

Azimuthal dependence of classical over-barrier hopping diffusion of hydrogen on a vicinal Ni(111) surface

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Using an unusual arrangement of optical techniques, we studied the full azimuthal dependence of hydrogen diffusion on a 0.1° -miscut Ni(111) surface vs temperature. From such a dependence, we arrived at the conclusion that the extra energy barrier for a hydrogen adatom to cross a [110] step edge must be less than 60 meV or 1.5 kcal/mol. [S0163-1829(98)51336-7]

Diffusion of adsorbates on crystalline surfaces is one of the most important subjects in surface science and materials research as it is involved in many fundamental material processes, such as epitaxy, catalysis, corrosion, and thermal annealing.¹⁻⁴ Many experimental methods have been devised in the past decades for studying such a process for various combinations of adsorbates and substrates.^{1,5-10} There has also been tremendous progress made in the theoretical understanding of atomistic and collective aspects of surface diffusion, both phenomenologically and in first-principles analysis.^{1,11-15} So far, most experimental and theoretical studies have been focused upon adsorbate diffusion on flat terraces of crystalline substrates. Even for this *relatively* simpler case, the task is already enormous both experimentally and theoretically.

In reality, however, topmost surfaces of crystalline substrates consist of flat terraces that are separated by steps or step bunches (clusters). The spacing between these steps or step bunches varies from a few lattice constants to micrometers, depending upon substrates, the orientation of the topmost surfaces, and how they are prepared. There are not many experimental techniques that are capable of measurements that readily separate the kinetics over flat terraces and those at steps. One of these techniques is scanning tunneling microscopy (STM).¹⁶ By invoking the nucleation theory, Bromann *et al.* found it feasible to deduce the Schwoebel-Ehrlich barrier or step-edge barrier by measuring the nucleation rate on two-dimensional islands as a function of island size and temperature.¹⁶ The laser-induced thermal desorption mass spectrometry used by George and co-workers is an example of macroscopic techniques that can be configured to measure the anisotropy of the diffusion rates on a substrate and in turn to extract the step-edge barrier.⁹

Zhu and co-workers and Reider *et al.* demonstrated another macroscopic technique that is capable of resolving the anisotropy of the diffusion rates on a substrate.⁵⁻⁸ This technique combines a laser-induced thermal desorption (using a pulsed optical interference pattern) to form a periodic distribution of adsorbates with a subsequent optical diffraction measurement from such a distribution to monitor the decay of the density modulation or grating. From the decay exponent, one directly extracts the diffusion rate along the direction perpendicular to the density grating. By varying the orientation of such a density grating with respect to a surface crystalline axis, one can readily obtain the azimuthal depen-

dence of the diffusion rates. Xiao *et al.* recently performed such measurements of CO diffusion on Ni(110) by rotating a Ni(110) sample with respect to its surface normal while keeping the optics of laser-induced desorption and optical diffraction unchanged.¹⁷

In this paper, we report an experimental study of the azimuthal dependence of hydrogen diffusion on a 0.1° -miscut Ni(111) using a different arrangement of laser-induced desorption and linear optical diffraction techniques. Our method is a variation of the one used by Xiao *et al.* Instead of rotating the substrate about the surface normal, we keep the substrate unchanged and rotate the incidence plane that contains both the desorption laser beams and the probe laser beam. Such an arrangement has the following advantages.

(i) As the substrate remains unchanged, we easily cover a full 360° range of azimuthal angles under cryogenic cooling conditions. The latter often severely limit the range of substrate azimuthal rotation under ultrahigh vacuum (UHV).

(ii) Since we rotate the entire desorption and probe laser assembly externally, we can easily and reproducibly vary the azimuthal angle with a precision optical stage. Such a precision is not readily achievable with conventional UHV sample holders that are usually poor optical mounts.

