PHYSICAL REVIEW B VOLUME 15, NUMBER 8 15 APRIL 1977

Electronic properties of adsorbed layers of nitrogen, oxygen, and sulfur on copper (100)

Gary G. Tibbetts, James M. Burkstrand, and J. Charles Tracy
Research Laboratories, General Motors Corporation, Warren, Michigan 48090

(Received 8 November 1976)

Adsorbed layers of nitrogen and oxygen in the $c(2\times 2)$ structure and sulfur in the (2×2) structure on copper (100) have been studied. Ultraviolet photoemission spectroscopy (UPS) shows that each of these layers induces a resonance above the "*d* band" of copper at about 1.3-eV binding energy with respect to the Fermi level and below the "*d* band" at about 6-eV binding energy. X-ray photoemission spectroscopy has been used to determine that the 1*s* electronic binding energies of adsorbed atoms of $c(2\times 2)$ nitrogen and oxygen are 396.3 and 529.8 eV, respectively, and that the 2*p* electronic binding energy of adsorbed 2×2 sulfur is 161.2 eV. The highest-energy Auger peaks excited by each of these core holes may be interpreted as arising from Auger transitions involving the surface electronic states measured in these UPS experiments. Good agreement with most features of the experimental Auger spectra has been obtained using measured and calculated data for the surface electronic binding energies under the assumption that Auger final-state effects are small. Therefore the evidence points to the formation of a copper-adsorbate surface complex in which these UPS-observed resonances have a high local density of states at the adsorbate atom cores and in which the final-state hole momenta are only loosely coupled.

INTRODUCTION

Electron spectroscopic studies of chemisorption can provide essential information concerning gas-surface interactions. Photoelectron spectroscopy, in both the far-ultraviolet and x-ray regions, has proven invaluable in determining the principal features of the electronic structure of the surface region.[1] Auger electron spectroscopy, while primarily used for surface compositional analysis, is finding increased usefulness as a source of spectroscopic information. With simultaneous application of these three spectroscopies, it is possible to obtain not only a more complete description of the surface chemical bond, but also a better understanding of processes upon which each spectroscopy is based.

In the present work, we have examined the adsorption of nitrogen, oxygen, and sulfur on copper (100). This study was prompted by our preliminary observations on a nitrogen-covered Cu(100) surface[2] of *two* adsorbate-induced surface-electronic states, one below the Cu *d* band corresponding roughly to the first ionization level of atomic nitrogen and a second quite-sharp resonance (0.5 eV wide) between the Cu *d* band and the Fermi level. The possibility that this electronic state above the *d* band might be a general feature of chemisorption on many metals suggested a more detailed examination of several adsorbates on several noble metals. Indeed, the present results as well as subsequent work on the adsorption of N, O, and S on silver (111) (Ref. 3) indicate that this new electronic state is characteristic of chemisorption of these atomic species on the noble metals. We believe that the observation of this level above the *d* band may have important implications in understanding the bonding of these atoms to transition metals.

An important feature of the present work is that our measurements were made primarily on crystallographically well-defined adsorbed surface layers. For example, extensive low-energy-electron-diffraction intensity profile analyses[2] indicated that the nitrogen in the $c(2\times 2)$layer on Cu(100) binds in a fourfold symmetric site, 0.145 nm above the first layer of copper atoms. X-ray photoelectron spectroscopy (XPS) verified that the core levels of the adsorbed layers observed here were in no case of complex form. This resulted presumably from adsorption in only one binding state and greatly simplified the analysis of the Auger spectra in terms of the XPS and ultraviolet photoelectron spectroscopy (UPS) measurements. For this reason, we have concentrated our experimental faculties on these well-defined surface structures without studying each as a function of coverage.

While electron spectroscopic studies of clean copper surfaces have been quite numerous,[4,5] similar studies on adsorbate-covered copper have been more limited in scope, because most gases do not adsorb appreciably on copper at room temperature.

Recently, Salmerón *et al.*[6] studied the Auger spectra of N, O, and S on copper and interpreted their results in terms of interatomic Auger transitions between adsorbate and substrate atoms. We will show how all of the lines in the valence region of these Auger spectra may be interpreted on a more experimentally consistent and physically plausible basis in terms of intra-atomic Auger transitions involving adsorbate electronic levels measured by XPS and UPS.

EXPERIMENT

This work was performed in a 30.5-cm stainless-steel vacuum chamber evacuated by ion and liquid-nitrogen-cooled sublimation pumps. The working pressure during these experiments was in the low 10^{-10} Torr range.

The electron-energy analyzer was a double-pass cylindrical-mirror analyzer[7] in which either 1.5- or 4.0-mm apertures may be selected. Only electrons emitted into a conical segment with half angle of 42.3° from the axis of the analyzer are collected. The Auger electron spectra presented here were excited by bombardment with a normally incident 5-kV electron beam of 6-μA intensity. A 0.5-V modulation potential was used in obtaining these spectra in the customary differential mode. The analyzer pass energy was set at 25 eV for 0.4-eV energy resolution.

