LBL-34612
UC-410

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

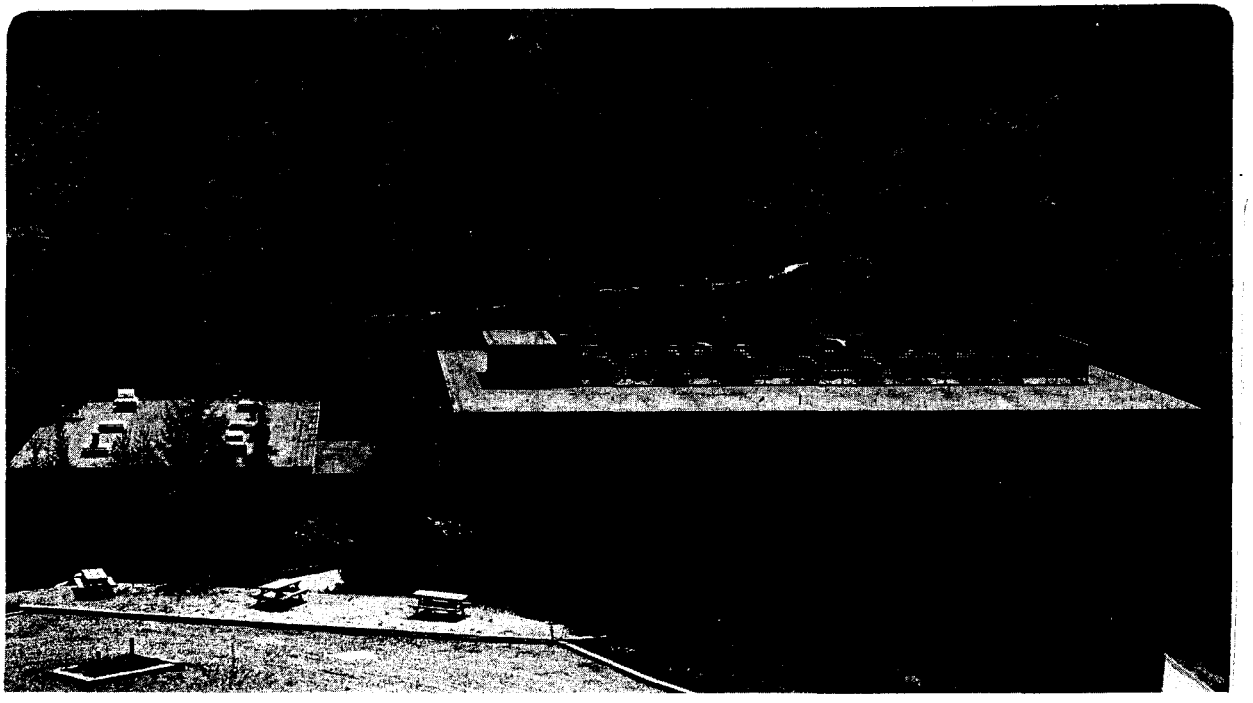
Materials Sciences Division

Presented at the Fourth International Conference on the Structures of Surfaces, Shanghai, China, August 16–19, 1993, and to be published in the Proceedings

New Vision on Surface Diffusion

X.-D. Xiao, Y. Xie, and Y.R. Shen

August 1993



LOAN COPY
Circulates
for 4 weeks
Bldg. 50 Library.
Copy 2
LBL-34612

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

LBL-34612
UC-410

New Vision on Surface Diffusion

Xu-Dong Xiao, Yuanlin Xie, and Y.R. Shen

Department of Physics
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

August 1993

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

LBL-34612
UC 410

New Vision on Surface Diffusion

Xu-Dong Xiao, Yuanlin Xie, and Y. R. Shen

Department of Physics, University of California
Materials Sciences Division, Lawrence Berkeley Laboratory
Berkeley, California 94720

