Energy Distributions of Field-Emitted Electrons from Tungsten in the Presence of Adsorbed CO†

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Measurements of the energy distribution in the presence of adsorbed CO are given for the (110), (210), and (100) planes of W. The results are discussed in terms of binding models.

Total energy distributions (TED) of field-emitted electrons from adsorbate-covered surfaces can reveal electronic structure associated with adsorption.[1-3] Specifically the local density of states, $\rho_a \equiv \pi^{-1}\mathrm{Im}G_{aa}$, is proportional to the enhancement of the density in energy $j(\epsilon)$ of the emitted electrons[3]:

$$\rho_a(\epsilon) \propto R(\epsilon) \equiv [j(\epsilon) - j_0(\epsilon)]/j_0(\epsilon), \quad (1)$$

where the subscript refers to emission in the absence of adsorbate.

We report here measurements for CO on tungsten. The results seem to confirm the existence of previously postulated adsorption states on some crystal planes, show the importance of substrate topography, and in some instances allow fairly unequivocal assignment of adsorbate-substrate geometry. In addition, some wholly unexpected features were seen.

An analyzer tube described previously[4] was modified by inclusion of a 127° cylindrical electrostatic velocity selector. Electrons emerging from the latter were counted with a Channeltron by standard techniques. The experiment was controlled by a Nova-1200 minicomputer which could scan repeatedly a preset energy interval. Resolution for clean W was estimated from the leading edge of the distributions to be 20–30 meV.[5] Ultrahigh vacuum and incremental dosing were achieved by immersing the whole apparatus in liquid hydrogen and using a sublimation gas source.[4] Dosing and measurements were carried out with the emitter at 20°K. Detailed descriptions will be reported elsewhere.[6] In the following energies are given relative to the Fermi energy E_F unless otherwise specified.

A TED for a clean (100) surface, showing the Swanson hump[7] at − 0.35 eV, is shown in Fig. 1. For $\theta_{CO} \geq 0.4$ monolayers, the Swanson hump virtually disappeared. Down to − 1.6 eV, no apparent enhancement was found. At 210°K a small enhancement at − 0.75 to − 1.1 eV and a shoulder at − 1.0 eV appeared. On further heating, $R(\epsilon)$ at − 0.75 eV gradually disappeared above 430°K while the resonance at < -1 eV increased, reaching its maximum at 750°K (Fig. 1). If it is valid to extrapolate the linear portion of the distribution, its maximum lies at − 2 eV with a half width at half-maximum of 0.35 eV. Redosing a virgin layer heated to 750°K caused no change,

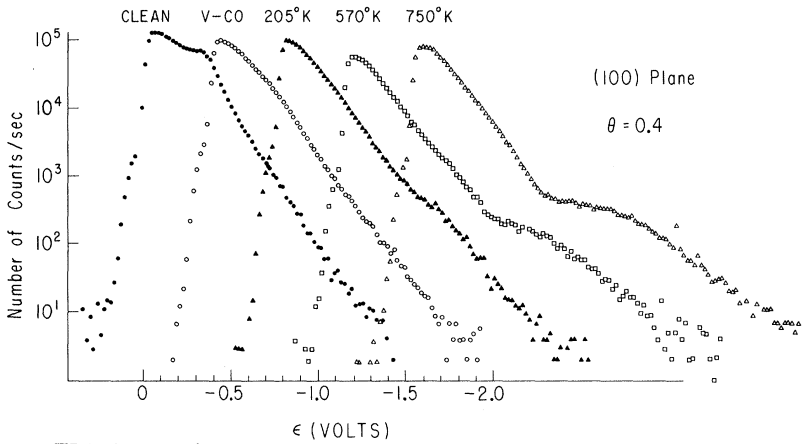

FIG. 1. TED's for (100). Curves are displaced for ease of viewing.

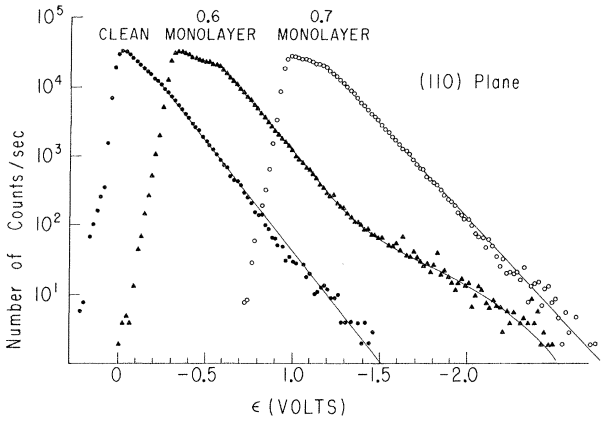

FIG. 2. TED's for (110) virgin CO. Curves displaced arbitarily.