The microwave excited ultraviolet resonance lamp is of our own design. Three capillaries 2.4 mm in diameter are incorporated in this windowless differentially pumped lamp, allowing an indicated He pressure in the sample chamber of 2×10^{-9} Torr during operation. The light strikes the target at an angle of incidence of 71.5° from the target normal. With 21.2-eV He I photons a maximum count rate of 3×10^{4} cps with a resolution of 0.08 eV is obtained from the Cu d band peak. The decreased intensity of the He II line at 40.8 eV necessitated degradation of the resolution to 0.4 eV before a maximum count rate of 2×10^{4} cps could be obtained. The surfaces described below were also studied with Ne I (16.7-eV) and Ne II (26.9-eV) radiation.

The x-ray source (Physical Electronics Model 4-151) has a Mg anode providing Mg $K\alpha_{1,2}$ x rays of energy 1253.60 eV. Operating at 400- W anode power, the d band of Cu gives 2500 cps at 0.8-eV resolution. The x-ray source is mounted so that the target is bombarded with x rays nearly parallel to the surface plane. Our spectrometer is calibrated by measuring the kinetic energies of electrons ejected from the Fermi level of cleaned Pt foil by photons of energy 21.2, 40.8, and 1253.6 eV. Our previous calibration[2] used the Cu LMM Auger peak energy of 918.02 eV determined by Kowalczyk *et al.*[8] as a fixed point and the kinetic energy difference for electrons ejected from the d band of Cu by photons of energy 1253.6 and 40.8 eV. This latter calibration was necessitated by the low density of states at the Fermi level of Cu, and assumes that a specific published value is correct. Using our Pt calibration, we obtain a value of 918.55 ± 0.2 eV for the LMM peak of copper, in good agreement with 918.6 eV measured by Kim, Gaarenstroom, and Winograd.[9]

In each of the experiments described below, signal averaging and data reduction was performed with a mini computer.

The copper target used in this work was grown with a nominal purity of 99.9999%, electropolished, and oriented so that the surface normal was within ±0.3° of the [100] direction. During these experiments the target surface was cleaned by successive cycles of 2-keV argon-ion bombardment; surface order was restored by annealing in vacuum to 720 K. Diatomic nitrogen gas does not adsorb on Cu surfaces even with exposures as large as 10^{-4} Torr for 10^{5} sec. However, large quantities of nitrogen adsorb after the gas is "activated" in an electron beam. By utilizing 100-eV electrons emitted by a filament in a nitrogen pressure of 5×10^{-5} Torr, we have been able to deposit more than $\frac{1}{2}$ a monolayer of nitrogen, the "disordered" surface in Fig. 1, in 10 min. After heating to

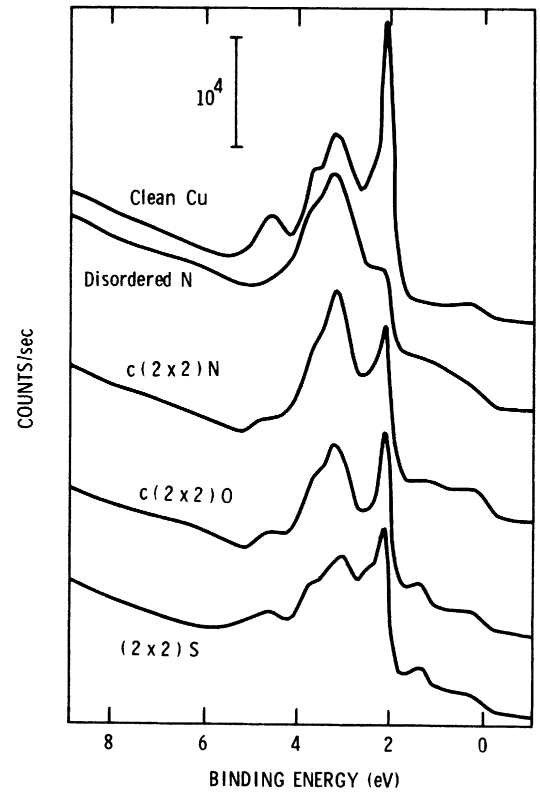

FIG. 1. He I photoemission spectra ($h\nu = 21.2$ eV) for various Cu(100) surfaces. Binding energies are referred to the Fermi level.

720 K for 10 sec, this disordered nitrogen overlayer changed to an ordered $c(2\times 2)$ overlayer. At the same time, the nitrogen Auger signal decreased by about 40%.

Adsorption of a $c(2\times 2)$ layer of oxygen on the copper crystal was obtained by exposure to 1×10^{-6} Torr of oxygen for 600 sec at 300 K. Heating the clean copper to 980 K for 600 sec allowed sulfur to segregate on the surface in sufficient quantities to form a well-ordered (2×2) layer.

