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Classical and quantum diffusion of hydrogen atoms on Cu(1 1 1)

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ABSTRACT

We measured diffusion constants of hydrogen adatoms on Cu(1 1 1) using a combination of enabling optical techniques. We observed a steep crossover from a strongly thermal activated hopping ($T > 130$ K) to a weakly thermal activated 'hopping' ($T < 130$ K). The diffusion at high temperatures is characterized by a large barrier $E_{\text{diff}}^{(1)} = 450$ meV and a large pre-exponential factor $D_0^{(1)} = 162$ cm²/s, indicating that it is dominated by the kinetics of crossing step edges. The weakly activated diffusion at low temperatures is characterized by a much smaller 'barrier' of $E_{\text{diff}}^{(2)} = 22$ meV and a pre-exponential factor $D_0^{(2)} = 6.8 \times 10^{-14}$ cm²/s, characteristic of a quantum under-barrier tunneling.

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Adsorbate diffusion on solids or solid-like materials such as polymer chains (e.g., DNA molecules) continues to draw great interest in the communities of condensed matter physics and now biophysics [1,2]. At high temperatures an adsorbate moves on a solid surface by phonon-assisted hopping over saddle points between neighboring potential energy minima (or adsorption sites), known as classical over-barrier hopping. In this 'classical' regime, single-particle and collective behaviors of adsorbate transport in different phases of adsorbate ensembles and how these behaviors affect growth and formation or conformation of surface-bound materials are some of the major impetuses to the sustained interest in this topic [1]. On the surface of single crystalline solid, atomic step edges play as important a role as atomically flat terraces in deciding the morphology of vapor-phase deposited materials and the mass transport over distance longer than the average separation of neighboring steps.

Furthermore at sufficiently low temperatures, an adsorbate may move between potential minima by quantum mechanically tunneling through the energy barrier when such a pathway is kinetically favorable. In practice, tunneling diffusion in and on solid surfaces has only been observed for light atoms such as positive muons (μ^+) and hydrogen atoms [3–6]. In 'quantum' tunneling regime, fluctuation and dissipative effects of phonons, conduction electrons, and other low-lying energy excitations in a host solid drive the interest in adatom diffusion from a different perspective [5–14]. For example, when conduction electrons near the Fermi surface of a solid dominate the dissipation of an adatom tunneling motion, the temperature dependence of the tunneling rate provides a measure of the Fermi surface, particularly when the solid enters from a normal metallic phase into a superconducting or charge density wave state [9]. In this Letter, we report an experi-

mental study of diffusion of hydrogen adatoms on Cu(1 1 1) that again shows the evidence of quantum tunneling diffusion.

We measured diffusion rate constants of hydrogen adatoms by following the decay of hydrogen adatom density 'gratings' on Cu(1 1 1) formed with monolayer Xe templates by using a combination of enabling optical techniques as illustrated in Fig. 1 [15]. A 10-mm dia. \times 1.5-mm thick Cu(1 1 1) disc with the miscut angle $\Delta\psi$ less than 0.1° or 0.0017 radians was used as the substrate. The experiment was performed with the Cu substrate inside an ultra-high vacuum chamber at a base pressure of 5×10^{-11} Torr. The substrate surface was cleaned with cycles of ion sputtering followed by thermal annealing to 800 K for a few tens of seconds. We formed hydrogen adatom density 'gratings' using monolayer-thick Xe templates. A Xe template was produced by photolithography from a uniform Xe monolayer on Cu(1 1 1). The thickness of the Xe layer was confirmed with an in situ nulling ellipsometer (an oblique-incidence reflectivity difference ellipsometer). By irradiating the substrate surface with the interference pattern of a pair of 7-ns optical pulses at 532 nm, the resultant thermal desorption produced a grating-like Xe template of monolayer thick. The mean thickness and the modulation depth of the Xe template are monitored with the nulling ellipsometer and the linear optical diffraction measurement system. By subsequently exposing the Cu(1 1 1) surface to hot hydrogen, dissociative adsorption of hydrogen molecules took place on the Xe-free part of the surface and formed a complementary density-modulated monolayer. We used a CreaTec Fischer Atomizer (HLC-40-200) to produce hot hydrogen molecules [16]. Afterward the monolayer Xe template was removed by briefly raising the temperature of the substrate above 78 K for a few seconds. To measure the diffusion rate constants of hydrogen adatoms at a temperature between 83 and 207 K, we heated the substrate quickly to the desired temperature (in a few seconds) and then monitored the intensity of a first-order diffraction of a weakly focused cw 532 nm laser from the hydrogen density grating covered

