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JAN 82 R VISWANATHAN, D R BURGESS, P C STAIR N00014-79-C-0794
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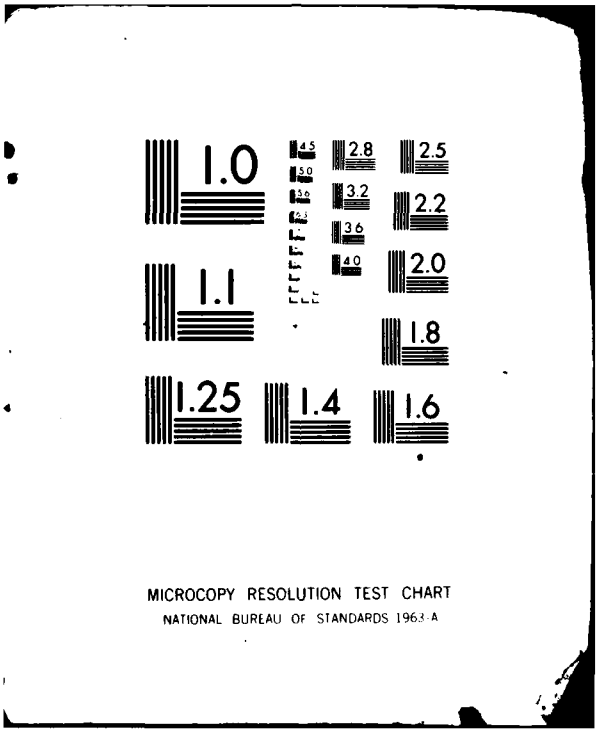
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Desorption of CO from both clean single crystal and polycrystaline copper has been achieved by means of ArF excimer laser irradiation of the crystal surface. A diffusion coefficient of $3.5 \pm 1.5 \times 10^{-6} cm^2 sec^{-1}$ has been determined for CO on the Cu(100) surface at $140^{\circ}K$ by monitoring the return of CO to the area depleted by the laser.

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Laser Flash Desorption of CO from Clean Copper Surfaces

by

R. Viswanathan, D. R. Burgess, Jr., P. C. Stair and E. Weitz

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Laser Flash Desorption of CO from Clean Copper Surfaces. R. Viswanathan, D. R. Burgess, Jr., P. C. Stair and E. Weitz, Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

The objective of this research is to utilize pulsed laser thermal desorption as a technique for studying the interaction of molecules with solid surfaces. This technique is similar to ordinary thermal desorption spectroscopy in many respects[1] but also has a number of advantages due to the rapid, localized heating of the surface made possible with focused, pulsed laser radiation. In the present study the pulsed laser desorption has been used to investigate the surface diffusion and desorption of carbon monoxide adsorbed on a polycrystalline copper surface as well as the copper (100) single crystal surface in ultrahigh vacuum. Surface diffusion was studied by observing the time dependence for the recovery of the desorption flux from a small area on the Cu(100) surface following the depletion of the adsorbed CO in that area by a series of laser pulses. The flux of desorbed CO was measured as a function of surface concentration and laser fluence by determining the time-of-flight into a mass spectrometer detector. Ordinary thermal desorption was performed to obtain relative coverages and to compare with the laser desorption measurements. The copper surface was chosen for this study because it is easily cleaned. Carbon monoxide was chosen as the adsorbate because its adsorption on copper is simple and well understood.

The ion pumped UHV chamber (base pressure 7×10^{-10} torr) is equipped with a UTI quadrupole mass spectrometer, ion sputter gun, gas introduction facilities and LiF windows for passing the laser beam into the chamber. The sample holder is mounted on a Huntington High Precision Manipulator for accurate sample positioning. The copper sample is heated by electron bombardment and cooled below 150 K using liquid nitrogen. The bulk temperature is measured via a chromel-

alumel thermocouple in contact with the edge of the sample. The laser desorption source is a focused or collimated ArF excimer laser beam with a pulse width of 10^{-8} sec and an energy range of 1-100 mJ/pulse at 193 nm. 10 μsec time resolution in the desorbed flux detected via the mass spectrometer is achieved using a fast amplifier and storing signals in a Biomation transient recorder. The copper surfaces were polished using standard metallography techniques and cleaned in UHV by a combination of oxidation at 1000 K and argon ion sputtering according to a recipe worked out in another UHV chamber equipped with Auger electron spectroscopy for verifying the surface cleanliness. The single crystal wafer was cut from a copper single crystal rod which was oriented by Laue X-ray diffraction. The CO was Matheson research purity used without further purification.

For the measurement of the diffusion coefficient we assume that the area on the surface which is depleted of adsorbed molecules is circular with the same diameter as the focused laser beam, ~0.20 cm. The solution to Fick's Law for this geometry is[2]

$$\frac{\bar{C}(t) - C_o}{C(o) - C_o} = 0.69 \exp(-5.8\ Dt/R^2) \qquad (1)$$

for times, t, long enough that $Dt/R^2 > 0.05$. In this equation C_o is the overall surface CO concentration, C(t) is the concentration within the irradiated area at time t after depletion by a series of laser pulses, D is the diffusion coefficient and R is the radius of the irradiated area. The fraction of the total adsorbed CO removed with each laser pulse is only 0.0001 as determined by a comparison of the integrated curves for laser desorption and ordinary thermal desorption. Thus C_o can be considered a constant for these experiments. A series of four (4) laser pulses at one second intervals was used to produce a depleted area, and the flux desorbed by these pulses was summed to obtain

Co-C(o). $\overline{C}(t) - C_o$ was determined from the flux desorbed by a second series of four pulses at time t after the first series. The diffusion coefficient, D, was obtained from the slope of $\ln[\frac{C(t)-C_o}{C(o)-C_o}]$ vs. t.