EXPERIMENTAL RESULTS

Figure 1 shows energy distributions of electrons ejected from clean and adsorbate covered Cu(100) by He I resonance radiation (21.2 eV). All electron-binding energies reported here are relative to the Fermi energy, and the spectra are made with the Cu(100) surface normal to the cylindrical-mirror-analyzer axis.

The spectrum from clean Cu(100) shows *d*-band emission with a complex structure extending from 2 to above 5 eV and an *s* band of lower intensity extending from 0 to 2 eV. Adsorption of a disordered layer of nitrogen induces a peak at 1.2 eV and a small very broad peak at 5.6 eV, with a decrease in size and sharpness of the copper *d*-band structure. The induced peaks become narrower when the nitrogen overlayer is annealed into a $c(2\times 2)$ structure, but they do not shift in energy. The *d*-band structure also sharpens considerably upon formation of the $c(2\times 2)$ overlayer from a disordered nitrogen overlayer. Thus, when a more uniform surface layer is established, the increased definition of the final state energy bands sharpen the entire UPS.

The most striking difference between the spectra of the ordered and disordered nitrogen is the increase in the 2.15-eV main *d*-band peak upon ordering. This peak is due to a high concentration of electrons 2.15 eV below the Fermi level and is prominent on spectra made with radiation of 16.8, 21.2, 26.9 and 40.8 eV.

Compared to the clean Cu(100) UPS spectrum, both spectra show a sizable reduction in intensity in the range from 2.0 to 5 eV, which is associated with the *d* band, and in the two peaks at 2.15 and 4.6 eV. The amplitude and energy position of these adsorbate-induced peaks are independent of the angle of the emitted electrons, whereas the amplitude of the *d*-band structure between 3 and 4 eV is dependent upon angle for both clean and nitrogen-covered copper. The amplitude but not the energy of the copper *d*-band peak at 2.15 eV decreases when the surface is either covered with nitrogen or tilted away from the normal.

Note the similarities between the He I spectra of N, O, and S overlayers. All three adsorbate layers induce levels at around 1.3-eV binding energy with smaller broad levels peaking between 5 and 6.5 eV, besides somewhat attenuating the *d*-band structure. N and O, in particular, are adsorbed in the $c(2\times 2)$ geometry and induce nearly identical changes in the He I UPS. The nitrogen overlayer can be annealed at a higher temperature without desorbing; this may account for the enhanced sharpness of its *d*-band peak at 2.15 eV.

Figure 2 compares the He II spectra of adsorbate-covered-Cu surfaces with clean copper. The additional structure at around 1.3 eV binding energy is readily observable on all the uv spectra for adsorbate covered surfaces. The N- and O-covered surfaces show definite peaks near 6-eV binding energy while the *S* covered surface shows some additional emission in the same energy region. On each of these adsorbate covered surfaces, the Cu *d*-band features are broadened compared to clean Cu.

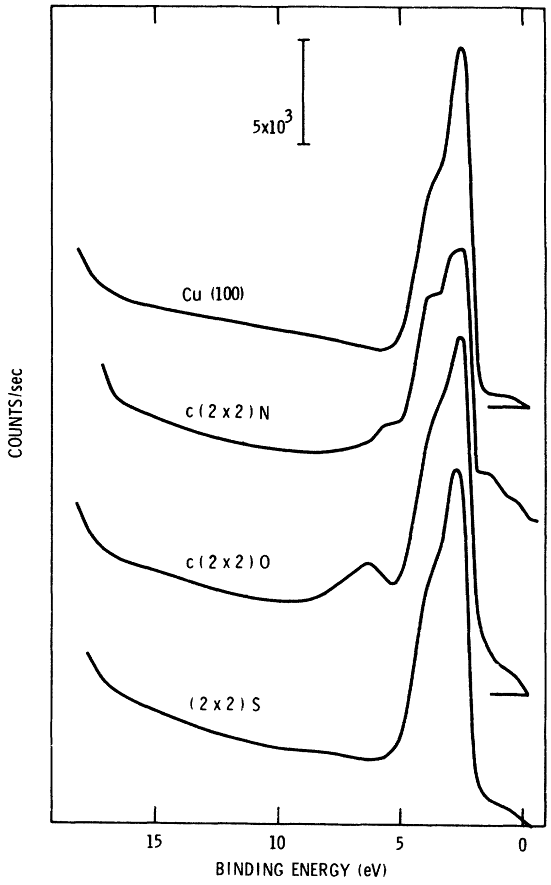

FIG. 2. He II photoemission spectra ($h\nu = 40.8$ eV) for various Cu(100) surfaces. Binding energies are referred to the Fermi level.

