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40.81-eV photoelectron study of Cu, Ag, and Au surfaces

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High-resolution photoelectron spectra from clean surfaces of Cu, Ag, and Au have been obtained using He I and He II radiation. The spectra have been corrected for instrumental transmission efficiency effects and have been deconvoluted to take account of finite instrumental linewidth. It has been established that 40.81-eV spectra do not contain large numbers of inelastically scattered electrons with kinetic energies $\gtrsim$ 20 eV and that the deconvoluted spectra reveal a number of features not previously reported. The present results have been compared with x-ray photoelectron spectroscopic measurements, with lower-energy photoelectron spectroscopic results, and with selected theoretical band-structure determinations. Preliminary data have been obtained relating to the adsorption kinetics of residual vacuum gases as a function of sample temperature in the range 30–300 °C.

I. INTRODUCTION

The study of the conduction-band regions of the noble metals has been of particular importance in the development of photoelectron spectroscopy as a tool for solid-state band-structure determination. Recent interest in these materials may be said to have been stimulated by the pioneering study of copper and silver by Berglund and Spicer,[1] who used photon energies below the LiF cutoff ($\simeq$ 11.6 eV), and by the similar study of gold by Krolikowski and Spicer.[2] That studies at such low photon energies reflect the energy distribution of the joint density of initial and final electron states is now well established.[3,4] Photoelectron studies at x-ray energies (XPS) constitute a probe for the determination of the conduction-band occupied density of states is also well known and the sensitivity of the technique has recently been examined in some detail by Shirley[5] for the conduction band of gold. Shirley compared an XPS spectrum taken with monochromatized x rays with a number of relativistic band-structure calculations and concluded, in particular, that the observed spectrum fitted the relativistic-augmented-plane-wave (RAPW) calculation of Christensen and Seraphin[6] and the Korringa-Kohn-Rostocker (KKR) calculation of Connolly and Johnson[7] equally well and was consequently able to distinguish these two results from other calculated band structures. He found, however, that the XPS result was unable to differentiate between the RAPW and KKR results. A second conclusion reached by Shirley was that matrix-element modulation was a small effect at XPS. Similar high-resolution XPS spectra for the Cu, Ag, and Au have been reported by Hufner *et al*,[8] who suggest that matrix-element modulation is significant, and by Lindau and Wilson[9] who, however, used Mg $K\alpha$ radiation without monochromatization.

Photoelectron spectroscopy using the He^+ resonance line at 40.81 eV (304 Å) has been used with success for the precise determination of binding energies in a number of d-band metals[10] and more recently in similar studies of the alkali halides.[11,12] It has been suggested[13] that the photon energy of 40.81 eV is sufficiently high for the resulting spectra to resemble closely the XPS results and by inference the occupied densities of states, and it is the intention of the present work to investigate this suggestion in detail for the noble metals Cu, Ag, and Au.

In the present work we report high-resolution 40.81-eV ultraviolet photoelectron spectra (UPS) of clean surfaces of Cu, Ag, and Au and compare these spectra with the XPS results, with lower-energy UPS, and with relativistic band calculations where available. These comparisons have been facilitated by correcting the measured spectra for the effects of instrumental transmission efficiency (dependent on photoelectron kinetic energy) and by the use of a deconvolution procedure[14] which accounts for finite instrumental linewidth. The use of a scraping technique[15] has enabled surfaces to be continuously cleaned; the extent to which the surfaces contaminate as a function of time has also been investigated and some preliminary data relating to the adsorption kinetics of residual vacuum gases has been obtained.

II. EXPERIMENTAL METHOD

The electron spectrometer and its associated photon source has been described elsewhere.[16] Briefly, it consists of a 90° sector spherical electrostatic energy analyzer with a resolving power of 50. Photoelectron spectra are accumulated in a multichannel analyzer by holding the analyzer at a fixed pass energy and by varying the accelerating/retarding voltage between sample and analyzer in synchronism with the channel advance clock of the multiscaler. The helium resonance lamp produces useful intensity at 21.22, 40.81, 48.37, and 51.02 eV. and when optimized for 40.81-eV production it is found that the intensity ratio 40.81/21.22 eV is close to 2. Under such conditions, typical detected count rates from the *d* bands of the noble metals were in the vicinity of 20 000 counts/sec.

