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X-RAY PHOTOEMISSION STUDIES OF THIN GOLD FILMS

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The *d*-band and the core-level spectra of gold deposited on aluminium and sapphire were investigated utilizing X-ray photoelectron spectroscopy (XPS). For thin deposits of gold, the *d*-band splitting was observed to be narrowed significantly with respect to that of bulk gold. The narrowing effect is attributed to the high surface to bulk ratio of the gold deposits. A shift of Au 4*f* core levels also occurs in correlation with the *d*-band effect.

1. INTRODUCTION

THE ELECTRONIC structures of different forms of gold, including pure solid, liquid, and alloyed phases, have been studied extensively using photoemission techniques.[1–4] The 5*d* portion of the valence band, which exhibits two distinctive peaks in the case of bulk gold, is of particular interest. The splitting is commonly attributed to the spin–orbit coupling effect.[1] Similar splitting was observed on liquid as well as solid gold.[2] This observation indicates that the lattice periodicity is not critical in determining the two-peak structure.

Recent theoretical studies of transition and noble metals predict that in samples of thin films (free standing or on simple metal substrate) of 10 atomic layers or less ($t \lesssim 30$ Å),[5,6] or in samples of small (10 ~ 50 Å) clusters,[7] dimensional effects on the electronic structure are expected. On the experimental side, certain inconsistencies have been encountered in using very thin gold films ($t \lesssim 20$ Å) on insulators as a calibration technique (gold "dressing" technique) in X-ray photoemission spectroscopy (XPS) work.[8] The inconsistencies are known to be associated with differences in thickness of the gold deposited. Angular dependent XPS studies, however, reveal that Au surface atoms on *bulk* gold samples do not exhibit a photoelectron spectrum (valence band or core levels) different from that of a bulk gold sample.

In this communication, we report the results of our observation of the XPS Au (4*f*) level and valence band spectra of thin ($t \lesssim 30$ Å) gold films and small clusters (dia. $\lesssim 30$ Å) of gold on various substrates. We have observed the systematic changes in the valence band and core-level spectra that occur when the thickness of the sample is increased in a smooth fashion by continuous vapor deposition.

2. EXPERIMENT

The substrates upon which gold was vapor deposited were chosen such that the interaction between the 5*d* electrons of gold and the substrate would be simple (gold on Al)[5] or eliminated (gold on Al_2O_3). The vapor deposition of Au onto sapphire (Al_2O_3) is well characterized.[9] Al_2O_3 is thermodynamically inert and does not react with gold under our experimental conditions. Gold also does not wet Al_2O_3, so that the gold deposited on Al_2O_3 forms islands instead of a uniform film.

The Al case is more complicated. Gold alloys with clean aluminum even at room temperature. However, our study shows that only the $AuAl_2$ phase grows at room temperature. A thin Au film can then be deposited on top of $AuAl_2$ without forming new Au–Al phases. Details of the phase formation will be discussed in the following section.

The experiments were carried out in an AEI ES200B photoelectron spectrometer using unfiltered Mg(K_α) radiation. Vapor deposition was accomplished at pressure ~ 1×10^{-9} torr onto sputter-cleaned substrates at a rate of about 6 Å/min., using a tungsten filament pre-wetted with pure gold. The pre-cleaning and pre-wetting of the tungsten filament was performed inside the spectrometer chamber to prevent possible contamination. The temperature rise of the substrate surface during deposition was estimated to be less than 10°C. Substrate core-level intensities (I) were monitored during the Au deposition to control sample thickness, using $I = I_0 \exp(-t/\lambda)$ with $\lambda = 20$ Å for 1.2 KeV photoelectrons.[10]

3. RESULTS

Figures 1 and 2 show the XPS valence bands and core electron levels, respectively, of gold deposited on pure aluminum. On both figures, spectrum (a) was taken on sputter cleaned aluminum (intensity ratio of O(1*s*)/Al(2*p*) ~ 0.06). This small oxygen contamination