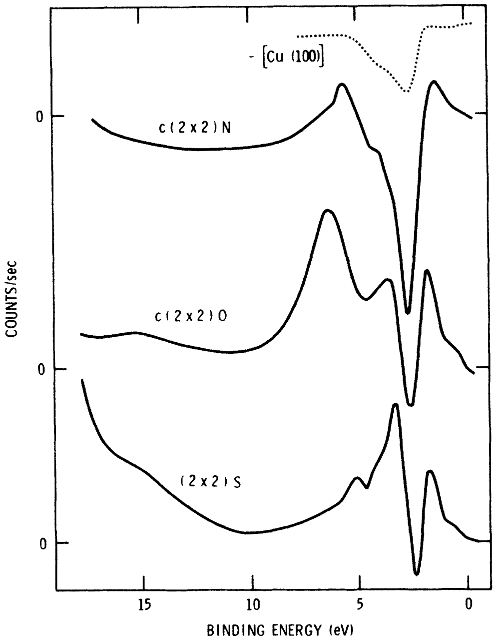

FIG. 3. He II difference curves for adsorbate covered Cu(100). Dashed line is $-\frac{1}{5}$ times the UPS of clean Cu(100).

TABLE I. Electronic binding energies in Cu(100) absorbates.

Surface	Level	Measured by	Binding energies (eV)[a] This work	Previous measurements
N $c(2\times2)$	I	UPS	1.2	
	II	UPS	5.6	
	1s	XPS	396.3	
O $c(2\times2)$	I	UPS	1.4	(~1.4)
	II	UPS	6.2	(~6.0)
	1s	XPS	529.8	(530.5)
$c(2\times4)$	I	UPS	1.4	
	II	UPS	6.2	
	1s	XPS	529.6	
S (2×2)	I	UPS	1.3	
	II	UPS	5.1	
	2p	XPS	161.2	

[a] Binding energies measured relative to the Fermi energy. The parentheses denote "monolayer" oxygen coverage on polycrystalline Cu (Ref. 14).

In order to clarify these adsorbate-induced changes, Fig. 3 presents point-by-point difference curves for the adsorbate-covered Cu spectra minus the clean-Cu spectra. Each of these difference curves shows structure above the *d* band around 1.3 eV, structure below the *d* band between 5 and 6.5 eV, and structure within the *d* band. The dashed line in Fig. 3 is an inverted spectrum of clean Cu which has been reduced by a factor of five. Note how the difference curve for each adsorbate within the 2- to 5-eV binding energy region resembles this inverted Cu curve. This is a manifestation of the attenuation and decreased sharpness of the adsorbate-covered surface's *d*-band peak noted above.

The positions of the adsorbate-induced levels are determined from these difference spectra and recorded in Table I. The positions of the levels around 1.3 eV are determined from the centroid of the composite peak because a slight shift of the upper *d*-band edge would unduly affect each of the peak positions. The other levels were positioned at the peaks in the difference curves.

Table II contains values for the work functions of each of the above surfaces. These values were determined from the widths of the photoemission energy distribution curves.

The nitrogen 1s XPS spectrum of a nitrogen-covered Cu(100) surface is shown in Fig. 4. No change in the region between the Fermi level and 50 eV below the Fermi level due to nitrogen adsorption was observed. Only small changes in the deeper copper levels were seen. The full width at half-maximum of the N 1s peak is about 1.3 eV, a value near the 1.1-eV composite width of the Mg $K\alpha$ peak (0.7 eV) and the operating resolution of spectrometer (0.8 eV). Thus, we observe no complex structure to this peak.

Similarly simple structures are observed for the 1s peak for $c(2\times2)$ and (2×4) oxygen. The 2p sulfur peak in the sulfur $p(2\times2)$ adlayer has a somewhat greater full width at half-maximum of 2 eV, possibly as a result of the spin-orbit splitting of the 2p level. The adsorbate core-binding energies are tabulated in Table I.

Figure 5 shows first-derivative $dN(E)/dE$ Auger electron spectra for the KLL transitions of N and O in the $c(2\times2)$ configuration and the $L_{2,3}MM$ transitions for $p(2\times2)$ S on Cu(100). The energy

TABLE II. Work functions of Cu(100) surfaces.

Surface	ϕ (eV)	Previous values (eV)
Cu(100)	4.77±0.05	4.65[a]
Cu–$p(2\times2)$ S	5.05	
Cu–disordered N	4.75	
Cu–$c(2\times2)$ N	4.59	
Cu–$c(2\times2)$ O	4.83	

[a] Polycrystalline Cu (Ref. 19).

