Identification of a Surface State on the (111) Terraces of Stepped Cu(211)

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Energy distribution measurements of field-emitted electrons reveal a free-electron-type behavior for clean Ir(100) and (110) surfaces. Adsorption of CO on Ir(100) causes the appearance of a structure at 0.6 eV below the Fermi level E_F which is identified with a chemisorption level created by "back donation" of metallic d electrons into the CO $2\pi^*$ level. Adsorption of atomic oxygen on Ir(100) and (110) leads to the formation of a maximum at 1.0 eV below E_F which is ascribed to a state derived from one of the O $2p$ levels.

Determination of the energy distribution of electrons field emitted from clean or adsorbate-covered surfaces may yield important information on the electronic properties of such systems.[1] Although the accessible energy range is limited to about 2 eV below the Fermi level E_F interpretation of the data may become more straightforward than of those obtained from photoemission, particularly if a high density of d states exists just below E_F which is the case with the transition metals. These two methods therefore supplement each other in a valuable manner. In the present work results for the chemisorption of carbon monoxide and oxygen on Ir planes will be presented. The observed structures are identified with the formation of chemisorption-induced states near E_F and are compared with the predictions of corresponding theoretical models for the bond formation.

Electrons field emitted from individual crystallographic planes of an Ir tip were energy analyzed by means of a two-stage 127° analyzer mounted into the tube of a field emission microscope. Experimental details will be described elsewhere.[2] Figure 1 shows energy distributions $\log j'(\mathcal{E})$ from clean Ir(111), (110), and (100) planes as well as from Ir(100) saturated with adsorbed oxygen and CO, respectively. The clean Ir(111) surface exhibits a pronounced peak at $\mathcal{E} = -0.40$ eV which was previously observed in a similar way also by Dionne and Rhodin.[3] Band structure calculations for iridium allow identification of this structure with the upper edge of an s-like band in this particular direction which is predicted to be located at -0.54 eV.[4] Adsorption of various gases (CO, O_2, H_2, NH_3) on this plane causes a complete suppression of this maximum, an effect presumably similar to that observed previously with adsorption on W(100).[5] A possible theoretical explanation of this effect has been offered by Duke and Fauchier.[6]

Emission from the clean (110) and (100) planes can by contrast be described almost perfectly by a free-electron model, i.e., $j'(\mathcal{E})$ is of the form $Ae^{\mathcal{E}/d}f(\mathcal{E})$, convoluted by a correction function for the resolution of the energy analyzer (15 meV), where $f(\mathcal{E})$ is the Fermi distribution function and d an energy parameter. Variations of the energy distribution caused by adsorption are commonly expressed by evaluating the enhancement factor $R(\mathcal{E}) = j'(\mathcal{E})/j_{\mathrm{cl}}'(\mathcal{E})$, where $j_{\mathrm{cl}}'(\mathcal{E})$ denotes the assumed energy distribution from the clean surface which would be obtained if the work function and the field were those corresponding to the adsorbate-covered surface.[1] If $j_{\mathrm{cl}}'(\mathcal{E})$ follows the behavior of a free-electron gas system [as is the case with the (100) and (110) planes] $R(\mathcal{E})$ is related to the local density of states on the adsorbate $\rho_a(\mathcal{E})$ through[7]

$$R(\mathcal{E}) - 1 \approx U^2(\mathcal{E})\rho_a(\mathcal{E}). \tag{1}$$

$U^2(\mathcal{E})$ is a term which compensates for the difference in tunneling from the adsorbate relative to tunneling from the metal. More precisely, a

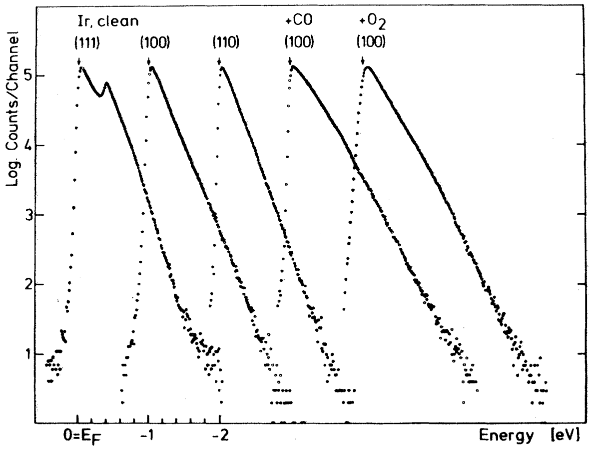

FIG. 1. Field-emission electron energy-distribution curves, $\log j'(\mathcal{E})$, for clean Ir(111), (100), and (110) planes as well as for Ir(100) surfaces saturated with adsorbed CO and O, respectively. The origins of the abscissa are arbitrarily shifted for clarity. Arrows indicate the position of the Fermi level.