Since the inelastic scattering mean free path for 20–40-eV electrons in metals is thought to be $\lesssim 10$Å,[17,18] UPS are extremely sensitive to surface contamination and it is essential that the surface under examination be free of adsorbed gases. Nilsson and Lindau[19] have made a comparison of surface preparation techniques including evaporation, ion bombardment, crystal cleaving and mechanical scraping in terms of their relative efficiency in a UPS study of Cu and β-brass. The technique of mechanical scraping was found to give results indistinguishable from those obtained by the other more conventional techniques and has been adopted for the present work. We have described our scraping technique in some detail in a paper on the UPS of Zn and Cd where it was found to be an excellent method of handling reactive surfaces.[15] An integral heater has been added to the sample holder for the present study (Fig. 1) and has permitted the acquisition of spectra at temperatures up to 300 °C. Samples were prepared by melting 99.99% pure material under argon in high-purity graphite crucibles followed by machining to cylindrical form (3-mm in diameter).

The presence of adsorbed gases, or the growth of chemisorbed layers was readily monitored in our spectrometer by the appearance of a broad band of photoelectrons from the adsorbate. This band, which appeared within seconds of halting sample rotation (and thereby scraping cessation) extended from $E_F - 5$ to $E_F - 12$ eV and appears to be predominantly due to photoelectrons from the first band of water vapor[20] which constitutes the main residual gas in our unbaked ($\sim 3\times10^{-7}$ Torr) vacuum system. Somewhat similar results have been reported by Brundle and Roberts[21] using 21-eV radiation.

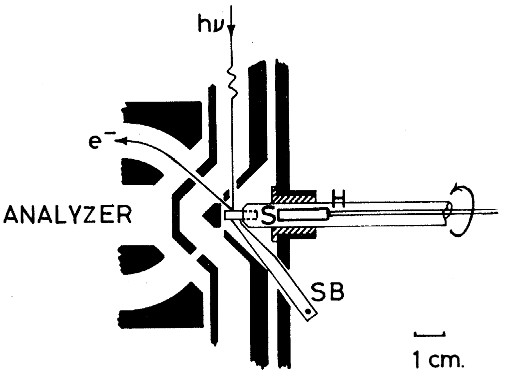

FIG. 1. Schematic diagram of the experimental arrangement providing mechanical scraping of the metal sample S; SB is the spring-loaded tungsten-carbide-tipped scraping blade; H is the sample heater.

III. DATA ANALYSIS PROCEDURES

An electron spectrometer operated in the constant energy mode[16] necessarily distorts an energy distribution in two fundamental ways: (i) by responding with varying transmission efficiency to electrons of initially different kinetic energies and (ii) by broadening intrinsic spectral structure due to its finite resolving power. Transmission efficiency effects may readily be corrected as explained by Kemeny *et al.*,[22] whereas numerical deconvolution procedures are available[14] for extracting the true spectrum from that detected, provided that an accurate description of the instrumental response to a monochromatic electron source is available. The spectra obtained in the present study were normally processed in the following sequence: (a) a Savitzky-Golay least-squares smoothing operation was used to reduce the effect of statistical fluctuations[23]; (b) the effective resolution was enhanced by application of the deconvolution procedure given in Refs. 14 and 15. Instrumental line profiles for this step were obtained by measuring the argon $3p_{1/2,3/2}$ or xenon $5p_{3/2}$ photoelectron lines; (c) the spectra were corrected for transmission efficiency variation using the procedure given in Ref. 22; and (d) the spectra were finally modified to subtract out the component due to inelastically scattered electrons. As may be seen from Fig. 2, for example for gold, correction for transmission effects shows that the 40.81-eV spectra from the noble metals do not in fact contain large numbers of inelastically scattered electrons with energies greater than 20 eV, but rather are characterized by a nearly constant inelastic tail reminiscent of XPS spectra from metals. We have consequently used the iterative procedure given by Shirley,[5] which essentially involves subtracting from each spectral point a contribution which is proportional to the spectral area at all higher (kinetic) energies. (This procedure is equivalent to an assumption that the inelastic-electron-scattering mean free path in the noble metals is relatively constant for kinetic energies in the 20–40-eV range—an assumption which has been verified by means of a Monte Carlo simulation of the photoemission process for 40.81-eV photons. Details of this calculation will be presented elsewhere.)

