Anisotropic Surface Diffusion of CO on Ni(110)

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Anisotropic surface diffusion of CO on Ni(110) has been studied using the newly developed technique of optical second-harmonic diffraction from a laser-induced CO monolayer grating. Two distinct orthogonal diffusion channels, along [1$\bar{1}$0] and [001], were found. The measured diffusion coefficients yield the diffusion activation energies $E_d(1\bar{1}0)=1.1\pm0.2$ kcal/mol and $E_d(001)=3.1\pm0.4$ kcal/mol and the preexponential factors $D_0(1\bar{1}0)=(3.8\pm2.0)\times10^{-9}$ cm^2/sec and $D_0(001)=(4.8\pm4.4)\times10^{-6}$ cm^2/sec. The anisotropy in the surface diffusion appears to cross over at $T\sim160$ K.

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Surface diffusion is often the limiting step controlling the rate of a surface process such as epitaxial growth, surface reaction, and catalysis, and hence a subject of great importance in surface science.[1] Anisotropy in surface diffusion on a crystalline surface is of special interest to researchers as it can prove direct information about the diffusion pathways. For microscopic diffusion of adatoms, there already exist many theoretical and experimental investigations on the subject.[2] Similar studies on macroscopic anisotropic heterogeneous surface diffusion, however, are very limited.[3] Experimentally, this is presumably because of difficulties inherent in the available experimental techniques.

We have recently developed a new technique for surface diffusion measurements.[4] First, by laser-induced thermal desorption (LITD) of adsorbates with two interfering laser beams, a monolayer adsorbate grating of a selected grating spacing is created on a sample surface. Then, optical second-harmonic generation (SHG) diffracted from the grating is detected and used to monitor smearing of the grating by surface diffusion of the adsorbates. The diffusion is one dimensional. Its direction with respect to the symmetry axes of the surface can be preselected by properly orienting the surface relative to the grating. Thus, the technique is ideally suited for the study of anisotropic surface diffusion. This is what we will demonstrate in this Letter. We studied the system of CO on Ni(110) since anisotropic surface diffusion of molecules has never been reported. We identified unequivocally two independent diffusion channels for CO on the surface, one along [1$\bar{1}$0] and the other along [001]. They have very different diffusion activation energies, significantly larger along [001], but both are much smaller than that for CO on Ni(111), leading to the surprising result that diffusion is significantly faster on Ni(110) than on (111) although the desorption energies of CO from the two surfaces are comparable. The preexponential factors in the diffusion coefficients are rather small, appearing also much larger along [001] and smaller along [1$\bar{1}$0] so that they compensate the effect of energy difference on the diffusion. We use the transition-state theory (TST) to *qualitatively* explain this observed compensation effect.

The experimental arrangement was described in an earlier publication.[4] The Ni(110) sample was mounted on a rotatable manipulator in an ultrahigh-vacuum chamber with a base pressure of 1×10^{-10} torr. It was cleaned and annealed by the usual procedure before the experiment.[5] The adsorption of CO on Ni(110) was carried out with the sample at ~100 K. The surface structure was monitored by low-energy electron diffraction (LEED). A clean Ni(110) surface produced a (1×1)LEED pattern, while an adsorbed full monolayer of CO produced a (2×1) pattern. To create a monolayer grating of CO on Ni(110) by laser-induced thermal desorption, a single-mode *Q*-switched Nd-doped yttrium-aluminum garnet laser at 1.06 μm was used. The intensities of the two interfering beams and the angle between the beams were properly adjusted to yield a grating that can be closely described by a periodic rectangular function with a period of 20 μm and an amplitude varying from $\theta=0$ to 1, where θ is the CO coverage. To detect the monolayer grating by SH diffraction, a frequency-doubled beam from the same laser system was used. Surface diffusion of CO was then monitored by the decay of the first-order SH diffraction signal. The diffusion measurements were conducted in a temperature range between 100 and 170 K. Readsorption of CO on Ni and desorption of CO by the probe beam during the experiment were found to be negligible.

The anisotropic surface diffusion measurements were carried out in the following way. The monolayer grating was first formed on Ni(110) along a selected direction. The sample was then heated to a certain temperature at which the CO diffusion was measured. This was repeated at a series of different temperatures. For each measurement, the sample surface was prepared anew as a precaution to avoid possible accumulative laser damage. We performed such measurements for a number of different grating orientations on Ni(110). The measured first-order diffracted SH signal as a function of time for diffusion along the two principal crystalline axes, [1$\bar{1}$0] and [001], are shown in Fig. 1. The SH signal from Ni(110) is ~5 times smaller than that from Ni(111).[5,6]