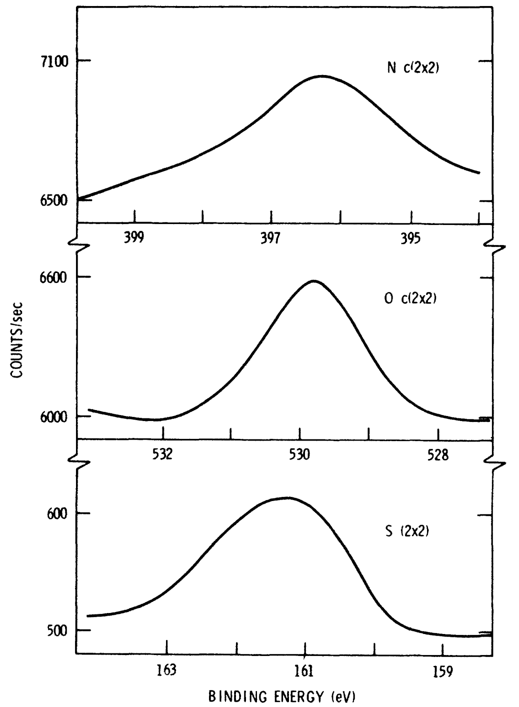

FIG. 4. X-ray photoemission spectra ($\hbar\nu = 1253.6$ eV) showing core levels of adsorbates on Cu(100).

scale in Fig. 5 is with respect to $E(k)$, the measured binding energy of the initial hole in the Auger process. The two *KLL* Auger spectra measured, those of oxygen and nitrogen, obviously do not satisfy the peak assignments for these elements in the atomic state, as given by Siegbahn.[10] For elements of very low atomic number where pure *LS* coupling predominates, a five-peaked Auger spectrum should be observed. (Note, however, that the electronic structure of the two hole final state of these *s-p* atoms does not have a rare-gas-like configuration, as required for Siegbahn's calculation.) The nitrogen experimental spectrum exhibits an eight-peaked structure, the oxygen shows seven peaks (including one around −50 V, visible in Fig. 6), and S shows a five-peaked structure.

DISCUSSION

Several previous UPS investigations of oxygen on copper have been made on evaporated films. Whereas, in the present work, we observe oxygen levels at binding energies lower and higher than the Cu *d* band, Nilsson and Lindau[11] observed only the peak at higher binding energy. Wagner and Spicer,[12] working with a maximum photon energy of 11.8 eV, indirectly observed both peaks. Recently, Yu *et al.*[13] have observed levels induced by oxygen above and below the Cu *d* bands which closely resemble ours. A more complete picture of the oxidation of polycrystalline Cu has been presented by Evans.[14] He observed oxygen-induced states above and below the *d* band, and made measurements of the 1*s* level of O in bulk CuO, CuO_2, and oxygen covered Cu. The emphasis of Evans' work is on relating the photoelectron spectra for oxidized Cu surfaces with spectra for bulk oxides. He concluded that the initial oxide layer resembles the monovalent bulk oxide Cu_2O. There are no other published photoemission studies of nitrogen or sulfur layers on copper.

Our data have shown remarkable similarities in the UPS results for these three adsorbate-covered surfaces. Each adsorbate bonds on copper by inducing filled electronic levels with energies smaller than *and* larger than the *d*-band energies. The picture of adsorbate electronic orbitals moving to decreasing binding energy due to adsorption (relaxation and binding energy shift) is by now well established.[1] The splitting of the N and O 2*p* orbitals into states above and below the

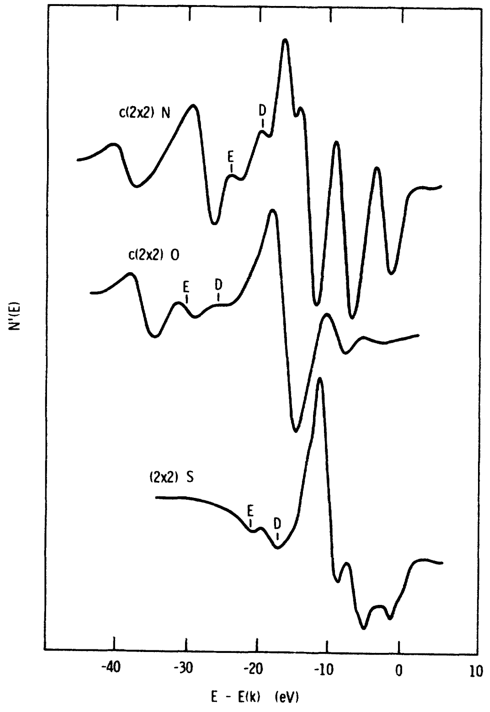

FIG. 5. First derivative Auger spectra $N'(E)$ for N, O, and S adsorbed on Cu(100). E is the energy of the emitted electron relative to the Fermi energy and $E(k)$ is the binding energy of the exciting core level. Marks show some calculated peak positions from Eq. (1), with $F-R=0$. They should line up with points of inflection of the $N'(E)$ curve.

