical prefactor $\Gamma_0 = 10^{10.7 \pm 0.3}$ Hz. When we increase the bias from -0.5 to

FIG. 3 (color). (a) Time-dependent tunneling current spectra taken above a center and a corner Si-atom site, respectively. A high current level represents a Cu atom moving to cause the respective sites to be brighter. (b) The bar distribution of the events with their resident time longer than the given time in the horizontal axis. The solids lines are exponential fits. The example here was taken at 208 K with a bias of -0.5 V.

-1.0 V, the measured hopping rates remain basically unchanged, indicating that the tip effect is minor. Only when the bias exceeds -2.0 V, a noticeable deviation (about a factor of 2 or more) in the hopping rate starts to appear at

FIG. 4 (color online). Arrhenius plot of the hopping rate, Γ , for the Cu atom from 200 to 320 K. The circles are data for the center Si-atom site, and the squares are data for the corner Si-atom site. Here, the open symbols represent data taken at the -0.5 V bias, and the filled symbols data taken at the -1.0 V bias.

low temperatures, a sign of the onset of tip-sample interaction.

There is contained more information than just the hopping rate in the tunneling spectra. As shown in Fig. 3(b) the fractional Cu occupation time at the corner site is 31.5%, and at the center site it is 3.2%. The total occupation time of 34.7% at these two sites is consistent with the threefold symmetry (ideally 33.3%) of the faulted half unit cell structure and indicates that the diffusion is truly random and has not been affected by the STM tip. The randomness of the events appearing in the spectra [e.g., Fig. 3(a)] further supports the negligible influence of the STM tip on Cu diffusion. The above fractional occupation times also lead to an estimate of adsorption energy at corner sites being ~ 40 – 50 meV larger than at center sites, consistent with the diffusion activation energy difference of ~ 40 meV shown above. The RT images [Fig. 2(c)] showing brighter spots at the corner sites than at the center sites already consistently indicate that the corner Si-atom site is the most stable adsorption site. While there is no independent data for Cu on this surface available, using a time consuming frame-by-frame imaging procedure, Tsong's group was also able to determine the relative adsorption energies for O_2 [26] and H [27] on the center and corner Si-atom sites, for which an energy difference of 50–150 meV was observed.

The present method has a number of advantages. First, it can measure much a faster diffusion rate without request for sophisticated instrumentation. Here, we have demonstrated 3–4 orders of magnitude faster hopping rate with the STM vendor's preamplifier (100 kHz). Further improvement can be achieved with commercially available broader bandwidth preamplifiers. Second, the hopping rate can now be measured for individual sites [26,27], as shown presently for the nonequivalent corner and center Si-atom sites. The ability of measuring site-specific hopping rates may further allow us to investigate diffusion heterogeneity, e.g., due to defects, and bring new understanding of the respective interactions. Third, owing to the significantly more diffusion events occurring at high temperatures, the data acquisition time for all systems that were studied by frame-by-frame imaging or atom-tracking methods at lower temperatures can now be significantly reduced for comparable statistics. Last, there is more information contained in the time-dependent tunneling spectra. For example, the fractional occupation time at a given site provides quantitative information on the relative adsorption energy. The statistical nature of the residence event and the site occupation time reveals important knowledge about the external field effect, e.g., the tip effect.

While the fluctuation of the tunneling current detected by a stationary blunt STM tip was proposed and demonstrated to measure the collective diffusion coefficient of a large number of adsorbates in the past [28,29], it was thought that single particle diffusion would not produce

such a current fluctuation to obtain an autocorrelation to deduce the diffusion coefficient. The key for the success of our mode is the surface potential energy heterogeneity that forces the diffusing species repeatedly to return to the site of interest. It is thus especially suitable for diffusion study on nanomaterial surfaces. This seems to shadow the present method as a general surface diffusion technique compared to the frame-by-frame imaging and the atom-tracking methods. However, by exploiting the Schwoebel barrier at the steps [1–5], one may form nanometer-sized islands on a flat surface with very few atoms. Diffusion on top of the islands, similar to the cases in field ion microscopy, becomes confined and measurable by our method. One can also build other nanostructures such as “quantum corral” by atom manipulation [30] for the confinement. With a reduced dimension, namely, diffusion along a trough on many anisotropic surfaces, confinement is much easier by simply placing two atomic reflection stoppers along the trough.

In summary, we have proposed and demonstrated a new STM mode that can measure fast surface diffusion confined in nanostructures. For Cu on Si(111)-(7 × 7), we have clearly shown that the RT triangular STM patterns are caused by fast diffusion of single atoms rather than by clusters of three or six atoms, or by the pure electronic effect. Quantitative site-specific hopping rates as well as the residence time at different sites have been unambiguously measured, revealing that the corner Si-adatom site corresponds to a stable adsorption site with ~40 meV lower energy than the center Si-adatom site. Future applications of our method to fast diffusion processes with practical interest are possible and may bring further understanding at the atomic scale.

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