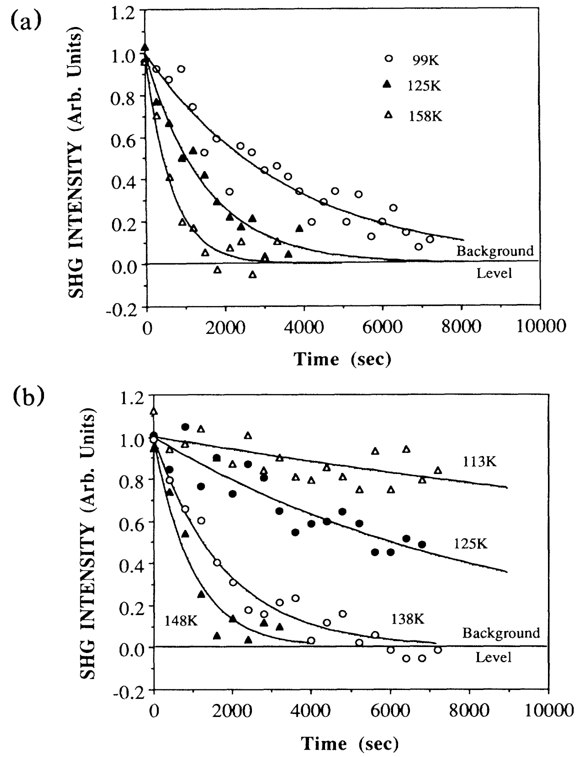

FIG. 1. Normalized first-order SH diffraction signal vs time at different temperatures for CO diffusion along (a) $[1\bar{1}0]$ and (b) [001] on Ni(110). The solid lines are the exponential fits with Eq. (1).

This made the present experiment somewhat more difficult in comparison with the same study on Ni(111). However, the signal-to-noise ratio was still sufficient to permit reasonable deduction of diffusion coefficients from the data.

To a good approximation, the first-order SH diffraction signal is proportional to the square of the first spatial Fourier component of the monolayer grating.[4,7] Its time variation resulting from CO diffusion is given by

$$S = S_0 \exp(-8\pi^2 Dt/s^2)\,, \tag{1}$$

where s is the grating period and D is the diffusion coefficient. We have neglected here the coverage dependence of D. A fit of the experimental data of $S(t)$ with Eq. (1) then yields the value of D. Figure 2 depicts D as a function of reciprocal temperature $1/T$ thus obtained for CO diffusion along $[1\bar{1}0]$, [001], and the direction bisecting the two. The existence of anisotropy in the surface diffusion is obvious from the figure. It is further illustrated in Fig. 3 showing how D varies with the grating orientation on the Ni(110) surface at $T = 110$ K.

The experimental results in Figs. 2 and 3 provide valuable information about the macroscopic CO diffusion on Ni(110). Since the surface has a C_{2v} symmetry, $\overleftrightarrow{D}$ as a tensor can be diagonalized. With $D(1\bar{1}0)$ and $D(001)$ specified, the diffusion coefficient along a direction at an angle ϕ from $[1\bar{1}0]$ can be determined from[8]

$$D(\phi) = D(1\bar{1}0)\cos^2\phi + D(001)\sin^2\phi\,. \tag{2}$$

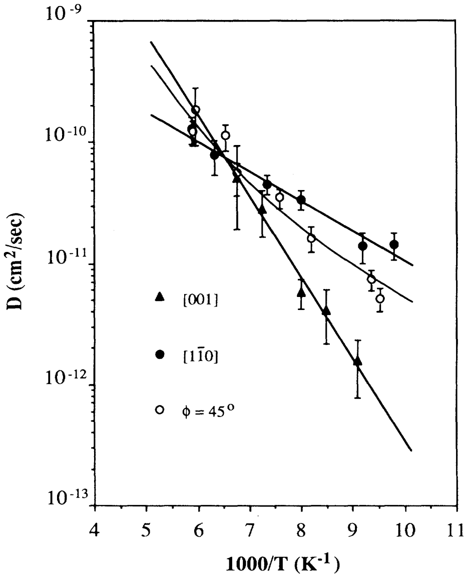

FIG. 2. Diffusion coefficient D vs reciprocal temperature $1/T$ in an Arrhenius plot for CO diffusion on Ni(110) along $[1\bar{1}0]$, [001], and the direction bisecting the two ($\phi = 45°$). The solid lines are least-square fits by Eqs. (2) and (3) with $E_d(1\bar{1}0) = 1.1$ kcal/mol, $D_0(1\bar{1}0) = 3.8\times10^{-9}$ cm²/sec and $E_d(001) = 3.1$ kcal/mol, $D_0(001) = 4.8\times10^{-6}$ cm²/sec.