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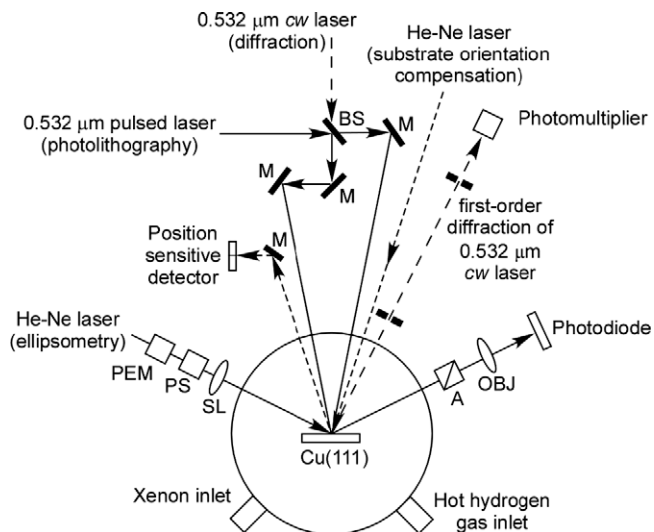


Fig. 1. A combination of four optical systems for preparation and characterization of hydrogen density 'gratings' for surface diffusion measurement: (1) a 0.532 μm pulsed laser, after being beam-split by BS, is used to form an interference pattern on Cu(111) and in turn make a Xe template for producing a hydrogen density 'grating'; (2) a He-Ne laser-based nulling ellipsometer is used to monitor the thickness of the Xe layer before and after template formation and the mean coverage of subsequently adsorbed hydrogen adatoms; (3) a 0.532 μm cw laser is used to produce optical diffraction from the Xe template and the subsequent hydrogen density grating for surface diffusion measurement; (4) another He-Ne laser and a position-sensitive detector are used to monitor the sample orientation change during heating and subsequent surface diffusion measurement for active feedback control.

region. The uncompensated thermal expansion of the Cu sample holding assembly during heating causes the substrate to rotate about the vertical axis by as much as a few mrad throughout the optical measurement. To compensate for such an angular drift, we employed a position-sensitive detector to monitor the reflection of a He-Ne laser from the Cu(111) surface. By using the imbalanced signal as a feedback to rotate the sample about the vertical axis (in the plane of incidence) in the opposite direction, we were able to maintain the sample orientation and thus the direction of the first-order diffraction to within ± 0.088 mrad during the temperature rise and subsequent diffraction measurement so that the temperature-induced sample orientation change had no observable effect on the detected diffraction signal. To measure diffusion constants that in the present experiment vary over 6 orders of magnitude, we used three optical set-ups to produce Xe templates with spatial periodicities of $2a = 0.38 \mu\text{m}$, $2 \mu\text{m}$, and $10 \mu\text{m}$ and detect the corresponding first-order diffractions. Fig. 2 shows the temporal evolution of the optical diffraction from hydrogen density gratings at different substrate temperatures, (a) with $2a = 10 \mu\text{m}$; (b) $2a = 2 \mu\text{m}$; (c) $2a = 0.38 \mu\text{m}$. The time-dependence of the diffraction signals was fit to single-exponential function $\exp(-\alpha(T)t)$, as shown in dashed lines in Fig. 2. From $\alpha(T) = (2\pi^2/a^2)D(T)$, we obtained $D(T)$ [15].