Stark shift of the order e_0Fx_a, where x_a is the location of the adsorbate potential, has to be taken into account.[8] This effect may cause a shift by about 0.5 eV of observed structures with respect to the interesting field-free case.[9]

Figure 2(a) shows $R(\mathcal{E})$ curves for CO-covered Ir(100) surfaces at two different coverages. A maximum at $\mathcal{E} = -0.60$ eV is growing up which exhibits at saturation coverage an additional shoulder centered at about −1.25 eV. The main peak has a half-width of about 0.7 eV. This structure is attributed to the formation of a chemisorption orbital below the Fermi level by coupling of metallic d states with the empty $2\pi^*$ orbital of CO as illustrated by Fig. 2(b). The creation of such a state in CO chemisorption on transition metals was first predicted by Grimley[10] on the basis of a rather crude model. Later semiempirical calculations for the system CO/Pd (which metal is chemically rather similar to Ir) yielded such a state at −0.7 or −0.2 eV.[11,12] A similar conclusion was reached with a cluster calculation for CO/Ni.[13] This state exhibits predominantly metallic d-like character, but is responsible for partial transfer of electronic charge to the adsorbate. Indirect experimental evidence for this effect is given by the observed increase of the work function and by the lowering of the C-O stretching frequency through partial occupation of the antibonding $2\pi^*$ level of CO. In photoelectron spectroscopy this state could never be clearly identified because of strong d-band emission in the region below the Fermi level which is usually strongly damped upon adsorption by antiresonance effects.[12] The origin of the shoulder in the energy distribution at −1.25 eV appearing at high coverages is still unclear. It might be due to the occupation of different sites at high surface concentrations, since adsorbed CO shows generally a tendency for the formation of close-packed layers near saturation.

The only other field-emission energy-distribution measurements with CO as adsorbate reported in the literature were those performed by Young and Gomer[9] with tungsten surfaces. These authors observed with different planes [except (100)] the formation of a pronounced maximum in the $R(\mathcal{E})$ curves at −2.0 to −2.5 eV which they tentatively interpreted in a similar way as arising from coupling of metallic d electrons with the CO $2\pi^*$ level. Since no calculations for CO/W are available it seems so far to be unclear whether these features have in fact the same origin as those described in the present context. It should be noted, however, that with CO/W additional much weaker resonances were observed in the energy range of −0.4 to −0.7 eV which were not discussed in detail.[9]

$R(\mathcal{E})$ curves for (dissociatively) adsorbed oxygen on Ir(100) and Ir(110) planes are reproduced in Fig. 3(a). In both cases a slightly asymmetric maximum centered at $\mathcal{E} = -1.0$ eV with a half-width of 0.9 eV is discernible. This structure is again ascribed to resonance tunneling via chemisorption-induced states. Cluster calculations[14] revealed that a few levels in the d-band region

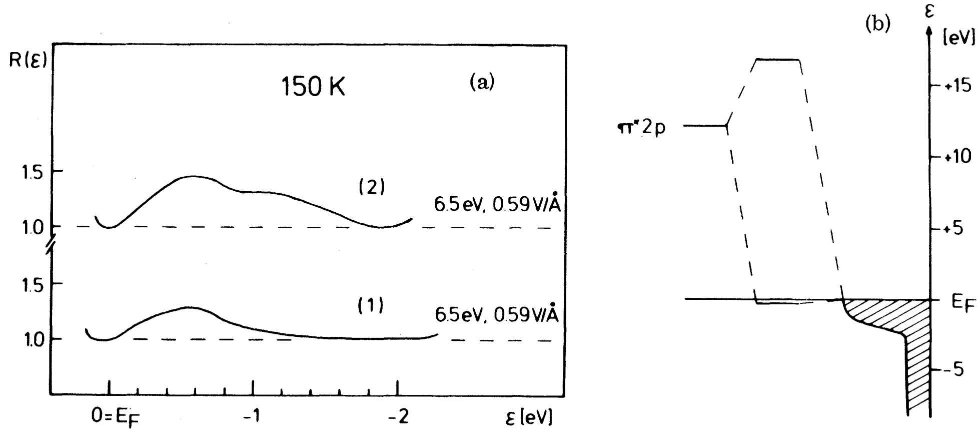

FIG. 2. (a) Enhancement factor $R(\mathcal{E})$ for Ir(100) saturated with CO (upper curve) and with about half the maximum CO coverage (lower curve). (b) Schematic energy level diagram for the coupling between metallic d states close to the Fermi level and the CO $2\pi^*$ state.