Following data processing as described above, the spectra were compared with selected band-structure calculations by broadening the density-of-states theoretical histograms with a Lorentzian followed by a least-squares fitting procedure which involved normalizing the broadened density of states to obtain the best possible fit. In each case the UPS was normalized so as to minimized, with respect to ϵ, the quantity

$$\Delta = \sum \frac{(E_i - \epsilon T_i)^2}{n},$$

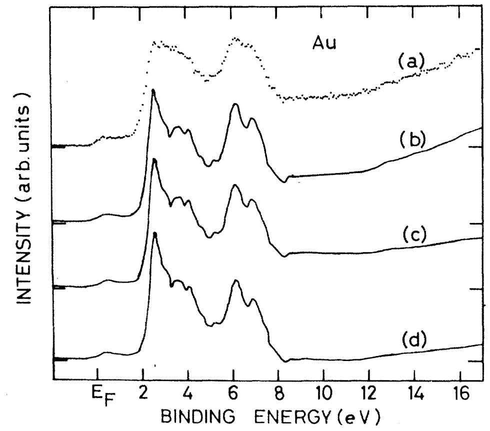

FIG. 2. 40.81-eV photoelectron spectra of clean gold showing data analysis procedures applied; (a) raw data; (b) after deconvolution procedures have been applied to (a) (see text). (c) spectrum of (b) corrected for analyzer transmission efficiency; (d) spectrum of (c) corrected for inelastic scattering (see text).

so that

$$\Delta_{\min}=\left[\sum E_i^2-\left(\sum E_iT_i\right)^2\Big/\sum T_i^2\right]\Big/n,$$

where E_i, T_i represent corresponding UPS and theoretical spectral values, and the summations are performed over n equispaced values. A rigid shift of one spectrum relative to the other along the energy scale was also introduced where necessary to minimize Δ in an attempt to allow for uncertainties in the absolute calibration of either spectrum. The magnitude of such shifts were almost always small (~0.1 eV) except for one particular comparison involving the Cu spectrum which will be discussed in detail below.

IV. RESULTS AND DISCUSSION

In. Figs. 2–4 we present 40.81-eV spectra from clean surfaces of Au, Ag, and Cu, respectively. In each figure, the raw data are displayed as curve (a), the result of smoothing and deconvolution is shown in curve (b), the result of correcting for transmission effects is shown in curve (c), and the result following background subtraction is shown as curve (d).

The curves (c) in Figs. 2–4 all show the almost constant inelastic scattered tail referred to earlier. The virtual absence of any broad contamination peak on this tail in the region from 5 to 12 eV below E_F is an excellent criterion of the cleanliness of the surface.

In Fig. 5(a), a 40.81-eV spectrum from Au which has been corrected for transmission effects and which has been modified to subtract scattered electrons but which has not been deconvoluted is compared with Shirley's XPS result[5] from which the scattered electron contribution had been removed by the procedure referred to above. Agreement between the two spectra is, in general, extremely good in regard to bandwidth and the location in energy of prominent structure but significant differences are also clearly apparent. A sharp Fermi edge is visible in the UPS result, a feature which is usually a good indication of surface cleanliness, and additional structure appears as a minor peak at $E_F-5.2$ eV and as a shoulder at $E_F-6.9$ eV. A more significant feature of the comparison of Fig. 5(a) relates to the different relative heights of the major d-band peaks. In this respect the present UPS result resembles the results published by Freeouf *et al.*,[13] who used photon energies in the 30–90-eV range.