In an earlier experiment, we established that the diffusion of hydrogen adatoms on a Ni(111) surface is dominated by a classical over-barrier hopping at above 110 K.⁶ In this regime, the energy barrier and the diffusivity for hydrogen over (111) terraces were determined to be $E_{\text{terrace}} = 200$ MeV (4.5 kcal/mol) and $D_{0,\text{terrace}} = 2.8 \times 10^{-3}$ cm²/s, respectively. In the present study, we determine the kinetic parameters of hydrogen hopping over step edges by investigating the azimuthal dependence of diffusion rates as a function of temperature.

The experiment is performed in an ultra-high-vacuum chamber with an operating pressure below 5×10^{-12} torr. A 1-cm-diameter Ni single-crystalline substrate disk exposes a (111)-oriented face with a miscut angle of 0.1° as determined by x-ray diffraction. Before the dissociative adsorption of hydrogen, the Ni(111) surface is cleaned with cycles of Ne ion sputtering at room temperature, followed by thermal annealing at 1000 K for a few minutes. The cleaned Ni(111) surface shows no traces of sulfur or carbon from a retarding-field Auger electron spectroscopy measurement. In a room-temperature scanning tunneling microscopy measurement, Maurice *et al.* showed that a clean Ni(111) surface with

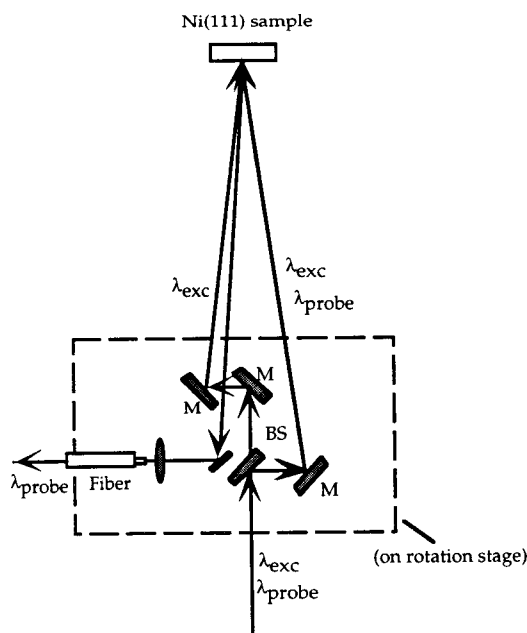


FIG. 1. Sketch of an optical assembly for preparation and monitoring of hydrogen adatom density gratings. The assembly is outside of the ultrahigh-vacuum chamber that hosts the Ni(111) sample. It consists of optics for laser-induced thermal desorption and for optical diffraction measurement all mounted on a precision rotation stage.

nominally 1° miscut was terminated with almost straight monatomic steps that ran perpendicular to the miscut direction with a density essentially determined by the miscut angle.¹⁸ The meanderingness along step edges is on the average less than ± 2 nm, which was a few percent of the averaged terrace width. We expect our 0.1° -miscut Ni(111) also to be terminated with straight monatomic steps with negligible meanderingness at or below room temperature. We also expect the step density to be roughly determined by the miscut angle of 0.1° .

We here elaborate in some detail on our optical arrangement for laser-induced desorption and optical diffraction. Other details of the experimental procedure have been described elsewhere.^{6,7} In Fig. 1 we show the sketch of our experimental setup. The beam splitting optics that produces the pulse pair to create an adsorbate density grating and the probe beam optics to monitor the first-order optical diffraction from such a density grating are mounted on a Newport precision rotation stage. For desorption, we use a single optical pulse from a Nd:YAG laser with a duration of 10 ns and a wavelength of $\lambda_{exc} = 1.064 \mu\text{m}$. In this study, hydrogen density gratings formed by laser-induced desorption have a spatial periodicity of $4.5 \mu\text{m}$.⁷ For optical diffraction measurement, we use a 2 mW He-Ne laser at $\lambda_{probe} = 0.6328 \mu\text{m}$. The incident He-Ne laser beam traces the path of one of the desorption laser beams. The first-order diffraction of the He-Ne laser beam is directed into one end of a flexible optical fiber. The other end of the fiber goes to a photomultiplier detector. We are able to freely and reproducibly rotate the optical assembly over the entire 360° range. By overlapping the axis of the rotation stage with the sample surface normal and with the two desorption beams on the sample, we are able to prepare and monitor the periodic dis-