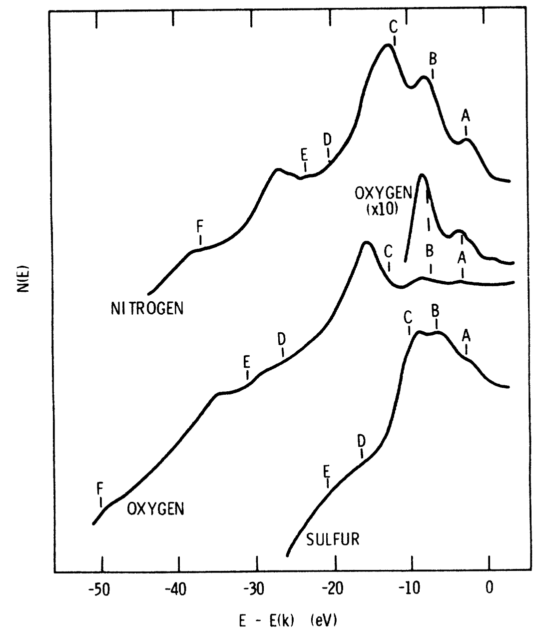

FIG. 6. $N(E)$ Auger spectra for N, O, and S adsorbed on Cu(100). E is the energy of the emitted electron relative to the Fermi energy and $E(k)$ is the binding energy of the exciting core level. Marks show calculated Auger peak positions from Eq. (1), with $F-R=0$.

densely occupied d bands resembles the formation of "bonding" and "antibonding" orbitals during the formation of diatomic molecules.[15]

In the case of the Cu surface, the "antibonding" orbitals are repelled only to the top of the d band, still considerably below the Fermi level. Therefore, the antibonding orbitals associated with these adsorbates on Cu are occupied. If this type of bonding occurred in metals with a high density of d states at the Fermi level, such an antibonding state would be above the Fermi level and would be unoccupied. This state will not be observable with UPS, but could in principle be observed by electron-energy-loss spectroscopy, partial-yield UPS, or appearance-potential spectroscopy. Indeed, Andersson and Nyberg,[16] in a recent appearance-potential study of the $3d$ transition metals have found consistent evidence that adsorbed layers of C, N, O, or S enhance the local density of unfilled-valence band states on the adatoms immediately above the Fermi level.

The photoemission data has now yielded an explicit picture of the adsorbate valence-band electronic level scheme, with XPS giving direct measurements of the $1s$ binding energies of N and O adsorbates and $2p$ binding energy for adsorbed sulfur. Unfortunately, the $2s$ electrons of N and O and the $3s$ electrons of S have too large a binding energy to be observed by us with UPS and too small a cross section to be observed with XPS using Mg $K\alpha$ radiation. These binding energies (Table III) may be approximated by the calculation of Hermann and Skillman[17] and are referenced to the Fermi level by subtracting the relevant work functions from Table II.[18]

If a k hole of binding energy $E(k)$ is filled by an Auger interaction between electrons in the j and l states, a (kjl) Auger process has occurred and the energy of the ejected electron may be designated as $E(kjl)$. The kinetic energy of the Auger electron is given by[8]

$$E(kjl)=E(k)-E(j)-E(l)-(F_{jl}-R_{jl}) , \qquad (1)$$

where F_{jl} is the hole-hole repulsion energy in the final state and R_{jl} is the excess relaxation energy which screens the two-hole final state. Multiplet configurations of the two-hole final state may further alter the energy of the Auger electron if the holes's momenta are sufficiently well correlated. In the case where the final hole states are not well localized, both F_{jl} and R_{jl} will be small.

These experimental Auger peak positions, tabulated as $E(k)-E(kjl)$, are listed in Table IV, column 4. Values of $E(j)+E(l)$ from all relevant adsorbate energy levels of Tables I and III are listed in column 5. The values of this sum are indicated by the tic marks in Fig. 6; they are identified by the letters listed in column 3. Because the D and E transitions are relatively small in the integrated spectra of Fig. 6, they are indicated in Fig. 5 also. Peaks in Auger current should be visible as the points of inflection in Fig. 5 where the $N'(E)$ curve has a negative tangent. It is easy in most cases to make an unambiguous assignment to the Auger process; these assignments are listed in column 2.

Considering the breadths of the peaks involved, the uniformity observed in the $F-R$ values derived from such a simple model is remarkable. The UPS peaks can be measured to about ±0.1 eV, the XPS to about ±0.2 eV, and the Auger peaks to about ±0.4 eV. Thus, the expected error in calculated $F-R$ values is about ±0.8 eV, a value not far below the 1.06 eV standard deviation actually

TABLE III. Herman-Skillman orbital energies with respect to E_F.

Element	Level	Binding energy (eV)
Nitrogen	$2s$	18.5
Oxygen	$2s$	24.3
Sulfur	$3s$	15.8

TABLE IV. Analysis of Auger spectra for N-, O-, and S-covered Cu.