The atomic arrangement of Ni(110) indicates that there are two major diffusion channels, one along $[1\bar{1}0]$ and the other along [001]. The corresponding diffusion coefficients versus T can be written in the Arrhenius form as

$$\begin{aligned} D(1\bar{1}0) &= D_0(1\bar{1}0)\exp[-E_d(1\bar{1}0)/kT]\,, \\ D(001) &= D_0(001)\exp[-E_d(001)/kT]\,. \end{aligned} \tag{3}$$

Indeed, Eqs. (3) describe the data in Fig. 2 fairly well. If the major diffusion channels were not along $[1\bar{1}0]$ and

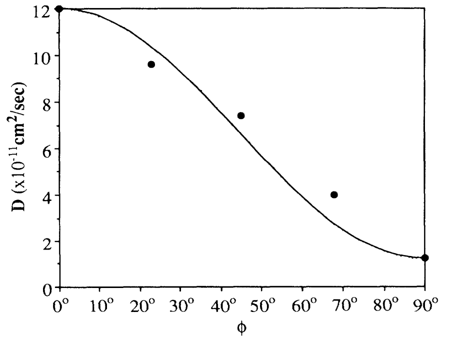

FIG. 3. Diffusion coefficient D for CO/Ni(110) as a function of angle ϕ away from $[1\bar{1}0]$ at $T \sim 110$ K. The solid line is predicted by Eq. (2) using the diffusion parameters given from Fig. 2.

[001], or if more than two channels existed, then it can be easily shown that $D(1\bar{1}0)$ and $D(001)$ would have more than one term with exponential dependence on $1/T$.[7] This is not observed in Fig. 2. We also notice that Eq. (2) describes the data in Fig. 3 very well. To the best of our knowledge, this is the first time two independent diffusion channels are clearly identified in a heterogeneous surface diffusion process.

From the fit of Eq. (3) with the data in Fig. 2, we can deduce the preexponential factors D_0 and the diffusion activation energies E_d for the two diffusion channels: $E_d(1\bar{1}0)=1.1\pm0.2$ kcal/mol, $D_0(1\bar{1}0)=(3.8\pm2.0)\times10^{-9}$ cm^2/sec and $E_d(001)=3.1\pm0.4$ kcal/mol, $D_0(001)=(4.8\pm4.4)\times10^{-6}$ cm^2/sec. With these values, Eq. (2) also gives a good fit to the $\phi=45°$ data as shown in Fig. 2. These results are most interesting. First, compared to CO on Ni(111) and Ni(100), with $E_d=6.8$ kcal/mol (Ref. 4) and 4.6–6.4 kcal/mol,[9] respectively, the values of E_d here for CO on Ni(110) are much smaller even though the desorption energies for the three cases are comparable [18–24 kcal/mol for CO/Ni(111),[10] 21–26 kcal/mol for CO/Ni(100),[11] and 28–32 kcal/mol for CO/Ni(110) (Ref. 12)]. This indicates that the surface potential corrugation along $[1\bar{1}0]$ and [001] on Ni(110) is much smoother than those along the diffusion pathways on Ni(111) and Ni(100). Next, we notice that associated with the small E_d, the values of D_0 for CO/Ni(110) are also quite small [compare to $D_0\sim10^{-5}$ cm^2/sec for CO/Ni(111) (Ref. 4)]. While $E_d(1\bar{1}0)<E_d(001)$ makes diffusion easier along $[1\bar{1}0]$, the preexponential factors with $D_0(1\bar{1}0)\ll D_0(001)$ appear to favor diffusion along [001]. This "compensation effect"[13] results in a diffusion process dominated by diffusion along $[1\bar{1}0]$ for $T<160$ K, but along [001] for $T>160$ K, as seen in Fig. 2. A similar effect has been observed for self-diffusion of Ni on Ni(110).[14]

To understand these results, let us first review how CO adsorbs on Ni(110). The Ni atoms of the surface layer of Ni(110) are more densely packed in the form of rows along $[1\bar{1}0]$. At sufficiently low temperatures, CO molecules can adsorb to both the top and the short-bridge sites along $[1\bar{1}0]$; the former has a slightly deeper potential well,[12] but we shall neglect this small difference in our discussion. Diffusion along $[1\bar{1}0]$ is then by hopping over energy barriers, $E_d(1\bar{1}0)$ from top-to-short-bridge sites and from short-bridge-to-top sites. Diffusion along [001] is by hopping over $E_d(001)$ from top-to-top sites and short-bridge-to-short-bridge sites of neighboring rows.