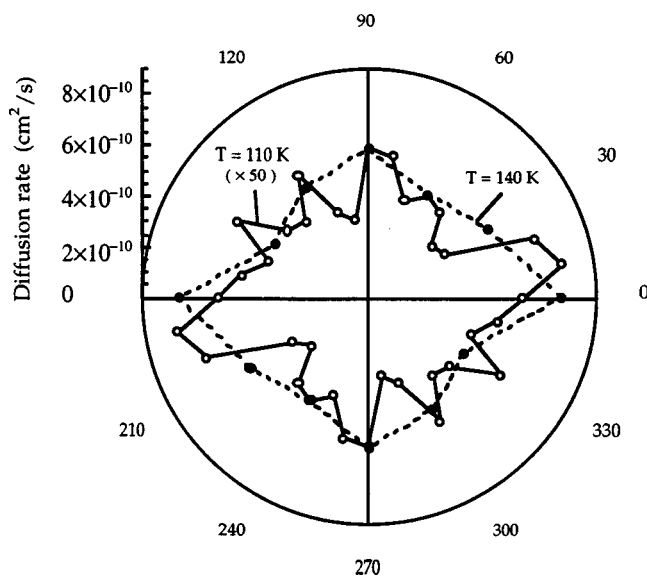


FIG. 2. Linear plots of the diffusion rates of hydrogen atoms vs azimuthal angle on a 0.1° -miscut Ni(111) surface measured at 140 and 110 K. The rates obtained at 110 K have been multiplied by a factor of 50 before being displayed.

tribution of hydrogen adatom density as a function of the azimuthal direction at the same spot on the sample.

In Fig. 2, we display the linear plots of the diffusion rates vs azimuthal angle measured at 140 K (dotted line) and 110 K (solid line). The mean coverage of hydrogen adatoms is $\theta_0 = 0.3$. $\Phi = 0^\circ$ corresponds to the diffusion along one of the $[110]$ axes in the surface plane. It is also the direction along which we earlier performed an extensive temperature-dependence measurement. Starting from $\Phi = 0^\circ$, we measured the diffusion rate at every 10° increment over the entire 360° range. The rates on the average decrease by a factor of 50 as the temperature drops from 140 to 110 K. To compare the azimuthal dependence at the two temperatures equitably, we have multiplied the rates obtained at 110 K by a factor of 50 before they are displayed in Fig. 2. The diffusion rates did not vary by more than a factor of four in the entire range of azimuthal angles. The maximum uncertainty in the measured diffusion rates are within 35% of the displayed values and these errors are random.

The most striking feature in Fig. 2 is that the azimuthal dependence shows a very weak anisotropy at 110 K and remains almost unchanged from 140 to 110 K even though the absolute rate has decreased by two orders of magnitude. It is noteworthy that while the decrease in the absolute diffusion rate measures the diffusion energy barrier over flat terraces,⁶ the anisotropy in the azimuthal dependence measures the difference between the energy barrier for crossing a step edge and the barrier for hopping over flat terraces.^{6,19} At 110 K, the minimum of the diffusion rate appears at either $\Phi = -37^\circ$ or 30° and it is no less than a factor of 3 smaller than the maximum rate. This means that the additional energy barrier for a hydrogen adatom to ascend or descend a step edge is small compared to the activation barrier over flat terraces (4.5 kcal/mol). This observation is significant considering that a 0.1° -miscut Ni(111) surface has roughly one step edge for every 400 terrace sites in the miscut direction or roughly 50 step edges over a distance of $4.5 \mu\text{m}$. In the

following, we offer a more detailed analysis of the step-edge effect and determine quantitatively the upper limit of the step-edge barrier.