Although surface diffusion has been a subject of extensive studies, its understanding is still rudimentary.[1] Experimental results are limited because of lack of widely applicable techniques. We have recently developed a novel technique ultilizing optical diffraction from a laser-induced one-dimensional monolayer grating to probe chemical surface diffusion.[2,3] Since the diffusion involved is one-dimensional, it can be easily analyzed. By varying the grating period, the measurable diffusion coefficient can have a dynamic range of about 9 orders of magnitude, from 10^{-6} cm^2/sec to 10^{-15} cm^2/sec. If the grating is properly oriented, anisotropic surface diffusion can be readily measured. Also the technique is applicable to both metals and semiconductors and probably even insulators or fluids. Finally, with linear optical diffraction, the sensitivity of the technique can be so high that a grating with a modulation of a few percent of a monolayer is easily detectable.[3] Therefore, the coverage dependence of surface diffusion can also be investigated. We have used this technique to study CO diffusion on Ni(110). We are interested in: i) the coverage dependence of anisotropic diffusion; ii) impurities effects on diffusion; and iii) defect effects on diffusion.

The experiment was performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 2.0×10^{-10} torr. The Ni(110) sample was cut and polished to within 0.2^{o} from the (110) plane. The sample surface was prepared in the usual way.[2] Auger spectra showed no detectable surface impurities (< 0.3% for S and C, and <3% for O) after the cleaning procedure. A sharp 1x1 LEED pattern from the bare Ni(110) surface and a clear 2x1 LEED pattern from a full CO monolayer on the surface could be observed.

To create a CO grating on Ni(110), laser-induced thermal desorption with two interfering pulsed laser beams from a single-mode Q-switched Nd:YAG laser was used. The depth of the adsorbate grating was controlled by properly adjusting the beam intensities.[2] We chose to have in our experiment a grating period of ~3μm and a coverage modulation of ~0.03ML on an adjustable average coverage $\bar{\theta}$. With such a small coverage modulation, the diffusion coefficient measured can be well approximated by a constant depending only on the average coverage. Linear optical diffraction could be used to probe the grating. In our experiment a signal-to-noise ratio of 10 was obtained.

Surface diffusion leads to smearing of the monolayer grating. As a result, the first-order optical diffraction signal decays as[3]

$$S(t) = S_0 \exp(-8\pi^2 Dt/s^2), \qquad (1)$$

where the decay constant is proportional to the diffusion coefficient D and inversely proportional to the square of the grating period s. Knowing s, we can deduce D from a fit of Eq.(1) to the measured S(t). Some typical results are shown in Fig. 1. From such data, D versus temperature T could be obtained and fit by the Arrhenius law

$$D = D_0 \exp\left(-\frac{E_{diff}}{k_B T}\right), \qquad (2)$$

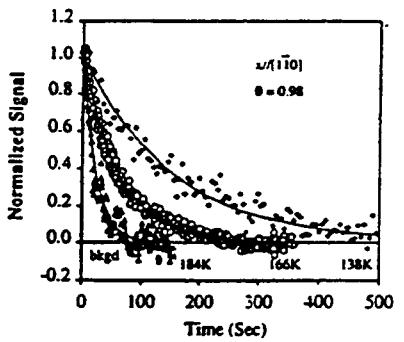


Figure 1: Linear diffraction signals versus time for coverage θ=0.98ML at three temperatures for diffusion along [1$\bar{1}$0]. The solid lines are single exponential fits by Eq. (1).

The preexponential factor D_0 and the diffusion activation energy E_{diff} could then be found.

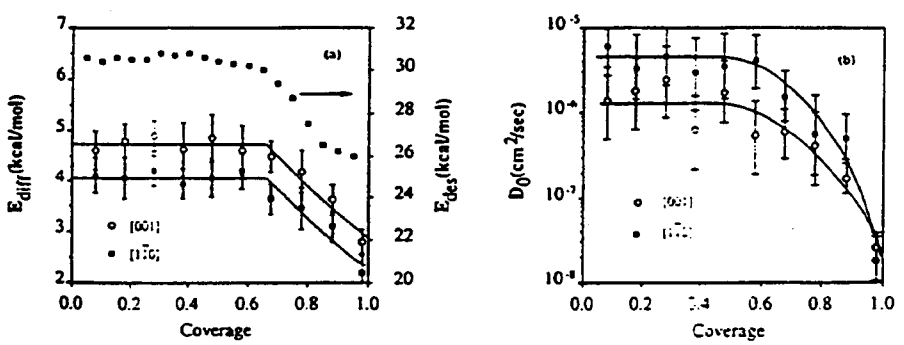


Figure 2: (a) Diffusion activation energy and (b) preexponential factor as a function of CO coverage θ for CO diffusion along [1$\bar{1}$0] and [001]. The solid lines in (a) are theoretical fits using a simple lattice gas model with mean field approximation, but the solid lines in (b) are only for eyeguide. The desorption energy as a function of coverage θ from Ref. 11 is reproduced in (a) for comparison.