Surface	Auger process	Label	Experimental value of $E(k)-E(kjl)$ (eV)	Values of $E(j)+E(l)$ (eV)	$F-R$
$c(2\times 2)$ N	K I I	A	2.6	2.4	0.2
	K I II	B	8.2	6.8	1.4
	K II II	C	12.7	11.2	1.5
		C'	15.5		
	KL_1 I	D	19.7	19.7	0
	KL_1 II	E	23.7	24.1	-0.4
		E'	27.9		
	KL_1L_1	F	39.0	37.0	2.0
$c(2\times 2)$ O	K I I	A	3.5	2.8	0.7
	K I II	B	8.3	7.6	0.7
	K II II	C	15.4	12.4	3.0
	KL_1 I	D	25.0	25.7	-0.7
	KL_1 II	E	30.2	30.5	-0.3
		E''	36.6		
	KL_1L_1	F	50.3	48.6	1.7
(2×2) S	$L_{2,3}$ I I	A	2.0	2.6	-0.6
	$L_{2,3}$ I II	B	6.7	6.4	0.3
	$L_{2,3}$ II II	C	9.4	10.2	-0.8
	$L_{2,3}M_1$ I	D	18.0	17.1	0.9
	$L_{2,3}M_1$ II	E	21.2	20.9	0.3
	$L_{2,3}M_1M_1$	F	not seen	31.6	

observed for the Auger peaks which can be identified. The uniformly small values observed imply that either the final-state holes do not strongly interact, or that the interaction energy is equal to the extra-atomic screening.

Recently, the Auger spectra of oxidized magnesium and sodium have been interpreted with good agreement to experiment under the assumption that $F-R$ is small.[20,21] This approximation may be justified because Na and Mg (and apparently, a thin oxide of either) sufficiently resemble a free electron metal so that final state effects are small. The final-state holes are not well localized enough for either hole-hole repulsion or dynamic polarization of the conduction electrons around the double hole state to be significant. In addition, the assumption that $F-R$ is small has been implicitly used in the identification of dissociative or nondissociative bonding of gases on metals[22] and in a recent calculation of the oxygen $KL_{2,3}L_{2,3}$ Auger line shape.[23]

The agreement of the N and O KL_1 I or II peaks and the $L_{2,3}M_I$ I and II peaks with the model is really excellent. These peaks are uniformly smaller than the peaks which involve two adsorbate levels. The largest $F-R$ value, probably representing a deviation from the simple model, is found in the oxygen K II II peak. As a matter of fact, close examination of each of the II II peaks in Fig. 5 indicates that this peak is composite in all three cases. The S and O peaks have a low-energy shoulder while the N subpeak is more clearly defined and is labeled C' in the table. The reason for this complexity could be related to the width of the II level on all the UPS's. Matrix effects applied to such a diffuse level could easily maximize different energy regions in the ultraviolet and Auger spectra.

The highest-energy Auger peak position is sensitive to the Cu surface coverage. For instance, as more nitrogen is adsorbed on the $c(2\times 2)$ surface the K I I Auger peak rises about 1.2 eV, bringing the $F-R$ values for these three adsorbate-induced Auger peaks into excellent agreement.

Almost all the features of these Auger spectra have been explained without invoking hole-hole correlation of momenta in the final state intense enough to yield multiplet effects. The model has already assigned all combinations of two hole final states, yet the peaks E' in nitrogen and E'' in oxygen are unexplained. The L_1L_1 final states, by virtue of their largest binding energies will be the ones most likely to have multiplet structure. However, no excited states of the N^{++} ion with $2p^2$ configuration exist which have the proper energy spacing to be consistent with peak E'. The situation for O^{++} is similar. Thus, there is no evidence of multiplet structure even for the KL_1L_1 Auger peaks. The absence of the $L_{2,3}M_1M_1$ sulfur peak predicted by our model could be assigned to a small matrix element yielding a small peak in a position too close to the 105 eV Cu *MNN* peak for reasonable measurement.

Complete justification for our model must, of course, await exact calculations for these relaxation and hole-hole repulsion effects, as well as the appropriate transition matrix elements.

It is appropriate to compare our explanation for these adsorbate Auger spectra with the work of Salmerón *et al.*[6] They attempt to explain the (K I I) Auger peak in N and O covered and the ($L_{2,3}$ I I) peak in S covered Cu(100) on the basis of "interatomic" transitions involving the Cu d band. In other cases where such "interatomic" transitions are observed, they are much smaller than the direct "intra-atomic" transitions. The reason for this may be seen by considering the form of a typical Auger matrix element

$$|\langle \phi_f \psi_c | e^2/r | \psi_1 \psi_2 \rangle|^2 ,$$

where ψ_1 and ψ_2 are the wave functions of the valence band electrons, ψ_c is the wave function of the core electron, and ϕ_f is the wave function of the ejected electron. The highly localized function ψ_c insures that only the local density of states on the adatom is important in the Auger process. Thus, it does not seem likely that the largest peaks in the Auger spectra of adsorbates having filled electronic states in the valence band would be due to such interatomic transitions.

