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Surface diffusion of Xe on Nb(1 1 0)

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Abstract

We studied Xe diffusion on Nb(1 1 0) from 48 to 70 K using the linear optical diffraction from laser-induced Xe density gratings. The diffusion rate is characterized by an Arrhenius behavior with an activation energy of $E_{\text{diff}} = 54$ meV and a diffusivity $D_0 = 1.7 \times 10^{-6}$ cm²/s. We also performed a density-functional theory calculation of the binding energy for Xe on Nb(1 1 0). Our preliminary result shows that Xe prefer on-top sites with a binding energy of 247 meV, and move by hopping over short-bridge sites with an activation energy barrier of 51 meV, in close agreement with the experimental value.

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1. Introduction

Rare gases on metals continue to serve as models for understanding adsorption, mass transport, and crystal growth (homogeneous and heterogeneous) of adsorbates on surfaces [1,2]. Experimentally low-temperature scanning tunneling microscopy (STM) studies of rare gases on metals have further enriched our understanding of how rare gases behave at atomic level [3–6]. Recent theoretical studies of rare gases on metals by Scheffler and coworkers have shed new light on general expectations and underlying physical mechanisms of rare gas adsorption on metals [7]. Close ties between experiments and corresponding theoretical efforts promise fruitful progresses in

gaining full understanding of rare gases on metals. Because binding energies of rare gases on metals are small and corrugations of the binding energies are even smaller, the diffusion of rare gas monomers on metals is generally too fast ($> 10^{-16}$ cm²/s for $T \geq 20$ K) for most low-temperature STM to follow [8–11]. As we had demonstrated previously, the method of linear optical diffraction from laser-induced adsorbate density gratings on metals is one of the macroscopic methods that are well suited for investigation of rare gas diffusion on metals under readily accessible experimental conditions [12,13].

In this Letter, we report an experimental study of Xe diffusion on Nb(1 1 0) using the method of linear optical diffraction. Combined with a density-functional theory calculation of the binding energy of Xe on Nb(1 1 0), we are able to propose the diffusion route for Xe on Nb(1 1 0) [14,15]. In addition the magnitude of the Xe binding energy

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corrugation, deduced from both the diffusion measurement and the theoretical calculation, is responsible for lack of long-range order for first two Xe monolayers and for subsequent growth behaviors of Xe [16].

2. Experimental procedures

The experiment is carried out in an ultrahigh vacuum chamber with a base pressure of 1×10^{-10} Torr during surface diffusion measurement. A 0.2-cm thick, 1.2-cm diameter single crystal Nb(110) disc with a miscut angle less than 0.1° is used as the substrate. The surface of the Nb(110) sample is cleaned with cycles of ion sputtering (using a 50–50% Ar–Ne mixture as the source) at room temperature, followed by annealing for a few minutes at 1170 K. Using a combination of a close-cycle Helium refrigerator and an electron beam heater, we can vary the sample temperature from 33 to 1500 K with a precision of ± 0.5 K. We monitor the temperature with a Type-K thermocouple spot-welded to the side of the Nb(110) disc, together with the reference junction in liquid nitrogen. For Xe adsorption, we back fill the chamber with 99.999% pure Xe gas. The coverage of Xe is controlled within a few percent of a monolayer using a calibrated oblique-incidence optical reflectivity difference probe [16].

The methods of laser-induced adsorbate density grating formation and linear optical diffraction from such a grating have been described previously [17]. The optical setup is same as in [17]. The laser-induced Xe density gratings in the present study have a spatial periodicity of $2b = 4.56 \mu\text{m}$. The grating is so oriented that we measure the diffusion rate along the direction at $\Phi = -70.9^\circ$ from the [001] azimuth of the Nb(110) surface. Immediately after the formation of a Xe density grating, we follow the evolution of the grating by monitoring the first-order diffraction of a 2-mW intensity-stabilized He–Ne laser (Spectra-Physics, Model-117A). The intensity of the first-order diffraction $S_1(t)$ decays with time as [12]

$$S_1(t) = S_1(0) \exp(-\pi^2 Dt/b^2) \sim \exp(-\alpha t). \quad (1)$$

From the decay exponent $\alpha = (2\pi^2/b^2)D$ that is extractable from the experiment, we find the value of diffusion rate D . In this study the mean coverage of Xe on Nb(110) is one half of the saturation coverage ($\theta_s = 0.47$) relative to surface atoms of the substrate, namely, $\theta/\theta_s = 0.5$.

We recently studied the adsorption and growth of Xe on Nb(110) with a combination of low energy electron diffraction (LEED) and an oblique-incidence optical reflectivity difference (OIRD) technique [16]. We did not observe well-defined LEED spots from the first and second monolayer of adsorbed Xe, indicating that near or at saturation coverage the two layers do not have a long-range crystalline order due to symmetry frustration and lattice mismatch [1]. The lack of long-range order for the first Xe monolayer on Nb(110) indicates that the binding energy variation on Nb(110) must be comparable to the strength of Xe–Xe interactions. Since a single Xe–Xe bond has a strength of 20 meV, we expect the corrugation of the Xe binding energy and thus the diffusion energy barrier on Nb(110) to be a few times of 20 meV.