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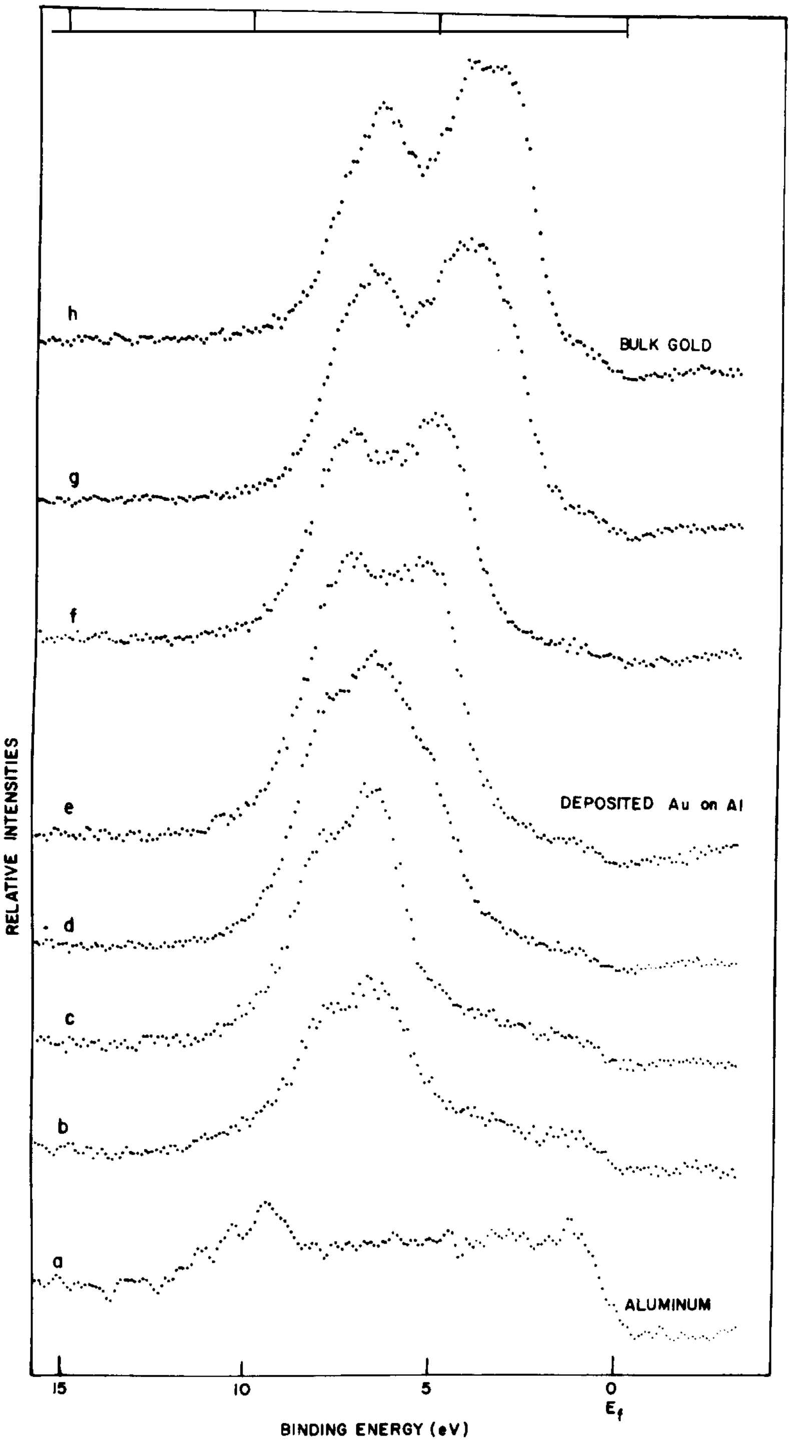

Fig. 1. Changes of the XPS valence band spectra of gold with the amount of Au deposited on aluminum.

is not critical for the discussion of this paper. Spectrum (h) was taken on bulk gold. Spectra (b) to (g) were taken at different stages of gold deposition. The effective thickness of the gold deposited at each stage is approximately 25 ± 5 Å.