In order to investigate this last point further it is informative to consider a comparison between the deconvoluted UPS result and certain relativistic

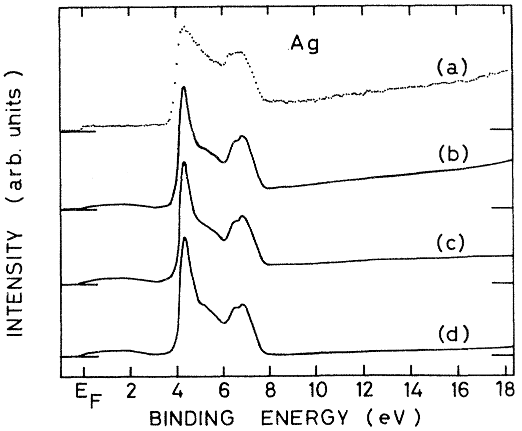

FIG. 3. 40.81-eV photoelectron spectra of clean silver for data analysis procedures as described in Fig. 2.

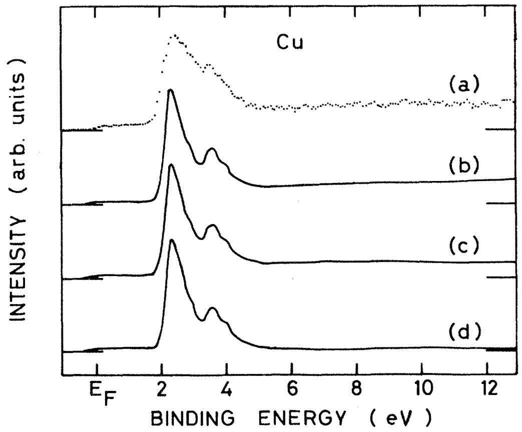

FIG. 4. 40.81-eV photoelectron spectra of clean copper for data analysis procedures as described in Fig. 2.

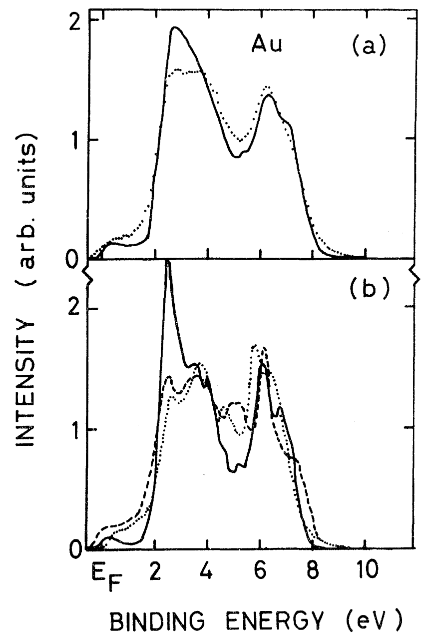

FIG. 5. (a) 40.81-eV photoelectron spectrum of clean gold which has been corrected for analyzer transmission efficiency and inelastic scattering, compared to the *XPS* result (Ref. 5). (b) Deconvoluted spectrum of (a) compared to theoretical density-of-states calculations: dashed line, Ref. 7; dotted line, Ref. 6.

band calculations. On the basis of Shirley's earlier study[5] we have chosen to make this comparison using the procedure outlined in Sec. III, with the published density of states histograms of Christensen and Seraphin[6] and of Connolly and Johnson[7] broadened by means of a Lorentzian of 0.3-eV half-width; Fig. 5(b). It is clear that while there is excellent agreement in terms of the location in energy of both major and minor structures, particularly in the case of the Connolly-Johnson comparison, considerable differences remain in the relative peak intensities, the least tightly bound *d* band and the intermediate peak at $E_F - 5.2$ eV being notable in this respect. Because of the similarity between the calculated density of states curves, obtained by different computational methods, it would appear that the discrepancies evident in Fig. 5(b) result from matrix element modulation effects in the UPS. As will be evident from the following discussion, the photoelectron cross section at a photon energy of 40.81 eV for less tightly bound *d* electrons is systematically higher than that for more tightly bound electrons in the *d* band of all three metals studied.