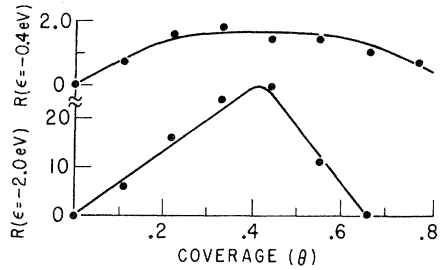

FIG. 3. Enhancements (at energies indicated) versus θ on (110) for virgin CO.

although the total intensity dropped.

Figure 2 shows TED's from (110). An enhancement sets in at -1 eV. The low emission from this plane made it impossible to determine the exact location or width of the peak. It showed little broadening with increasing coverage, but $R(\epsilon)$ at a given energy first increased almost linearly to $\theta = 0.45$ and then decreased sharply, as shown in Fig. 3. At $\theta = 0.7$ the resonance disappeared completely. On heating a $\theta = 0.4$ layer the resonance disappeared irreversibly at 200°K.

In addition to the resonance at < -1 eV a strong modulation of the distribution was observed near E_F (Fig. 2), which disappeared irreversibly at 100°K. On redosing a virgin layer heated to 400°K no new structure appeared in the TED, although the intensity dropped.

Figure 4 shows results for (210). An enhancement centered at -2.7 eV with a half width at half-maximum of 0.47 eV occurred for the virgin layer. Its intensity increased monotonically with θ. The resonance disappeared irreversibly at 350°K. Redosing at 20°K after heating a virgin layer to 350°K caused an enhancement at ~2.7 eV. Similar behavior was found on (123).

Amplitudes at $\epsilon = 0$ agree well with those calculated from the Fowler-Nordheim equation taking into account field, work function, and pre-exponential changes[8] except on the (110) plane where agreement can be obtained only by assuming no pre-exponential decrease, or a corresponding increase in observed current. All the resonances on any plane were suppressed by small amounts of carbon on the surface, and could be restored after oxygen treatment of the emitter.

The bonding of CO to single transition-metal atoms in carbonyls is believed[9] to consist of a dative δ bond involving the 5σ orbital of CO (mainly a lone pair on C) and a metal d orbital (for instance d_{z^2}) as well as π bonds formed from metal t_{2g} (i.e., d_{zx} and/or d_{zy}) orbitals and CO antibond-

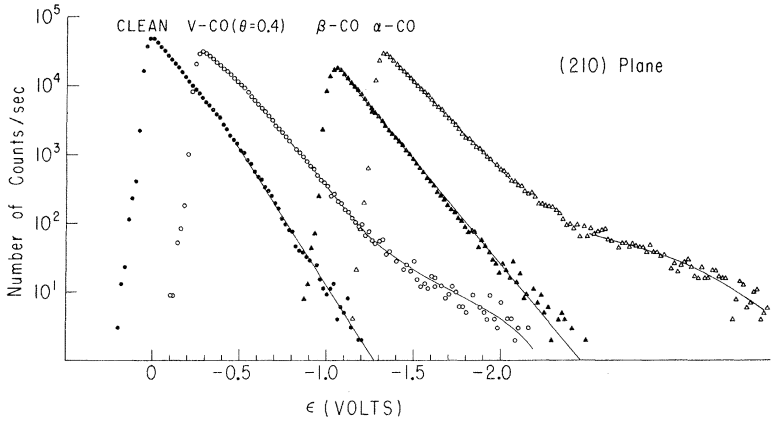

FIG. 4. TED's for (210). Curves arbitarily displaced.

ing 2π orbitals (with energy ~ -8 eV relative to vacuum). A level believed to correspond to such π bonds has been seen in photoelectron spectroscopy of $W(CO)_6$ at -8.5 eV (relative to vacuum).[10] It seems very probable therefore that the enhancements seen at < -1 eV on the (110) and at -2.7 eV on the (210) and (123) planes (e.g., -7.7 eV below vacuum) in the low-temperature (virgin) layer correspond to such π bonding. The virgin state on these planes thus corresponds in all probability to adsorption on top of single W atoms via a σ bond and via π bonds, the latter involving mainly t_{2g} tungsten orbitals and the 2π CO antibonding orbital. Such a structure was previously suggested[11] for the (110) plane by the fact that virgin CO yields CO^+ as the principal ionic desorption product in electron-impact desorption. It is interesting that the resonances on (110) and (210) disappear approximately at the temperatures at which the CO^+-yielding virgin state goes over into an O^+-yielding state in electron-impact desorption.[12] The formation of the latter requires some activation energy, and thus in all probability some CO rearrangement, for instance to a sp^2 hybridization of C. For such an arrangement the 2π levels of CO no longer exist as such and the disappearance of the resonance is explained.

The absence of a π resonance for virgin CO on (100) is puzzling. If adsorption occurred on the corner atoms of the unit mesh, π bonding should certainly occur. Since these have only four nearest neighbors they might behave more nearly like free W atoms, so that the resonance could be narrow and sufficiently far below E_F to be invisible in our experiments. If adsorption occurred at the center of the unit mesh, a strong σ bond with the atom directly underneath would be expected. π bonding might occur by interaction with $d_{x^2-y^2}$ orbitals from atoms at the corners of the unit mesh, but might be weak, and/or partially discriminated against in field emission by the fact that the CO molecule is partially "buried" in the surface.