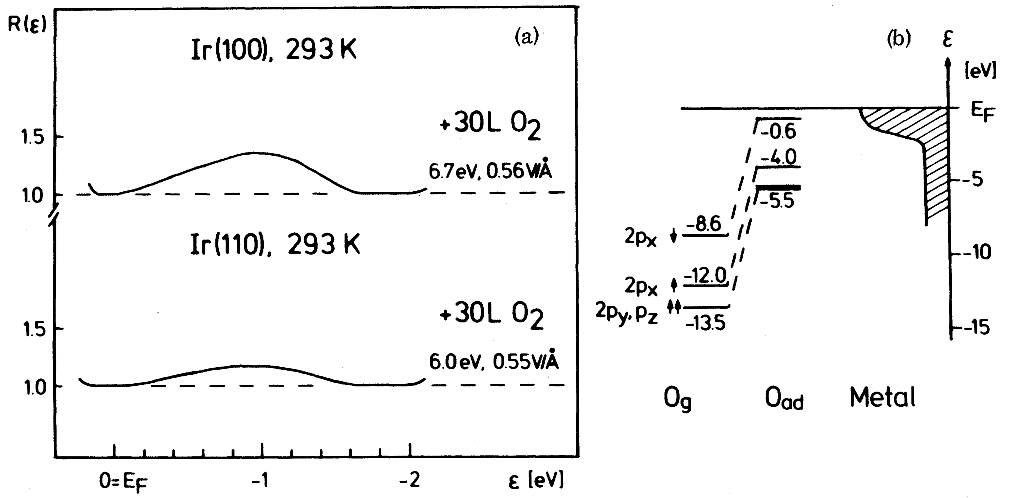

FIG. 3. (a) Enhancement factor $R(\mathcal{E})$ for oxygen-covered Ir(100) and (110) surfaces. (b) Energy level diagram for the coupling of an oxygen atom to the metal (Ref. 14).

have some charge population on oxygen which might be responsible for this effect; however, a somewhat different explanation is preferred: The energy levels of the $2p$ electrons of the free triplet oxygen atom are indicated in Fig. 3(b). According to semiempirical calculations[15] coupling to the metal causes an upward shift of these levels. The lower two states show up as a relatively broad maximum at $\mathcal{E} \approx -6$ eV in the photoelectron spectrum,[16] whereas the highest level is predicted to be close to the Fermi level and is identified with the reported structure in the field-emission energy distribution. As a consequence this orbital is predicted to be mainly adsorbate-like, in contrast to the situation found with CO.

Again Young and Gomer[17] reported on measurements with O/W(100) where a strong maximum at −1.9 eV was observed. However, the clean W(100) surface does not exhibit a free-electron behavior which is a prerequisite for the validity of Eq. (1).[7]

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[1] J. W. Gadzuk and E. W. Plummer, Rev. Mod. Phys. 45, 487 (1973); E. W. Plummer, in *Interactions on Metal Surfaces*, edited by R. Gomer (Springer-Verlag, Berlin, 1975), p. 143.

[2] H. F. Kempin, K. Klapper, and G. Ertl, to be published.

[3] N. J. Dionne and T. N. Rhodin, Phys. Rev. Lett. 32, 1311 (1974), and Phys. Rev. B 14, 322 (1976).

[4] O. K. Anderson, Phys. Rev. B 2, 883 (1970).

[5] E. W. Plummer and J. W. Gadzuk, Phys. Rev. Lett. 25, 1493 (1970); E. W. Plummer and A. E. Bell, J. Vac. Sci. Technol. 9, 583 (1972); C. Lea and R. Gomer, J. Chem. Phys. 54, 3349 (1971); E. W. Plummer and R. D. Young, Phys. Rev. B 1, 2088 (1970).

[6] C. B. Duke and J. Fauchier, Surf. Sci. 32, 175 (1972).

[7] D. Penn, Phys. Rev. B 9, 844 (1974).

[8] C. Caroli, D. Lederer, and D. Saint James, Surf. Sci. 33, 228 (1972).

[9] P. L. Young and R. Gomer, J. Chem. Phys. 61, 4955 (1974).

[10] T. B. Grimley, in *Molecular Processes on Solid Surfaces*, edited by E. Drauglis *et al.* (McGraw-Hill, New York, 1969), p. 299.

[11] G. Doyen and G. Ertl, Surf. Sci. 43, 197 (1974).

[12] G. Doyen and G. Ertl, Surf. Sci. 69, 157 (1977).

[13] I. P. Batra and O. Robaux, J. Vac. Sci. Technol. 12, 242 (1975); B. H. Chen, D. C. Foyt, and J. M. White, Surf. Sci. 67, 218 (1977).

[14] G. Doyen and G. Ertl, to be published.

[15] I. P. Batra and O. Roubaux, Surf. Sci. 49, 653 (1975).

[16] H. Conrad, J. Küppers, F. Nitschké, and A. Plagge, Surf. Sci. 69, 668 (1977).

[17] P. L. Young and R. Gomer, Surf. Sci. 44, 247 (1974).