This feature is clearly apparent in Fig. 6(a) which provides a comparison, similar to that in Fig. 5(a) for gold, between an undeconvoluted UPS of clean silver and an XPS spectrum published by Hufner *et al.*[8] with a quoted resolution of 0.5 eV. The location and width of the *d* band are again in excellent agreement.

As may be seen in Fig. 6(b), the resolution enhancement obtained by applying the deconvolution technique to the UPS of Fig. 6(a), emphasizes the splitting of the *d* band which is less clearly visible in Fig. 6(a). The importance of including relativistic effects in any band calculation of gold has been recognized for some time[5,24] and it would appear from the present result that such effects are also important in the case of silver. We are unaware of any fully relativistic calculation of the band structure of Ag and consequently our comparison in Fig. 6(b) is with the nonrelativistic calculations of Snow,[25] interpolated by Williams and Janak as quoted by Eastman,[4] and with Smith's interpolation[3] of the calculation by Ballinger and Marshall.[26] The latter calculation predicts the location and width of the *d* band with precision but is clearly inadequate because of the noninclusion of spin-orbit interaction. Hufner *et al.*[8] have obtained reasonable agreement with their XPS result by arbitrarily increasing the width of the *d* band calculated by Snow[25] by 16% and subsequently incorporating spin-orbit effects, but a fully relativistic calculation is clearly to be preferred.

We consider that the present 40.81-eV studies of Au and Ag are encouraging insofar as the spectra

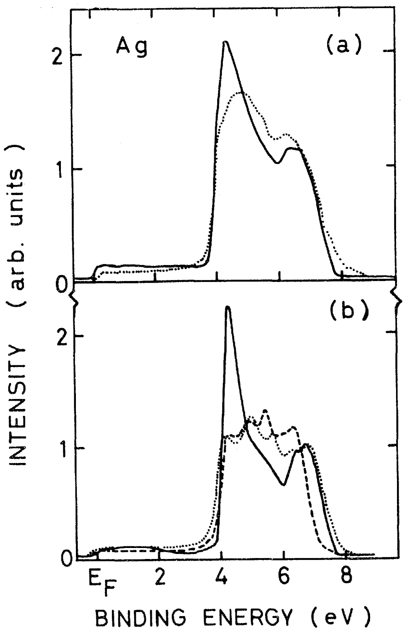

FIG. 6. (a) 40.81-eV photoelectron spectrum of clean silver which has been corrected for analyzer transmission efficiency and inelastic scattering, compared to the XPS result (Ref. 8). (b) Deconvoluted spectrum of (a) compared to density of states calculations: dashed line, Ref. 4; dotted line, Ref. 3.

obtained clearly duplicate the structure (if not the relative amplitude of structure) previously observed using premonochromatized XPS. Indeed the present high energy UPS, after deconvolution, reveals additional detail which we believe reflects previously unresolved structure in the initial density of states. This latter conclusion is supported by the correspondence between the UPS and the band calculation by Connolly and Johnson, in particular.

High-energy UPS from copper have also been obtained but we have found it difficult to correlate these as precisely with either XPS data or available band calculations as was the case with Au, and to a somewhat lesser extent, with Ag. An undeconcoluted 40.81-eV spectrum from clean Cu is compared with the XPS spectrum of Hufner *et al.*[8] in Fig. 7(a). Although the bandwidth of 3.2 eV obtained from the present spectrum agrees closely with earlier determinations which employed lower-energy UPS, it is clearly less than that observed by XPS. Figure 7(b) consists of a comparison between the deconvoluted 40.81-eV spectrum and two somewhat dissimilar band calculations. One such calculation is due to Smith[3] who used the Hodges *et al.*[27] interpolation scheme on the band calculation of Burdick.[28] The second calculation is from Snow's[29] self-consistent-field program which predicts a significantly reduced *d* bandwidth, but in this instance the location of the *d* band had to be shifted by 0.9 eV to bring theory into optimum correspondence with experiment.