Let α be the fractional density of monatomic steps along the miscut direction, and ϕ be the angle between the directions of the diffusion and the miscut. Let E_{step} be the largest of the ascending and descending energy barriers across a step edge. We define an effective diffusion constant over steps as $D_{\text{step}} = D_{0,\text{step}} \exp(-E_{\text{step}}/k_B T)$. The diffusion rate over a flat terrace of Ni(111) $D_{\text{terrace}} = D_{0,\text{terrace}} \exp(-E_{\text{terrace}}/k_B T)$ was determined previously with $D_{0,\text{terrace}} = 2.8 \times 10^{-3}$ cm²/s and $E_{\text{terrace}} = 200$ meV. It can be easily shown that

$$D(\phi) = D_{\text{terrace}} \sin^2 \phi + \cos^2 \phi / [\alpha / D_{\text{step}} + (1 - \alpha) / D_{\text{terrace}}]$$

(Refs. 6 and 19), or after a rearrangement,

$$D(\phi) = D_{\text{terrace}} \left[1 - \cos^2 \phi \frac{\alpha (D_{\text{terrace}} / D_{\text{step}} - 1)}{1 + \alpha (D_{\text{terrace}} / D_{\text{step}} - 1)} \right]. \quad (1)$$

The second term in the square brackets gives rise to the anisotropy. The aspect ratio of the anisotropy can be defined as $\gamma \equiv D(\phi = 90^\circ) / D(\phi = 0^\circ)$ or $\gamma = 1 - \alpha (D_{\text{terrace}} / D_{\text{step}} - 1) / [1 + \alpha (D_{\text{terrace}} / D_{\text{step}} - 1)]$. We now apply this analysis to our experimental result. From the STM study by Maurice *et al.*, we can assume that the averaged step density on our 0.1°-miscut Ni(111) is predominantly determined by the miscut angle so that $\alpha \approx 2.5 \times 10^{-3}$. Using $\alpha \approx 2.5 \times 10^{-3}$ and assuming $D_{0,\text{step}} \approx D_{0,\text{terrace}} = 2.8 \times 10^{-3}$ cm²/s, we arrive at $\exp[(E_{\text{step}} - E_{\text{terrace}}) / k_B T] \leq (1 - \gamma) / (\gamma \alpha) \sim 10^3$. With $T = 110$ K, we obtain an upper limit of the Schwoebel-Ehrlich barrier $E_{\text{step}} - E_{\text{terrace}} \leq 1.5$ kcal/mol (or 60 meV/atom). This means that the extra barrier for a hydrogen atom to descend or ascend a step edge on Ni(111) is no more than 1.5 kcal/mol or less than 1/3 of the diffusion energy barrier over flat terraces ($E_{\text{terrace}} = 200$ meV). Even if we use the ratio of 1/4 between the minimum diffusion rate and the maximum diffusion rate over the entire azimuthal range as the extreme measure of the aspect ratio, we would arrive at the upper limit of the Schwoebel-Ehrlich barrier $E_{\text{step}} - E_{\text{terrace}} \leq 1.56$ kcal/mol.

Our experimental results qualitatively support an effective-medium theory calculation of hydrogen energy surfaces by Nordlander *et al.*¹² On a Ni(111) surface miscut along either $\Phi = -37^\circ$ or 30° , the resultant step edges consist of long segments of close-packed rows jointed by kinks as shown in Fig. 3. Near a step edge, it resembles a Ni(110) surface. Since hydrogen atoms reside at threefold hollow sites on both Ni(111) and Ni(110), crossing a step edge on a vicinal Ni(111) is equivalent to crossing a close-packed row on Ni(110). It is between a threefold hollow site on an upper terrace and a threefold corner site on the lower terrace over a twofold short-bridge site.²⁰⁻²² Nordlander *et al.* calculated the hydrogen adsorption energy surfaces on Ni(111) and Ni(110).¹² On (111) terraces these authors found that the diffusion of a hydrogen adatom took place between a pair of fcc and hcp threefold hollow sites (e.g., A, B, C, E, F, and G) over a twofold bridge site (e.g., S₁, S₂, S₅, and S₆) with a barrier of 100 meV or 2.3 kcal/mol. On Ni(110) along [001]