3. Results and discussion

In Fig. 1, we display the Arrhenius plot of the measured surface diffusion rates as a function of sample temperature. In the studied temperature range between 48 and 70 K, the diffusion rate of Xe deduced from the linear optical diffraction method is described by an Arrhenius function $D(T) = D_0 \exp(-E_{\text{diff}}/k_B T)$. By fitting the data in Fig. 1, we find the diffusion activation energy barrier $E_{\text{diff}} = 54$ meV (1.24 kcal/mol) and the diffusivity (preexponential factor) $D_0 = 1.7 \times 10^{-6}$ cm²/s. The magnitude of the diffusion energy barrier is three times the strength of a Xe–Xe bond.

To determine the adsorption sites and the diffusion routes of Xe on Nb(110) and whether the measured diffusion rate is dominated by hopping of Xe adatoms or by dissociation of Xe from adatom islands, we performed a preliminary density-functional theory calculation of Xe binding energy on a frozen Nb(110) using the commercially

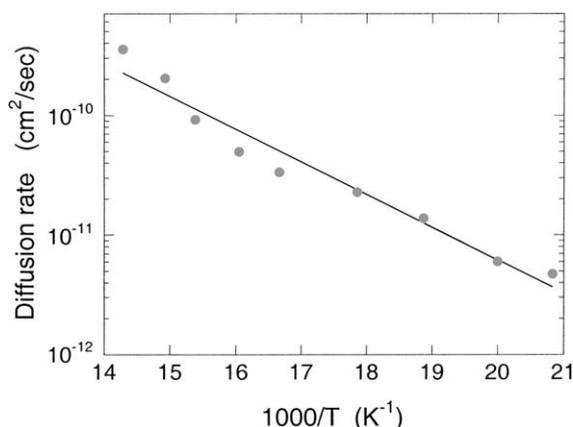


Fig. 1. Arrhenius plot of surface diffusion rates for Xe on Nb(110) from 48 to 70 K. The solid line is a fit to an Arrhenius function $D(T) = D_0 \exp(-E_{\text{diff}}/k_B T)$, yielding $E_{\text{diff}} = 54$ meV and $D_0 = 1.7 \times 10^{-6}$ cm²/s.

available VASP code [18,19]. We used plane waves as basis functions with a cutoff energy of 200 eV and used ultra-soft pseudopotentials for Nb and Xe in the calculation. Seven special k -points were used to generate the charge densities to build a self-consistent potential. The Nb(110) surface was modeled by a slab consisting of 11 layers of Nb and a vacuum region of same thickness. The dimension of the super-cell in the surface plane measures 6.6 Å (two times the lattice constant) along [001] azimuth and 9.33 Å along [110] azimuth, as shown in dotted line in Fig. 2. In the calculation, we fixed the positions of all the Nb atoms and the in-plane position of Xe at one of

three sites on Nb(110) (on-top site, short-bridge site, and long-bridge site, as shown in Fig. 2), while allowing the out-of-plane position (height) of Xe atom to relax until the total energy was minimized. The difference between the total energy for Xe placed in the middle of the vacuum region and that for Xe placed at one of sites on Nb(110) gives the binding energy.

Our calculation shows that Xe at the on-top site has the largest binding energy of 294 meV. Xe at the short-bridge site has a binding energy of 240 meV. Xe at the long-bridge site has a binding energy of 226 meV. The calculation suggests that Xe adatoms prefer on-top sites on Nb(110), and move between neighboring on-top sites by hopping over short-bridge sites with an activation energy of 54 meV, instead of over long-bridge sites with a higher activation energy of 68 meV. The finding of on-top sites being the preferred adsorption site has been reported experimentally and theoretically for rare gas on a number of other metals [1,5–7,20]. It is attributed to relatively donor-like characters in on-top regions on a metal. The theoretical value of 54 meV closely agrees with the experimental value of 54 meV. We caution that the close numerical agreement between our preliminary calculation and the experiment may be fortuitous, given the limitation of the density functional theory, the assumption of a frozen Nb lattice, and limited k -points used in the calculation. The key findings of the calculation should be that (1) the binding energy corrugation along Nb(110) is in the range of 50–70 meV, as observed experi-