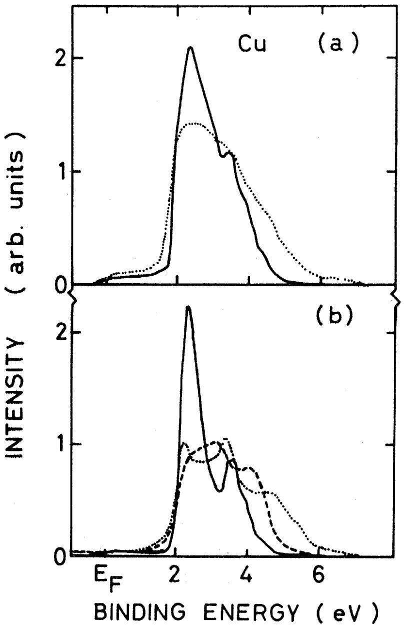

FIG. 7. (a) 40.81-eV photoelectron spectrum of clean copper which has been corrected for analyzer transmission efficiency and inelastic scattering, compared to the XPS result (Ref. 8). (b) Deconvoluted spectrum of (a) compared to density of states calculations: dashed line, Ref. 27; dotted line, Ref. 3.

Since the observed *d* bandwidth in the 40.81-eV spectrum is narrower than either theory or the XPS determination it would appear that an explanation must be found which involves some feature which would not affect the XPS result. Since the UPS technique samples a region nearer the surface than does the XPS technique (the electron scattering mean free path at ~40-eV kinetic energy is approximately $\frac{1}{3}$ of its value at ~1500 eV) the present result may reveal a surface density of states of the type predicted by Haydock *et al.*[30] Similarly, local disordering near the surface may have a narrowing effect on the *d* bandwidth[30] although it is not clear to us why either of these effects should be so much more noticeable in Cu than in either Au or Ag.

We prefer an explanation based on a strong variation of subshell photoionization cross section across the band which leads to a vanishingly small contribution to our spectrum from deep-lying *d* states. This explanation is is consistent with our earlier observation of preferential emission from the $d_{5/2}$ states in Au and Ag compared with emission from the $d_{3/2}$ states, and may well be related to the fact that the final-state wavelength of an electron excited by 40.81-eV radiation from a $d_{3/2}$ state is comparable to that of the initial-state radial wave function with consequent cancellation in the dipole overlap integral.

For completeness we show 21.22-eV UPS from Cu, Ag, and Au in Fig. 8. These spectra are very similar to those reported by Eastman *et al.*[31] for Au and by Lindau and Wallden,[32] and have been corrected for the effects of instrumental transmission efficiency only. We have previously reported[33] that the subshell photoionization cross section (SPC) for *d* electrons does not differ greatly over the photon energy range 21–41 eV; whereas the SPC for *s* or *p* derived states is a strong function of photon energy, reducing by a factor of $\lesssim 0.1$ from 21 to 41 eV. Surface contamination observed during the present work has been tentatively attributed to chemisorbed water molecules (see below) and as such is more clearly visible in 21-eV spectra than in those reported above when 40.81-eV photons were employed. In particular the Cu spectrum of Fig. 8 displays some emission from such contamination at approximately $E_F - 6$ eV. This is consistent with the Eastman *et al.* finding[31] that Cu is more sensitive to vacuum conditions than either Ag or Au. An alternative explanation for the increased contamination sensitivity at $h\nu = 21$ eV requires that the electron-electron scattering length be longer for ~20-eV electrons than for ~40-eV electrons. As there is some indirect evidence that the electron scattering mean free path is nearly constant over this energy