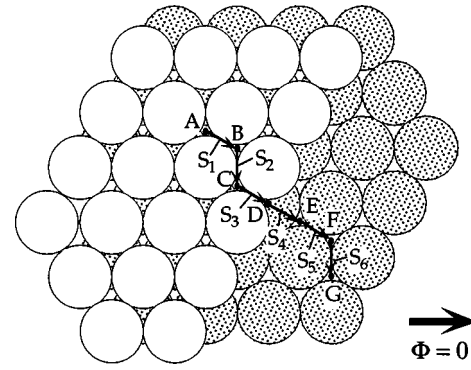


FIG. 3. Sketch of a vicinal Ni(111) surface with step edges running along close-packed rows. The large arrow points along the direction corresponding to $\Phi = 0$ in Fig. 2. The connected arrows form a possible diffusion path for a hydrogen adatom. A, B, C, D, E, F, and G are adsorption sites with three-fold coordination. S₁, S₂, S₃, S₄, S₅, and S₆ are saddle points along the diffusion path.

direction (e.g., $S_3 \rightarrow D \rightarrow S_4 \rightarrow E \rightarrow S_5$), they found that the energy barriers for hopping from the upper terrace site C to the lower terrace corner D over S₃ and from D to another lower terrace site E over S₄ are also 100 meV or 2.3 kcal/mol. In addition, the binding energy at the corner site D is the same as that at threefold hollow sites on (111) terraces and thus the corner site does not act as a trap. Although the energy barrier predicted by the effective medium theory is a factor of two smaller than the experimental value of $E_{\text{terrace}} = 200$ meV, the theory correctly reproduces the qualitative feature of our experimental observation. Such a small step-edge barrier on Ni(111) may be understood if we assume that the binding energy of hydrogen along its diffusion path is mostly determined by the binding coordination number with the Ni substrate atoms.¹⁴ Since the corner site D has a coordination number of 3, it should not be surprising that the binding energy is almost the same as that at a threefold hollow site on (111) terraces. By the same token, as a hydrogen adatom traverses from the upper terrace site C to the lower terrace corner D, the saddle point S₃ has the same coordination number (=2) as the saddle points on open (111) terraces (e.g., S₁, S₂, S₅, and S₆). Therefore we also expect the saddle-point energy at S₃ to be the same as at S₁, S₂, S₅, and S₆. It is noteworthy that a hydrogen atom at the corner site D does not have to hop over S₄ in order to move onto the open lower terrace. It may hop to a neighboring threefold coordinated corner site over a twofold short-bridge site and then onto the open terrace. This makes a vicinal Ni(111) surface appear very smooth for a hydrogen adatom.

In conclusion, we have devised a convenient experimental method to study the azimuthal dependence of adsorbate diffusion on a substrate. Our investigation of hydrogen diffusion on a 0.1°-miscut Ni(111) surface using this technique reveals that the extra energy barrier to descend or ascend a step edge is less than 1/3 of the diffusion energy barrier on an open (111) terrace.

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- ⁶By symmetry, $D(\phi) = D_{\parallel} \sin^2 \phi + D_{\perp} \cos^2 \phi$, where $D_{\parallel} = D_{\text{terrace}}$ is the rate of diffusion parallel to steps and D_{\perp} is the rate of diffusion perpendicular to the steps. Let $\tau_{\text{step}} = \tau_0 \exp(E_{\text{step}}/k_B T)$ be the residence time at a step site and $\tau_{\text{terrace}} = \tau_0 \exp(E_{\text{terrace}}/k_B T)$ be the residence time at a terrace site. Perpendicular to steps, a tracer adatom traverses a mean distance of Na_l in a time interval τ by making N^2 jumps of length a_l . As τ is the total residence time it is given by $\tau = N^2[\alpha \tau_{\text{step}} + (1 - \alpha) \tau_{\text{terrace}}]$. By definition $D_{\perp} = (Na_l)^2/4\tau$. From $D_{\text{step}} = a_l^2/4\tau_{\text{step}}$ and $D_{\text{terrace}} = a_l^2/4\tau_{\text{terrace}}$, we arrive at $D_{\perp} = 1/[\alpha/D_{\text{step}} + (1 - \alpha)/D_{\text{terrace}}]$ and Eq. (1) in the text.
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