For measurements of anisotropic surface diffusion, the CO monolayer grating could be oriented on Ni(110) along various directions. The average CO coverage $\bar{\theta}$ was also varied for studies of coverage dependence in the diffusion. Figure 2 shows how our experimentally determined E_{diff} and D_0 for CO diffusion on Ni(110) along $[1\bar{1}0]$ and [001] vary with the average CO coverage $\bar{\theta}$. In both directions, E_{diff} is essentially constant up to a CO coverage of 0.7ML and then decreases monotonically towards full coverage, with D_0 behaving the same way. The CO-CO interaction is clearly important for surface diffusion with $\bar{\theta}$ higher than 0.7ML, but does not seem to have contributed additional anisotropy to E_{diff} since the difference in E_{diff} along $[1\bar{1}0]$ and [001] remains unchanged with $\bar{\theta}$.

It is known that below θ=0.7ML, CO adsorbs on both short-bridge and top sites along the Ni atomic rows with a coverage independent occupation ratio.[4,5] The separation between adsorbed CO molecules is at least 3.74Å in the $[1\bar{1}0]$ direction. Above this coverage the need to accommodate more CO molecules on the surface pushes more molecules to either top or short-bridge sites[4,6,7] and the close packing causes such CO molecules to tilt alternatively towards [001] and $[00\bar{1}]$ with a tilt angle of 19° with respect to the surface normal.[8,9,10] The electron orbital overlap of the neighboring CO molecules along $[1\bar{1}0]$ is now appreciable considering that the diameters of Ni atoms and adsorbed CO molecules are 2.49Å and 2.80Å, respectively. This leads to a short range CO-CO repulsive interaction which is significantly relieved if one of the molecules would move to a neighboring saddle point on a diffusion pathway. Thus, the diffusion energy barriers are effectively reduced. The above picture qualitatively explains the decrease of E_{diff} with increasing $\bar{\theta}$ above 0.7ML and indicates that it is the short-range CO-CO interaction responsible for the observed coverage dependence.

For comparison, the desorption energy E_D of CO/Ni(110) measured earlier by Feigerle *et al* [11] is reproduced in Fig. 2(a). The resemblance of E_D to E_{diff} as a function of coverage further suggests that the long-range CO-CO interaction has negligible influence on the potential variation around the adsorption sites.

We have also investigated the impurity effect on surface diffusion. Figure 3 presents the effect of S impurity on CO diffusion along $[1\bar{1}0]$ for $\bar{\theta}$~1.0. In this experiment, S was deposited on Ni(110) by exposing the surface with a proper amount of H_2S. It is seen that even with ~.01 to .02ML S, the diffusion coefficient D for CO diffusion is already appreciably different from that of a clean surface. The activation energy E_{diff} monotonically increases from its clean surface value of

2.1kcal/mol to a saturation value of ~7kcal/mol as the S coverage increases to 0.05ML, above which D is further reduced through change in D_0. In the low temperature region (~160K), CO diffusion on Ni(110) with ~0.05ML of S impurities is already 2 orders of magnitude slower than on the clean surface.

The existing theory cannot explain such a dramatic change in the CO diffusion coefficient due to impurities, including the saturation effect, with any realistic S-CO interactions.[12] It is possible that such adsorbed S atom could induce a local surface reconstruction of Ni(110),[13] resulting in a change of local potential barrier for diffusion and hence an increase in the diffusion activation energy. Another possible mechanism is that S adsorbates may migrate to the step sites, strongly enhancing the energy barriers at the steps which then dominates the CO surface diffusion.