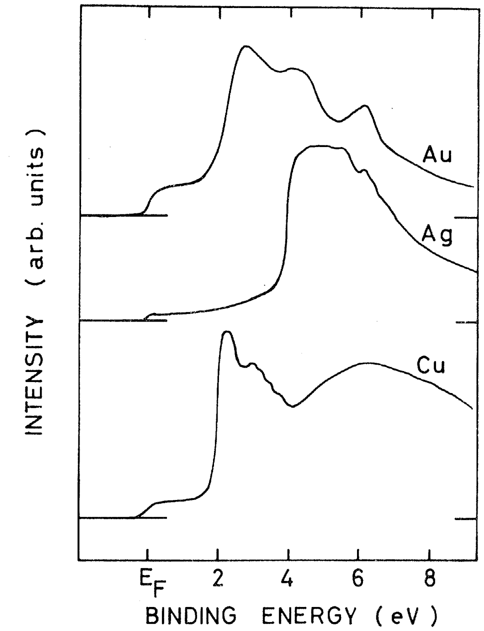

FIG. 8. 21.22-eV photoelectron spectra of clean Cu, Ag, and Au.

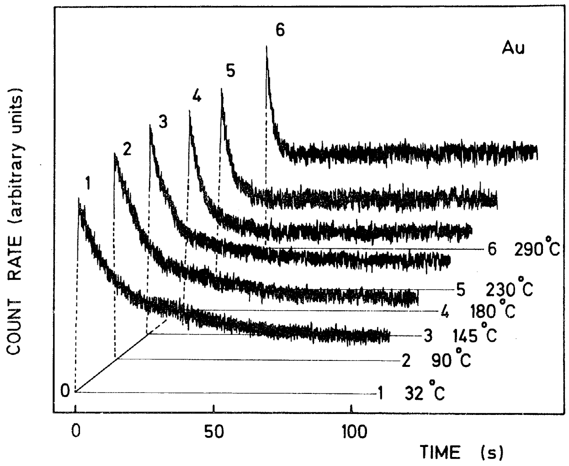

FIG. 9. Rate of adsorbate growth on a clean gold surface illustrated by the decay in intensity of Au $5d_{5/2}$ photoelectrons (energized by 40.81-eV photon) vs time following the cessation of sample cleaning. The decay curves are shown for different gold temperatures.

interval[34] we tend to favor the above explanation based on SPC considerations.

V. SURFACE ADSORPTION KINETICS

We have previously discussed a technique[15] for observing surface adsorption by monitoring the decay in intensity of a photoelectron peak as the surface adsorbs a contaminant. This technique was successfully applied to a study of the adsorption of water vapor on clean surfaces of zinc and cadmium. In the present work, a sample heater was added and curves of the decay in intensity with time of selected d-band peaks were measured for sample temperatures up to 300 °C. Residual gas analysis of the target area revealed water vapor to be the principal component with traces of N_2 or CO detected.

Figure 9 shows the decrease in photoelectron intensity from the more intense d-band of gold ($5d_{5/2}$) as a function of time following the cessation of sample scraping for a number of sample temperatures, the pressure during these measurements being ~ 3 $\times 10^{-7}$ Torr. One significant aspect of the curves is the abrupt change in slope particularly visible at the higher temperatures. We suggest that this change of slope corresponds to the formation of a monolayer of adsorbate since subsequent multilayers cannot readily form at these higher temperatures. The d-band intensity consequently remains essentially constant at temperatures of ~ 300 °C at nearly one-half the initial intensity for up to 30 min. At room temperature, no significant change of slope is observed and the initial rate of decrease is much slower. The final d-band intensity after 160 sec is approximately one-third of the initial intensity and still decreasing. We suggest that there is no distinct monolayer formation at room temperature but rather a gradual build up of adsorbate into multilayers. The initial rate of decrease within the first 10 sec following scraping is observed to be greater for gold at 300 °C than at 30 °C. (See Table I for times to decrease to 75% of initial value.)