No reliable surface potential map of Ni(110) is presently available with or without adsorbates. To facilitate our discussion, we assume the following model potential:

$$V(x,y)=E_d(1\bar{1}0)\sin^2\left(\frac{2\pi x}{a}\right)+E_d(001)\sin^2\left(\frac{\pi y}{\sqrt{2}a}\right), \tag{4}$$

where a is the lattice constant along $[1\bar{1}0]$, and $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ refer to $[1\bar{1}0]$ and [001], respectively. Such a potential yields around the bottom of the potential wells two vibrational modes with frequencies $f_x=(2/a)[E_d(1\bar{1}0)/M]^{1/2}\sim3.3\times10^{12}$ Hz (110 cm^{-1}) along $\hat{\mathbf{x}}$ and $f_y=(1/\sqrt{2}a)\times[E_d(001)/M]^{1/2}\sim1.9\times10^{12}$ Hz (65 cm^{-1}) along $\hat{\mathbf{y}}$, where M is the mass of a CO molecule. These vibrational modes can be compared with their equivalent "frustrated translation" modes which were measured recently for a full CO monolayer on Ni(110) by electron-energy-loss spectroscopy.[15] Both frustrated translation modes exhibited a frequency dispersion between 60 and 113 cm^{-1} with little anisotropy. The good agreement can be taken as a confirmation of the measured values of $E_d(1\bar{1}0)$ and $E_d(001)$. Furthermore, the small activation energy $E_d(1\bar{1}0)$ along the $[1\bar{1}0]$ direction is supported by the observation of streaky $c(4\times2)$ and $c(8\times2)$ LEED patterns, which suggest that CO may occupy intermediate positions other than the high-symmetry sites (namely, the top and short-bridge sites).[16]

As we mentioned earlier, the smaller D_0 appears to go alongside with the smaller E_d. In the absence of any simple theory for collective (chemical) diffusion coefficients, we will use the microscopic picture of CO diffusion in the above model surface potential to *qualitatively* explain the observed compensation effect. We implicitly assume here that the thermodynamic factor and the velocity cross correlations relating the chemical and tracer (microscopic) diffusion coefficients[1] are the same for diffusion along different directions. We then have, for microscopic diffusion,[8]

$$D_0^*=\tfrac{1}{4}\langle l^2\rangle\nu_0, \tag{5}$$

where the mean-square hopping length $\langle l^2\rangle$ is proportional to $a^2/4$ along $[1\bar{1}0]$ and $2a^2$ along [001]. This difference in the mean-square hopping length partly accounts for the anisotropy in D_0^*. The major part of the anisotropy in D_0^* (or D_0) is expected to come from the trial frequency ν_0. In the transition-state theory we have[17]

$$\nu_0=(kT/h)Q_s/Q_w, \tag{6}$$

with Q_w being the partition function for the molecule in the adsorption well and Q_s the partition function at the saddle point excluding the diffusion coordinate. Along $[1\bar{1}0]$ and [001], Q_w is the same, but Q_s is different. One generally finds that at sufficiently high temperatures, Q_s is larger for a shallower potential well at the saddle points. Thus $Q_s(001)>Q_s(1\bar{1}0)$ for CO on Ni(110) with $E_d(1\bar{1}0)<E_d(001)$, as can be explicitly shown using the potential in Eq. (4).[7] We then have $\nu_0(001)>\nu_0(1\bar{1}0)$ and hence $D_0(001)\gg D_0(1\bar{1}0)$.

One may wonder if the observed surface diffusion was dominated by line defects on the surface. In our case, the miscut of Ni(110) was less than 0.3° along the [001] direction so that a step could appear only after a terrace with a width of about 70 lattice constants. For diffusion dominated by hopping across the steps, we would have $1/D(\text{step}) \gg 70^2[1/D(\text{terrace})]$ knowing that the mean-square hopping length is $\langle x^2 \rangle = 2Dt$, and hence, $E_d(\text{step}) \gg E_d(\text{terrace}) + 8.5kT$ assuming that the trial frequency ν_0 is the same for hopping at the steps and on the terraces. Then, if $E_d(\text{step}) = E_d(001) = 3.1$ kcal/mol, we would find $E_d(\text{terrace}) \ll 0.56$ kcal/mol for $T = 150$ K, which is only about twice as much as the thermal energy kT (0.3 kcal/mol). This would make the stable adsorption of CO on top and short-bridge sites unlikely. We therefore believe that, in our case, the contribution from the steps were negligible.

In summary, we have studied anisotropic CO diffusion on Ni(110) using the technique of SH diffraction from CO monolayer gratings. The results enable us to identify two major diffusion channels, along $[1\bar{1}0]$ and $[001]$, respectively, and deduce the preexponential factors and activation energies of the corresponding diffusion channels. They are very different from those for isotropic diffusion of CO on Ni(111) and Ni(100). A reversal in the anisotropy of CO diffusion along $[1\bar{1}0]$ and $[001]$ at sufficiently high temperatures was observed and can be understood with the transition-state theory.

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