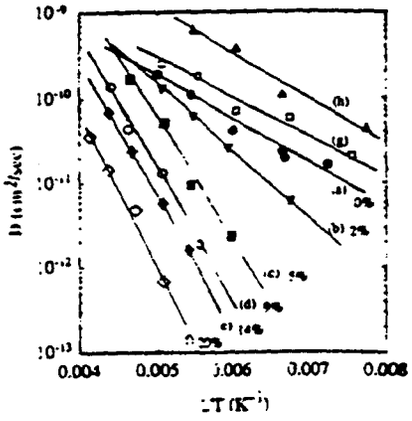


Figure 3: CO Diffusion coefficient at full coverage $\bar{\theta}$~1.0 along [1$\bar{1}$0] of various Ni(110) surfaces as a function of reciprocal temperature: (a) normally prepared clean surface; (b) - (f), surfaces with S coadsorbate concentrations of 2%, 5%, 9%, 14%, (f) 20%, respectively; (g) surface flash-annealed after Ar^+ sputtered, (h) surface normally prepared followed by 5min Ar^+ sputtering.

The effect of surface point defects, created by Ar^+ sputtering, on CO diffusion on Ni(110) has also been studied. The data in (f) and (g) of Fig. 3 were taken on Ni(110) surfaces with different defect densities for an average CO coverage of $\bar{\theta}$~1.0. In (f) the surface after 30 minutes of Ar^+ sputtering (at 10^{-4} torr and 500V) was flash-annealed at 1120K for ~ 1 minute. In (g) the surface after Ar^+ sputtering was first annealed at 1120K for 10 min. After it was cooled down to room temperature, it was Ar^+ sputtered for 5min. These two cases are compared to the normally prepared surface (a), which was annealed at 1120K for 10 minutes after Ar^+ sputtering. CO diffusions in cases (f) and (g) are significantly faster, but E_{diff} remains unchanged.

It is clear that the defect density must increase from (a) to (f) to (g). Our experimental results therefore show unambiguously that CO diffuses along [1$\bar{1}$0] on Ni(110) faster if the defect density is higher. The change comes via the preexponential factor D_0. Instead of blocking sites in the diffusion pathways, the defects must have increased the apparent jump length in the diffusion process.

In summary, we have shown that linear optical diffraction off an adsorbate grating is an effective and versatile technique for surface diffusion studies. We

have used it to probe anisotropic CO diffusion on Ni(110). The coverage dependence of the diffusion has also been measured and proven to be dominated by short-range CO-CO interaction. The sulfur impurities on Ni(110) effectively impede CO diffusion on Ni(110) with a significant increase in the diffusion energy barrier. Defects on the surface, on the other hand, speed up the diffusion mainly through an increase in the preexponential factor.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-ACO3-76SF00098.

References

[1] For a recent review, see R. Gomer, Rep. Prog. Phys. **53**, 917(1990).

[2] Xu-dong Xiao, X.D. Zhu, W. Daum and Y.R. Shen, Phys. Rev. Lett. 66, 2352(1991); Phys. Rev. B **46**, 9732(1992).

[3] Xu-dong Xiao, Yuanlin Xie and Y. R. Shen, Surf. Sci. **271**, 295(1992).

[4] R. J. Behm, G. Ertl and V. Penka, Surf. Sci. **160**, 387(1985); S.Haq, J.G.Love and D.A.King, Surf. Sci. **275**, 170(1992).

[5] J. Bauhofer, M. Hock, and J. Kuppers, Surf. Sci. **191**,395(1987).

[6] D. J. Hannaman and M.A.Passler, Surf. Sci. **203**, 449(1988).

[7] B. Voigtlander, D. Bruchmann, S. Lehwald and H. Ibach, Surf. Sci. **225**, 151(1990).

[8] W. Riedl and D. Menzel, Surface Sci. **163**, 39(1985).

[9] M. D. Aley, M. J. Yates, Jr., Surface Sci. **165**, 447(1986).

[10] D.A.Wesner, F.P.Coenen and H.P.Bonzel, Phys. Rev. Lett. **60**, 1045(1988);Phys. Rev. B **39**,10770(1989).

[11] C.S.Feigerle, S.R.Desai and S.H.Overbury, J.Chem.Phys. **93**,787(1990).

[12] V. P. Zhdanov, Surf. Sci. 194, 1(1988); Phys. Lett. A **137**, 225(1989).

[13] D. R. Warburton, G. Thornton, D. Norman, C. H. Richardson and R. Mcgrath, Surf. Sci. **189/190**, 495(1987); R. Baudoing, E. Blanc, C. Gaubert and Y. Gauthier, Surf. Sci. **128**, 22(1983).