In Fig. 3, we show the Arrhenius plot of $D(T)$ from 207 to 83 K. The diffusion rate constants are characterized by a strongly thermal activated region between 207 and 130 K and a weakly thermal activated region from 130 to 83 K. In the high temperature region, $D(T)$ are fitted well to an Arrhenius function $D(T) = D_0^{(1)} \exp(-E_{\text{diff}}^{(1)}/k_B T)$ with $E_{\text{diff}}^{(1)} = 450$ meV and $D_0^{(1)} = 162 \text{ cm}^2/\text{s}$. In the low temperature region, $D(T)$ are also fitted well to an Arrhenius function $D(T) = D_0^{(2)} \exp(-E_{\text{diff}}^{(2)}/k_B T)$ with $E_{\text{diff}}^{(2)} = 22$ meV and $D_0^{(2)} = 6.8 \times 10^{-14} \text{ cm}^2/\text{s}$. The dash line shows $D(T) = D_0^{(1)} \exp(-E_{\text{diff}}^{(1)}/k_B T) + D_0^{(2)} \exp(-E_{\text{diff}}^{(2)}/k_B T)$. The sharp transition is the result of two different diffusion kinetics, each of which dominating differ-

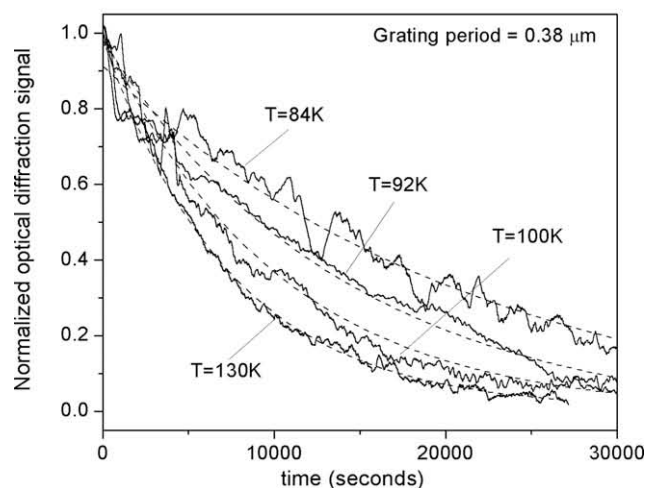
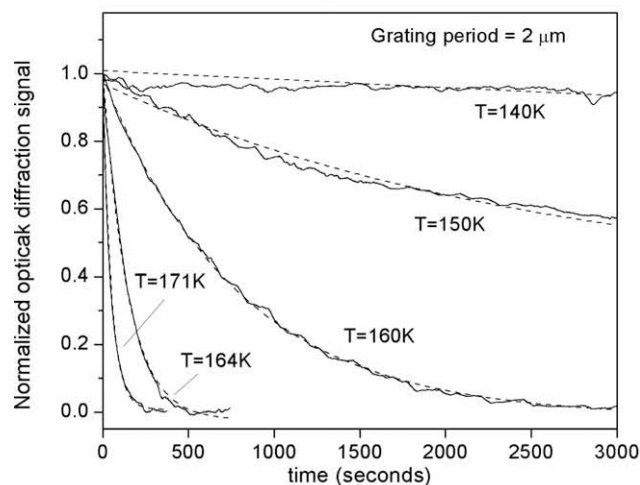
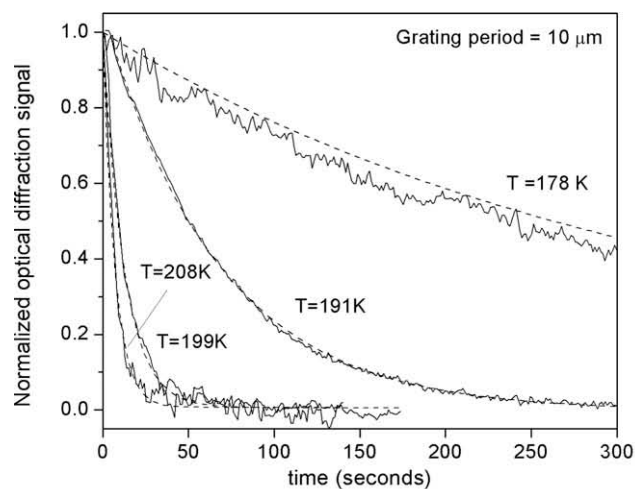


Fig. 2. Optical diffraction signals vs. time at various substrate temperatures: (a) $2a = 10 \mu\text{m}$; (b) $2a = 2 \mu\text{m}$; (c) $2a = 0.38 \mu\text{m}$. The time range increases successively by one order of magnitude from (a) through (b) to (c). The dash lines are fit to single-exponential functions $\exp(-\alpha(T)t)$.