The effect of sample temperature or contamination adsorption kinetics of gold is particularly evident in Fig. 10 which shows spectra taken at a variety of times following the cessation of sample scraping. In Fig. 10(a) the rapid deterioration of the characteristic gold spectrum and its replacement by the broad contamination peak centered at $E_F - 6$ eV at room temperature may be contrasted

TABLE I. Values of t, f, and $\langle E_a \rangle$ for Au, Ag, and Cu at 30 and 300 °C for a pressure $\simeq 3 \times 10^{-7}$ Torr, where t is the time taken in sec for the d-band photoelectron intensity to decrease to 75% of its initial value after the production of a clean surface, and f is the intensity of the d-band photoelectrons 90 sec after the production of a clean surface, expressed as a fraction of the initial value. $\langle E_a \rangle$ is the mean activation energy for initial chemisorption of water vapor.

	t (sec)		f		$\langle E_a \rangle$ (eV)	
Metal	30 °C	300 °C	30 °C	300 °C	30 °C	300 °C
Gold	9	2	0.3	0.5	0.04	0.006
Silver	13	7	0.4	0.45	0.04	0.05
Copper	7	5	0.4	0.5	0.04	0.04

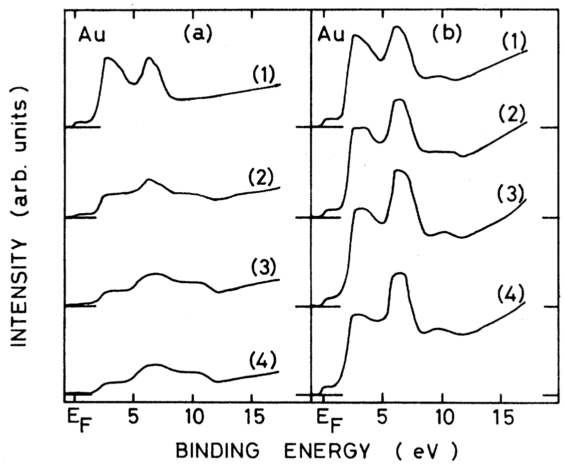

FIG. 10. Effect of adsorbate contamination on the photoelectron spectrum of clean gold at temperatures of (a) 30 °C and (b) 300 °C. Spectrum (1) taken within 1 sec of sample cleaning; spectrum (2) taken 90 sec following sample cleaning. Spectra (3) and (4) taken, respectively, at 7 and 20 min following sample cleaning. At 30 °C, the adsorbate contamination peak centered at a binding energy of 6 eV grows rapidly; at 300 °C the adsorbate is evident 1 sec following sample cleaning but remains relatively constant with little deterioration of the Au photoelectron spectrum.

with the relatively uncontaminated spectra obtained from gold at ~ 300 °C, even after some minutes delay. If we accept the conclusion reached above that a monolayer of adsorbed water vapor is formed in ~10 sec, spectrum 2 of Fig. 10(b) represents the result to be expected from gold with a monolayer of adsorbed water vapor and consequently exemplifies the extreme sensitivity of the UPS technique for surface studies.[35–37]

Similar data were recorded for the contamination of copper and silver surfaces but in neither case was evidence obtained which might be construed as indicating a limited adsorption process such as that proposed above for gold at 300 °C. Relevant parameters are given in the table which also includes calculated mean activation energies derived on the basis of the model previously used for zinc and cadmium.[15]

VI. CONCLUSION

40.81-eV photoelectron spectra of Au, Ag, and Cu have been found to agree closely with previously published monochromatized XPS spectra. Comparisons of the present UPS results with theoretical density-of-states calculations have been presented which show good over-all agreement with respect to *d* bandwidth and position relative to Fermi energy for Au and Ag but which reveal rather poorer agreement for Cu. Deconvolution procedures have revealed previously unresolved fine structure which coincides with structure in the density of states calculation for Au as given by Christensen and Seraphin.[6] The variation in intensity of photoelectrons from points wihtin the *d* band of each metal does not mirror the variation as predicted theoretically. This being most probably due to matrix element modulation across the band. This effect is clearly seen to be more prominent at a photon energy of 40.81 eV than has been reported at XPS energies.[5,8]

An *in situ* scraping technique has been used to demonstrate a novel way of determining data on adsorption kinetics at different sample temperatures, as evidenced by the preliminary data presented here.

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