The weak resonance appearing at 210°K and vanishing >430°K at $-(0.75-1.0)$ eV is probably associable with an α-like state, which may be formed together with a β or a β precursor in this temperature interval. The latter state is responsible for the broad resonance peaking at -2 eV, which persits into the true β regime at 700°K. It is doubtful whether this resonance has anything to do with π bonding. The fact that it is seen by Plummer and Waclawski[13] in photoemission with many adsorbates on (100) suggests that it may arise from surface reconstruction, or from a modification of the tungsten density of states, as suggested by these authors.

The existence of a resonance for α-CO (the state formed by readsorption on a β layer) on (210) suggests that on this plane α-CO corresponds to single site adsorption, and sufficient back donation to populate π orbitals. It is interesting that α-CO on this plane leads to a reduction in work function,[8] so that at least some of the back-donated electron density may be drawn from β-CO via the metal. On (110) no resonance is observed for α-CO. This is consistent with a model previously advanced for this plane,[11] in which α-CO corresponds to adsorption between two W atoms. π-bond formation would then be improbable.

One of the most interesting features of the present work is the relatively sharp disappearance of the virgin resonance at ~ -2 eV on (110) at $0.6 < \theta < 0.7$ monolayers. Since this is not seen on (210) which corresponds to terraces of one unit cell of (110) and steps of one unit cell of (100) the phenomenon probably corresponds to the higher density of (110)-like sites on (110). Since CO is not mobile in the chemisorbed layer at 20°K a phase change is unlikely; further, the diminution of the resonance, while rapid, is not abrupt. Since there is no evidence that broadening accompanies the diminution in intensity, overlap of the π-bonding orbitals into a band, followed by a Mott transition, is unlikely. In any case this band would be unlikely to be so wide as to make the resonance invisible. It is more likely that the effect can be attributed to Pauli exclusion of electrons from the π-bonding region when overlap with the 1π and 5σ orbitals from adjacent adsorbed CO molecules becomes appreciable. An effect of this kind has been invoked by Fano and co-warkers[14] to explain the x-ray absorption spectrum of SF_6 and other molecules. Onset of overlap should occur when $\theta > 0.5$, and apparently is sufficiently strong at $\theta = 0.7$ to kill the resonance entirely. The binding energy of virgin CO decreases markedly with increasing θ on (110)[11]; this supports the exclusion argument, since the binding energy should increase, if band formation occurred.

The final item deserving comment is the modulation observed on (110) near E_F. The apparent symmetry of its width as a function of θ about $\theta = 0.5$, and its disappearance after heating a $\theta = 0.4$ layer to 100°K, suggest that it is related to the creation of an aperiodic potential on the sur-

face by randomly adsorbed CO (or vacancies in the CO layer at high θ); heating to 100°K could permit rearrangement to a symmetric structure. The relaxation of surface symmetry might lead to orbital rearrangement of the surface atoms with a resultant change in the surface density of states, reflected in the TED.

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Plasma Heating by an Intense Electron Beam*

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An intense pulsed electron beam ($v/\gamma \sim 2$) was used to heat electrons in a target plasma in a magnetic field. A strong beam-plasma interaction was observed. Measured heating levels were found to be consistent with a two-stream instability calculation and return-current heating estimates. Energetic counter-streaming electrons were detected in the plasma during the beam pulse and possible sources of these electrons are suggested.

Experiments using intense pulsed relativistic electron beams to heat plasma electrons have been reported recently.[1-6] New results from an energetic beam-plasma experiment are reported here. A strong interaction between beam and plasma electrons has been observed. Both a two-stream beam-plasma instability and return-current heating were considered in the interpretation of our measurements.

A Nereus accelerator[7] produced a 350-kV, 60-nsec pulse of electrons with the current rising throughout the pulse to a peak of 50 kA. the 2.5-cm-diam beam was injected into a 10-cm-diam, 30-cm-long Pyrex tube. An 8-cm-diam Faraday cup collected beam current which was transported through the plasma. A hydrogen plasma was formed by first preionizing the gas by a spark between two electrodes spaced 1 mm apart and located 2 cm from the axis. This was followed by a pulsed longitudinal discharge which raised the degree of ionization substantially. The electron beam was then injected into the afterglow plasma after a preselected delay. The plasma column at beam injection time was ~3 cm in diameter; a lower-density background plasma was present near the walls. The electron density was measured with a 35-GHz interferometer; for densities below $\sim 10^{13}$ cm^{-3}, interferometer fringe measurements were used. Low backfill pressures ($\lesssim 2\times 10^{-3}$ Torr) ensured that avalanche during the beam pulse was small. Bounds on densities above 10^{13} cm^{-3} were estimated from microwave cutoff behavior, avalanche considerations, and complete ionization limits on density. Backfill pressures up to 1.5×10^{-2} Torr were used to obtain these plasmas. Upper limits to avalanche rates for electron impact ionization were calculated from published