ent temperature regions. As will be clear shortly, the unusually large pre-exponential factor in the high temperature region results from step edge crossing as the rate-limiting process in the overall diffusion kinetics, thus making the apparent hopping length close to the average step edge separation instead of the distance between neighboring 3-fold hollow sites. The reduction of the

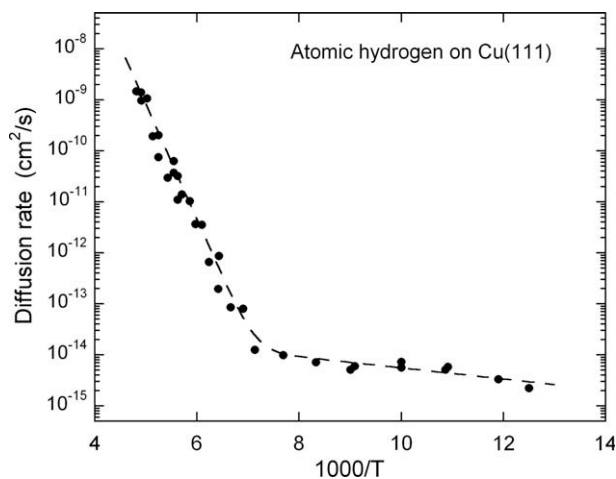


Fig. 3. Arrhenius plot of diffusion constants of hydrogen adatoms on Cu(1 1 1) from 207 to 83 K. The dash line is fit to two thermally activated diffusion rates $D_0^{(1)} \exp(-E_{\text{diff}}^{(1)}/k_B T) + D_0^{(2)} \exp(-E_{\text{diff}}^{(2)}/k_B T)$ with $E_{\text{diff}}^{(1)} = 450$ meV, $D_0^{(1)} = 162$ cm²/s, $E_{\text{diff}}^{(2)} = 22$ meV, and $D_0^{(2)} = 6.8 \times 10^{-14}$ cm²/s.

pre-exponential factor by 15 orders of magnitude in the low temperature region is characteristic of tunneling across a step edge between vibrational ground-states of hydrogen adatoms on two sides of the step edge, similar hydrogen tunneling between the ground-states of two neighboring 4-fold hollow sites on a terrace of Cu(1 0 0).

The diffusion from 207 to 130 K is a characteristic over-barrier hopping with a large energy barrier of 450 meV. This value is large compared to the activation energy (197 meV) for hydrogen hopping on flat terraces of Cu(1 0 0) observed by Lauhon and coworkers from an STM measurement. On flat terraces of Cu(1 1 1), hydrogen adatoms reside on 3-fold hollow sites for adsorption [17–19]. One generally expects the diffusion energy barrier for an adsorbate on the more close-packed Cu(1 1 1) to be smaller than that on the more open Cu(1 0 0). The clue is in the pre-exponential factor $D_0^{(1)} = 162$ cm²/s which is 4–5 orders of magnitude larger than the expected value from the transition-state theory. This suggests that the effective hopping distance is orders of magnitude larger than the nearest neighbor distance between 3-fold hollow sites. This is only possible if the observed diffusion of hydrogen adatoms on Cu(1 1 1) is dominated by crossing step edges that are far apart and pose an understandably large activation energy barrier for hydrogen adatoms to cross. This is not unexpected as the optical diffraction method measures the diffusive motion of $\sim 10^9$ hydrogen adatoms across a (macroscopic) distance from 0.4 to 10 μm along which they are likely to encounter step edges. Whether the step edge crossing dominates the decay rate of hydrogen adatom density modulation is usually determined by whether the pre-exponential factor of the measured diffusion rate in the classical over-hopping regime is significantly larger than the expected value of the transition-state theory. In contrast the STM method used by Lauhon and Ho on hydrogen adatom diffusion on Cu(1 0 0) enabled these authors to follow the diffusive motion of $\sim 10^2$ individual adatoms over atomic distances on a single [1 0 0] terrace of Cu(1 0 0) and thus avoid the direct effect from step edges. As shown by Nabighian and Zhu [20] and independently by Merikoski and Ying [21], the rate of a step-crossing dominated surface diffusion has the form as $D(T) \cong (1/\theta_{\text{step}}) a_s^2 v_{s0} \exp(-E_{\text{step}}/k_B T)$ (when there is a significant barrier for either upward or downward crossing, but not both) or $D(T) \cong (1/\theta_{\text{step}}^2) a_s^2 v_{s0} \exp(-E_{\text{step}}/k_B T)$ (when there exists a significant barrier for both upward and downward crossing). θ_{step} is the fractional density of step edges (the ratio of the number of step edges to the total