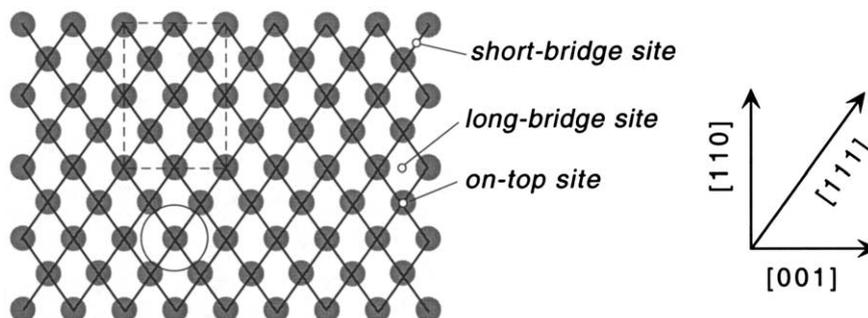


Fig. 2. Arrangement of Nb atoms on Nb(110) (solid circles). The large open circle shows the size of a Xe adatom residing at an on-top site. Small open circles indicate three high symmetry sites where we computed the binding energy of Xe using a density-functional theory. The dotted line shows the dimension of the super-cell used in the binding energy calculation (see text for details).

mentally, and (2) hopping over short-bridge sites is the most probable route of Xe diffusion, as shown in grid lines in Fig. 2. As a result it is safe to conclude that the diffusion of Xe on Nb(110) measured in our experiment is dominated by diffusion kinetics of Xe monomers and the diffusion consists of jumps over short-bridge sites along $[1\ 1\ 1]$ or $[1\ 1\ \bar{1}]$ azimuths. This also means that the same diffusion kinetics should hold in the low coverage limit. In addition the diffusion rate is expected to have an azimuthal dependence of $D(T, \Phi) \sim [1 - (\cos 2\Phi)/3] \exp(-E_{\text{diff}}/k_B T)$, where Φ is the angle between the diffusion direction and the $[00\ 1]$ azimuth of Nb(110) surface. In our case, $\Phi = -70.9^\circ$ and $[1 - (\cos 2\Phi)/3] = 1.26$.

The diffusion of Xe on Nb(110) should be compared to that of Xe on W(110) [21]. Both substrates are (110) planes of bcc metals, with W(110) having a 5% smaller lattice constant. Chen and Gomer measured the surface diffusion rate of Xe on W(110) using field-emission current fluctuation method. They found that at $\theta = 0.13$ (relative to surface atoms of the substrate), $E_{\text{diff}} = 48$ meV and $D_0 = 7 \times 10^{-8}$ cm²/s. These kinetic parameters are comparable to what we found on Nb(110). One key distinction between the diffusion behaviors on these two bcc metals is that on W(110) Xe adatoms form a $p(2 \times 2)$ superlattice at $\theta = 0.25$ (relative to surface atoms of the substrate) [1,22]. The saturation Xe coverage on W(110) is $\theta_s = 0.43$. The propensity to forming a Xe $p(2 \times 2)$ superlattice on W(110) caused the experimentally measured diffusion rate near $\theta = 0.25$ to behave anomalously as reported by Chen and Gomer. On Nb(110) we did not observe any evidence of anomalous behaviors in the evolution of the Xe density gratings and in the temperature dependence of the extracted rate constants. This is consistent with the fact that we did not observe such a Xe superlattice on Nb(110) [16].

Diffusivities of Xe on the (110) plane of both bcc metals [10^{-6} cm²/s on Nb(110) and 10^{-7} cm²/s on W(110)] are 3–4 orders of magnitude smaller than the expected value of 10^{-4} – 10^{-3} cm²/s from the transition-state theory [23–25]. A very small diffusivity (10^{-9} cm²/s) was also reported for Xe on Ni(111) by Nabighian and Zhu [26]. For Xe on

Pt(111) however, George and coworkers observed the ‘typical’ value of 10^{-4} cm²/s. It is intriguing and yet not understood that diffusivities of rare gases and other adsorbates on metals vary over a wide range at finite as well as nearly zero surface coverage [27]. It cannot be a trivial consequence of adatom–adatom interaction on metal surfaces. We should note that the experimental observations of small diffusivities have been reported with microscopic techniques such as field-ion microscopy and scanning tunneling microscopy [10,28] as well as macroscopic techniques such as the present optical diffraction method, laser-induced thermal desorption mass yield (hole-filling), and field-emission current fluctuation [1,29]. Consequently experimentally observed small diffusivities cannot be simply attributed to thermodynamic factors that are inevitably involved when surface diffusion rates are measured with macroscopic means such as in the present work. For rare gases on metals the experimental data of surface diffusion are still scarce at this point for useful consensus on the plausible cause for small diffusivity.

4. Conclusion

Surface diffusion of Xe on Nb(110) at coverage near $\theta/\theta_s = 0.5$ is characterized by an activation energy of $E_{\text{diff}} = 54$ meV and diffusivity of $D_0 = 1.7 \times 10^{-6}$ cm²/s. Our preliminary density-functional theory calculation of the binding energy for Xe on Nb(110) suggests that the Xe diffusion proceeds by hopping between on-top sites over short-bridge site with an activation energy barrier of 54 meV. The good agreement in activation energy between the experiment and the theory favors the diffusion kinetics of Xe monomers on Nb(110) as the dominant contributor to the observed Xe diffusion rate, instead of the kinetics of Xe dissociation from edges of distorted or disordered adatom islands.

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