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EXTENSIONS OF ELECTRON STIMULATED DESORPTION
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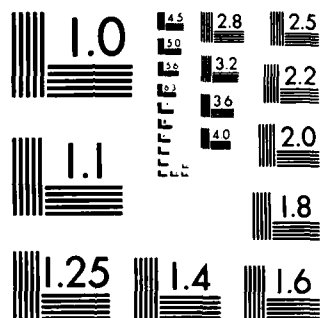
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Work carried out consisted of determining energy thresholds for neutral CO, CO ⁺ , and O ⁺ from chemisorbed CO on W(110) in electron stimulated desorption. Arguments explaining the results are given and it is shown that the most probable electron energy which can be utilized at threshold is $E_{\text{patt}} + \phi_{\text{emitter}} - \phi_{\text{collector}}$. Current distributions in ESD diodes were also measured and shown to be triangular. The implications of these findings are discussed. Adsorption of CO and of oxygen on 1-4 Cu layers, adsorbed on a W(110) crystal			

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ANNUAL SUMMARY REPORT ON ONR CONTRACT N00014-77-C-0018

July 1, 1983 - June 30, 1984

Work carried out during this period has consisted of extensions of electron stimulated desorption measurements and of a continuing investigation of gas adsorption on Cu layers deposited on a tungsten (110) surface.

Electron Stimulated Desorption

(J.-C. Lin and R. Gomer)

Accurate thresholds and yield vs. electron energy curves have been measured for neutral CO, using the square wave modulation technique devised earlier. Threshold and near threshold behavior has also been determined for CO^+ , O^+ from molecularly adsorbed CO, and O^+ from dissociated, i.e., β -CO. The nominal threshold for neutral virgin CO is 5.5 eV; this value is not correlated with any σ - π excitation, but may correspond to a $2\pi_a \rightarrow 2\pi_b$ excitation. For CO^+ the threshold, 12.5 eV, could correspond to a 4σ to E_F transition. For O^+ from molecular CO the threshold, 20.6 eV, is much higher than that from dissociated CO, 16.8 eV because of CO bond breaking. A value of the W-C bond (after dissociation of CO) of 5.5 eV can be deduced from our data. The above correlations assume that the available electron energy is $E_{\text{battery}} + \phi_{\text{emitter}} - \phi_{\text{collector}}$, i.e. that the electron cannot use all the energy available if it wound up at the Fermi level of the substrate. For the O^+ threshold from CO the latter assumption leads to a negative binding energy for C on W, thus confirming the assumption $E_b - \phi_{\text{emitter}} - \phi_{\text{collector}}$. For atomic systems, however, the full electron energy can sometimes be utilized. In addition to the thresholds noted above additional channels were seen to open for $E_{\text{batt}} = 28.6$ eV for both neutral CO and CO^+ . This corresponds to a W core level excitation if it is assumed that the full electron energy, $E_{\text{batt}} + \phi_{\text{emitter}}$ is available. This is reasonable since the electron winds up at a W atom in this case. This finding suggests that

a new channel opens up via a Knotek-Feibelman mechanism¹ and that there is some contribution to neutral CO from reneutralization of CO⁺. This work will be extended somewhat and then written up for publication. An attempt to look for neutral O desorption with a mass analyzer, using the square wave modulation technique has not been successful. This means either that O atoms are electron desorbed with such high velocities that they cannot be ionized with adequate efficiency in the mass spectrometer or that they come off so slowly that the square wave technique fails. It is planned to investigate this system further.

A detailed study of current distribution in ESD diodes, which consist of a thin W filament in front of the crystal as electron source was made by simulating the experimental geometry with a "crystal" of 80% transmission molybdenum Lektromesh with a filament at variable distances in front of it. Behind the "crystal" a probe, consisting of a 0.01 "diameter W rod inside a 0.025" O.D. stainless steel capillary but insulated from the latter by a glass coating could be moved over the "crystal" surface to probe current distribution. In a separate experiment a solid Pt foil cut to the shape of the crystal was used with one of its support leads electrically insulated from it (but at the same potential) so that current to the leads could also be estimated. It was found that current distribution along the narrow dimension of the crystal was nearly uniform, but that it was nearly triangular along the long dimension, peaking at the center. This resulted from the fact that the middle section of the electron emitting filament is hottest. It was also shown that uniform current distributions over the crystal can be obtained by using a filament in the form of a spiral at each end with a straight section in the middle. For many purposes the triangular distribution is actually an advantage, however, since it concentrates emission in the central region. It was also shown that some emission current hits the leads to the crystal. The amount depends on

the particular arrangement used i.e. whether the crystal is at ground or at negative or positive voltage with respect to the main chamber. Measurements of apparent cross sections of Kr ESD in the real system, using these various electrical arrangement confirmed these findings. Finally an arrangement simulating a geometry previously used by Leung, Vass and Gomer² was used and it was found that no current then reaches the crystal leads. It was also possible to calculate corrections to cross section measurements for triangular current distributions. By a combination of these findings it could be shown that the apparent discrepancy between the CO ESD cross section reported by Leung, Vass and Gomer² and by Opila and Gomer³ can be resolved in terms of corrections to the current distribution. This work is being written up for publication.

Adsorption of Gases on Cu Overlayers on W(110)

(I. Hamadeh and R. Gomer)

The adsorption of Co and O₂ on 1-4 atomic layers of Cu deposited on a W(110) crystal is being studied. For CO the thermal desorption measurements described in last year's report have been extended to isothermal desorption and to XPS measurements. Isothermal measurements indicated that the peaks seen in temperature programmed desorption do not obey simple first order kinetics, but consist of at least two first order regimes with different rate constants. In XPS only a single peak for O 1s from CO is seen throughout the heating regime, indicating that unlike CO on W⁴ there is no dissociation (which is also obvious from the temperature regime of desorption) and thus only one general type of binding, despite the multiple peaks seen in desorption. This suggests that the various desorption peaks result either from substrate dereconstruction or from CO-CO interactions. The XPS shifts of both O and Cu after CO adsorption could be studied. For 1 Cu layer there is a shift to higher binding energy for O 1s from CO, relative to clean W by 1.3 eV. At the same time the

Cu $2p_{3/2}$ peak shifts from 932.6 to 933.2 eV binding energy on CO adsorption. This suggests that there is some electron transfer from both the O atom of CO and from Cu, presumably to the underlying W substrate.

In the course of these measurements it was also noticed that appreciable peaks at apparent binding energies of 536 and 523 eV were seen when > 3 Cu layers were adsorbed. After some searching it appears that these are unusually strong Cu Auger peaks, resulting from photoexcitation of core holes. This could be confirmed by searching for other Cu Auger lines. It was found, however, that all the photon induced Auger transitions are shifted to lower kinetic energies by 5-10 eV. The origin of this shift is not yet understood.

Experiments with O_2 adsorption still in a preliminary state indicate that the sticking coefficient of O_2 decreases drastically from that on clean W when the Cu layer thickness exceeds 2.

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- 3) R. Opila and R. Gomer, Surf. Sci. 129, 563 (1983).
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Publication Resulting from this Contract

A Photoelectron Spectroscopic Study of Changes Produced in CO Adsorbed on the W(110) Plane by Electron Impact, R. Opila and R. Gomer, Surf. Sci. 129, 563 (1983).

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