number of adsorption sites) along the ‘diffusion’ direction (perpendicular to the hydrogen density grating). a_s is the width of the step edge and is of the order of 10^{-8} cm. v_{s0} is the pre-exponential hopping frequency and is of the order of 10^{13} Hz based on the transition-state theory. E_{step} is the largest energy barrier for crossing the step edge regardless upward or downward. If we assume that θ_{step} is dominated by the miscut angle such that $\theta_{\text{step}} \approx \Delta\psi \approx 1.7 \times 10^{-3}$, $D_0^{(1)}$ will expectedly be $1/\theta_{\text{step}}$ to $1/\theta_{\text{step}}^2$ or 3–5 orders of magnitude larger than the expected value ($a_s^2 v_{s0}$) from the transition-state theory. This is what we observed for hydrogen adatom on Cu(1 1 1) at high temperatures. It means that the average spacing between neighboring step edges is $a_s/\theta_{\text{step}} \sim 0.1$ μm , small compared to the smallest grating periodicity (0.38 μm). It is not surprising that the activation energy barrier $E_{\text{diff}}^{(1)} = 450$ meV, with the contribution from extra barriers at step edges, is even larger than that for hydrogen adatoms on terraces of Cu(1 0 0).

At 130 K, the diffusion of hydrogen adatoms sharply crosses over into another thermal activated regime with small activation energy of 22 meV. It is indicative of another kinetic pathway for crossing step edges with a higher hopping rate than $D_0^{(1)} \exp(-E_{\text{diff}}^{(1)}/k_B T) \cong (1/\theta_{\text{step}})^2 a_s^2 v_{s0} \exp(-E_{\text{step}}/k_B T)$ ($1 \leq \gamma \leq 2$) below 130 K. The only available pathway is quantum mechanical tunneling through the energy barrier at a step edge. Since the activation energy barrier $E_{\text{diff}}^{(2)} = 22$ meV is much less than the energy needed to excite the in-plane vibration of hydrogen adatom on Cu(1 1 1) from the ground-state to the first-excited state, $\hbar\omega_{\text{in-plane}} = 100$ meV [22], the tunneling has to take place between the ground-states of two neighboring potential minima across a step edge [23]. The tunneling matrix element J can be deduced from the expression of the tunneling diffusion rate $(1/\theta_{\text{step}})^2 (J^2/\hbar\omega_{\text{in-plane}}) \exp(-E_{\text{diff}}^{(2)}/k_B T)$ and the experimental values of $D_0^{(2)}$ and $D_0^{(1)}$,

$$J \cong \hbar\omega_{\text{in-plane}} \sqrt{D_0^{(2)}/D_0^{(1)}} = 2.0 \times 10^{-9} \text{ eV}.$$

The energy barrier $E_{\text{diff}}^{(2)}$ is either due to the misalignment of the vibrational ground-states at the two potential minima across the step edge or the small polaron effect (coincidence energy) [11].

In conclusion, on Cu(1 1 1) we observed yet another example of quantum tunneling diffusion of hydrogen on metal surfaces. In the present experiment both the classical and quantum diffusion of hydrogen are dominated by the kinetics of hydrogen adatom crossing step edges. By introduction of an active sample orientation control, we now have a fully enabling experimental apparatus for studying macroscopic surface diffusion of adsorbates on metal or semiconductor surfaces in ultrahigh vacuum: (1) a pulsed laser system for making thermal erasable rare gas templates on a solid substrate by photolithography; (2) a nulling ellipsometry system for characterizing the thickness of a rare gas template; (3) a linear optical diffraction system for characterizing the rare gas template and the subsequently formed adsorbate density ‘grating’; (4) a position-sensitive detected linear reflection system for controlling sample orientation during substrate heating. Such a combination of optical systems for controlled preparation and characterization of modulated adsorbate density profiles makes the linear optical diffraction technique a truly versatile experimental method that will expand and facilitate surface diffusion studies in a major way.

Acknowledgement

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