The measured diffusion coefficient for CO on the clean Cu(100) surface at 140 K is $3.5 \times 10^{-6}cm^2sec^{-1} \pm 1.5 \times 10^{-6}cm^2sec^{-1}$. The large uncertainty is due to poor signal-to-noise on the desorption fluxes caused by the small signals. For an activated diffusion model $D = D_o \exp(-E_a/RT)$. Assuming a reasonable value for D_o (0.1 to 0.01) the calculated activation energy is 2-3 kcal/mole. This activation energy should be fairly accurate since the calculated value is insensitive to the values of D and D_o. 2-3 kcal is a reasonable value for E_a, it is roughly 1/5 of the heat of adsorption of CO on Cu(100) in agreement with surface diffusion activation energies measured for other surface-adsorbate systems.[3] It is also approximately the energy required to force CO out of its lowest energy adsorption site which occurs in the formation of the high coverage compression structure on Cu(100).[4]

The laser fluence and surface coverage dependence of the CO flux desorbed from Cu(100) and polycrystalline copper have been investigated only qualitatively. Poor pumping in the region of the mass spectrometer prevented the quantitative determination of the CO velocity distribution via time-of-flight measurements. For both polycrystalline copper and Cu(100) there is a marked threshold for the onset of desorption as a function of laser fluence. An increase in fluence of 30% from threshold doubles the desorption signal from Cu(100). Increasing the fluence above threshold increases both the desorption flux and the mean molecular velocity as judged by the time-of-flight spectrum. In general the desorption cross-section on the polycrystalline surface was several orders of magnitude higher than on the single crystal Cu(100) surface.

With increasing coverage, the time-of-flight spectrum of CO on the polycrystalline copper surface showed a pronounced shift toward decreasing molecular velocities. We interpret this to be due to sequential filling of sites with decreasing heats of adsorption with increasing coverage.

Perhaps the most important result of this work is the demonstration that surface diffusion can be studied on macroscopic single crystals using pulsed laser desorption. Surface diffusion is important in chemical reactions on surfaces. However, convenient tools were not available for its study except for systems that were compatible with field emission experiments.[3] Laser desorption should be useful for studying any surface-adsorbate system where the adsorbate can be thermally desorbed.

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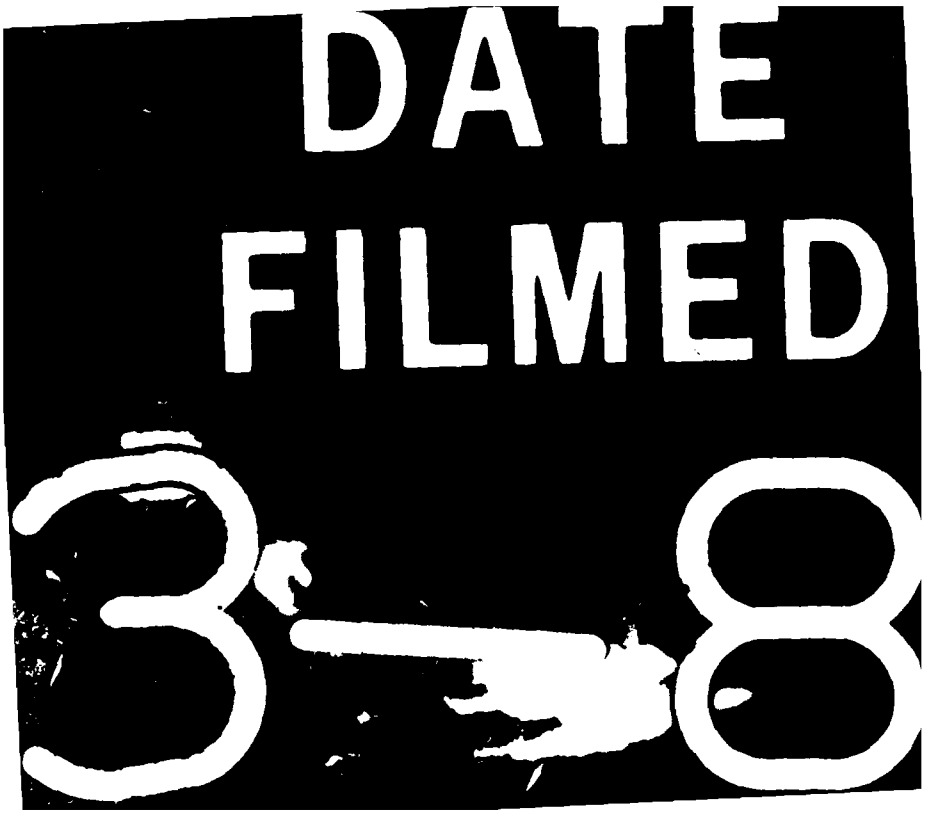
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