Our work shows that it is not surprising that a relationship (derived by Salmeron *et al.*[6] exists between the Auger energy and the position of the d-band peak. This relationship arises because the binding level of the adsorbate peak labeled I lies between the d-band peak and the Fermi energy.

CONCLUSIONS

We have shown that for N, O, and S adsorbed on Cu(100), electronic levels of the adsorbate are induced above and below the d band of Cu. These levels occur at about 1.3-eV binding energy and from 5.1- to 6.2-eV binding energy, respectively.

The splitting of the adsorbate orbitals into states above and below the densely occupied d bands resembles the formation of bonding and antibonding orbitals and may be a general feature of adsorbate-metal bonding.

Core level energies of these adsorbed gas layers were measured with XPS. Using the above data, we have calculated, in the approximation that final-state effects are small, the peak positions of the Auger spectra of these three adsorbate atoms. These peak positions agree well with experiment. This model of intra-atomic Auger processes explains all of the features in the valence band portion of the adsorbate Auger spectra, in contrast to an interatomic model which could not explain two of the three prominent features.

The observation of high-energy peaks in the Auger electron spectrum which can be correlated with adsorbate-induced electronic states observed with UPS is a first. This analysis verifies that these bonding electrons have a sizable local density of states near the adsorbate core.

ACKNOWLEDGMENTS

The skillful technical assistance of D. W. Gorkiewicz and R. B. Hall was valuable in this investigation.

---

[1] See, for example, D. E. Eastman and M. I. Nathan, Phys. Today 28, No. 4, 44 (1975); and references cited therein.

[2] J. M. Burkstrand, G. G. Kleiman, G. G. Tibbetts, and J. C. Tracy, J. Vac. Sci. Technol. 13, 291 (1976).

[3] G. G. Tibbetts and J. M. Burkstrand (unpublished).

[4] D. R. Lloyd, C. M. Quinn, and N. V. Richardson, J. Phys. C 8, L371 (1975).

[5] L. Ilver and P. O. Nilsson, Solid State Commun. 18, 677 (1976).

[6] M. Salmerón, A. M. Baró, and J. M. Rojo, Phys. Rev. B 13, 4348 (1976).

[7] P. W. Palmberg, J. Vac. Sci. Technol. 12, 378 (1975).

[8] S. P. Kowalczyk, L. Ley, F. R. McFeely, R. A. Pollack, and D. A. Shirley, Phys. Rev. B 9, 381 (1974).

[9] K. S. Kim, S. W. Gaarenstroom, and N. Winograd, Chem. Phys. Lett. 41, 503 (1976).

[10] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, *ESCA-Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy* (Nova Acta Regiae Societatis Scientarum, Uppsala, Sweden, 1967), Ser. IV, Vol. 20.

[11] P. O. Nilsson and I. Lindau, *Band Structure and Spectroscopy of Metals and Alloys*, edited by D. J. Fabian and L. M. Watson (Academic, New York, 1973).

[12] L. F. Wagner and W. E. Spicer, Surf. Sci. 46, 301 (1974).

[13] K. Y. Yu, W. E. Spicer, I. Lindau, P. Pianetta, and S. F. Lin, Surf. Sci. 57, 157 (1976).

[14] Stephan Evans, Faraday Trans. II, Chem. Phys. 71, 1044 (1975).

[15] F. L. Pilar, *Elementary Quantum Chemistry* (McGraw-Hill, New York, 1968), p. 460.

[16] S. Andersson and C. Nyberg, Surf. Sci. 52, 489 (1975).

[17] F. Herman and S. Skillman, *Atomic Structure Cal-*

culations (Prentice-Hall, Englewood Cliffs, N.J., 1963).

[18] Orbital energies should, in principle, be reduced by a relaxation-energy term before identifying them as binding energies. However, available measured binding energies agree well with values from Table II. For example, an O 2*s* binding energy of 24.2 eV has been measured by P. H. Citrin, J. E. Rowe, and S. B. Christman [Phys. Rev. B 14, 2642 (1976)], and ~24 eV has been measured by Z. A. Weinberg and R. A. Pollack [Appl. Phys. Lett. 27, 254 (1975)].

[19] D. E. Eastman, Phys. Rev. B 2, 1 (1970).

[20] A. P. Janssen, R. C. Schoonmaker, A. Chambers, and M. Prutton, Surf. Sci. 45, 45 (1974).

[21] A. P. Janssen, R. Schoonmaker, J. A. D. Matthew, and A. Chambers, Solid State Commun. 14, 1263 (1974).

[22] J. T. Grant and M. P. Hooker, J. Elect. Spectrosc. 9, 93 (1976); K. Kunimori, T. Kawai, T. Kondow, T. Onishi, and K. Tamaru, Surf. Sci. 54, 525 (1976).

[23] H. Nozoye, Y. Matsumoto, T. Onishi, T. Kondow, and K. Tamaru, J. Phys. C 8, 4131 (1975).