For the first stage of deposition, the *d*-band of gold has two peaks at about 6.3 and 7.5 eV [Figs 1 (b) and (c)]. The 4*f* core levels of gold are also shifted toward higher binding energy side by about 1.5 eV from those of bulk gold [Figs. 2(b) and (c)]. Similar *d*-band structure[3] and core level shift were previously reported on bulk $AuAl_2$. The observed spectra (b) and (c) of Figs. 1 and 2 correspond to the formation of $AuAl_2$.

As the deposition of gold increases beyond the stage

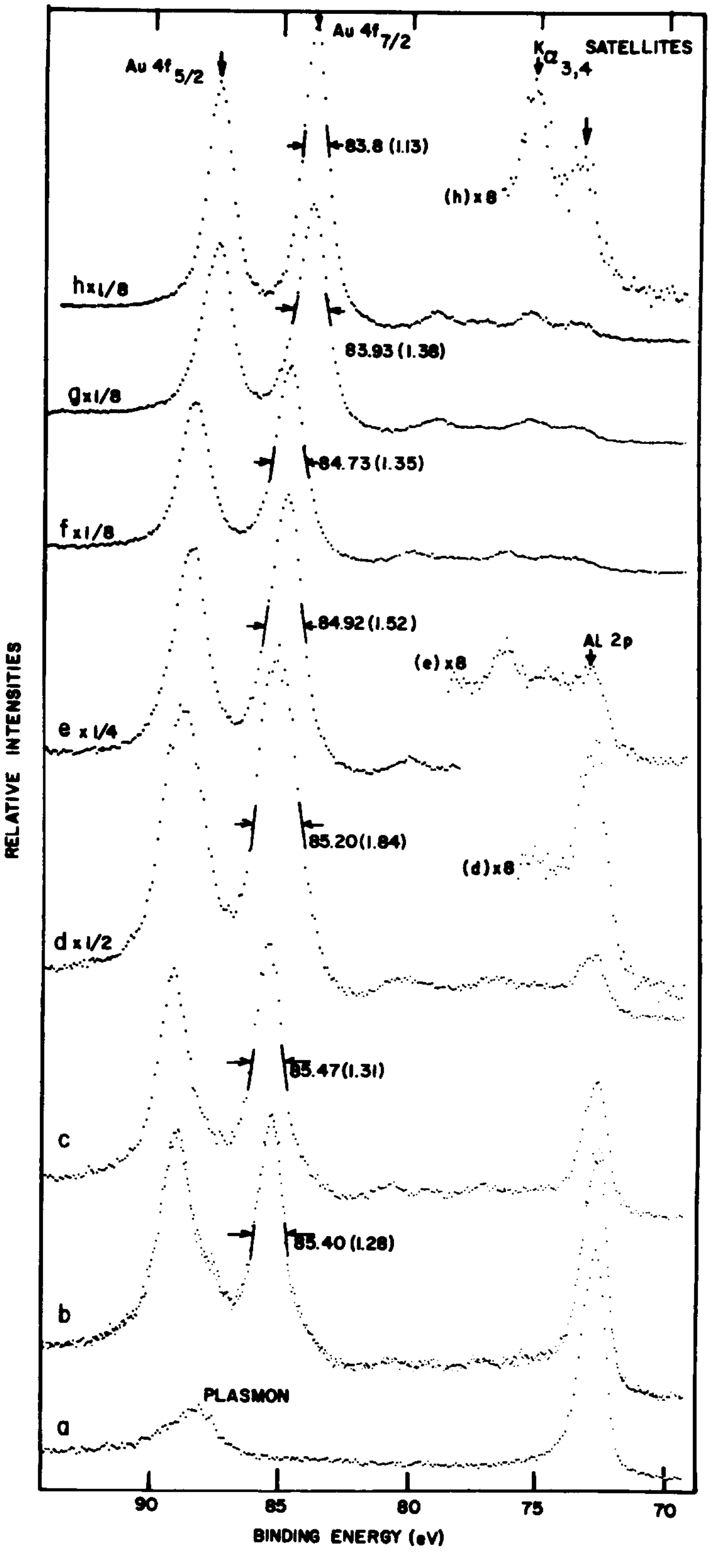

Fig. 2. Changes of the XPS spectra of Au 4*f* and Al 2*p* levels with the amount of Au deposited on aluminum.

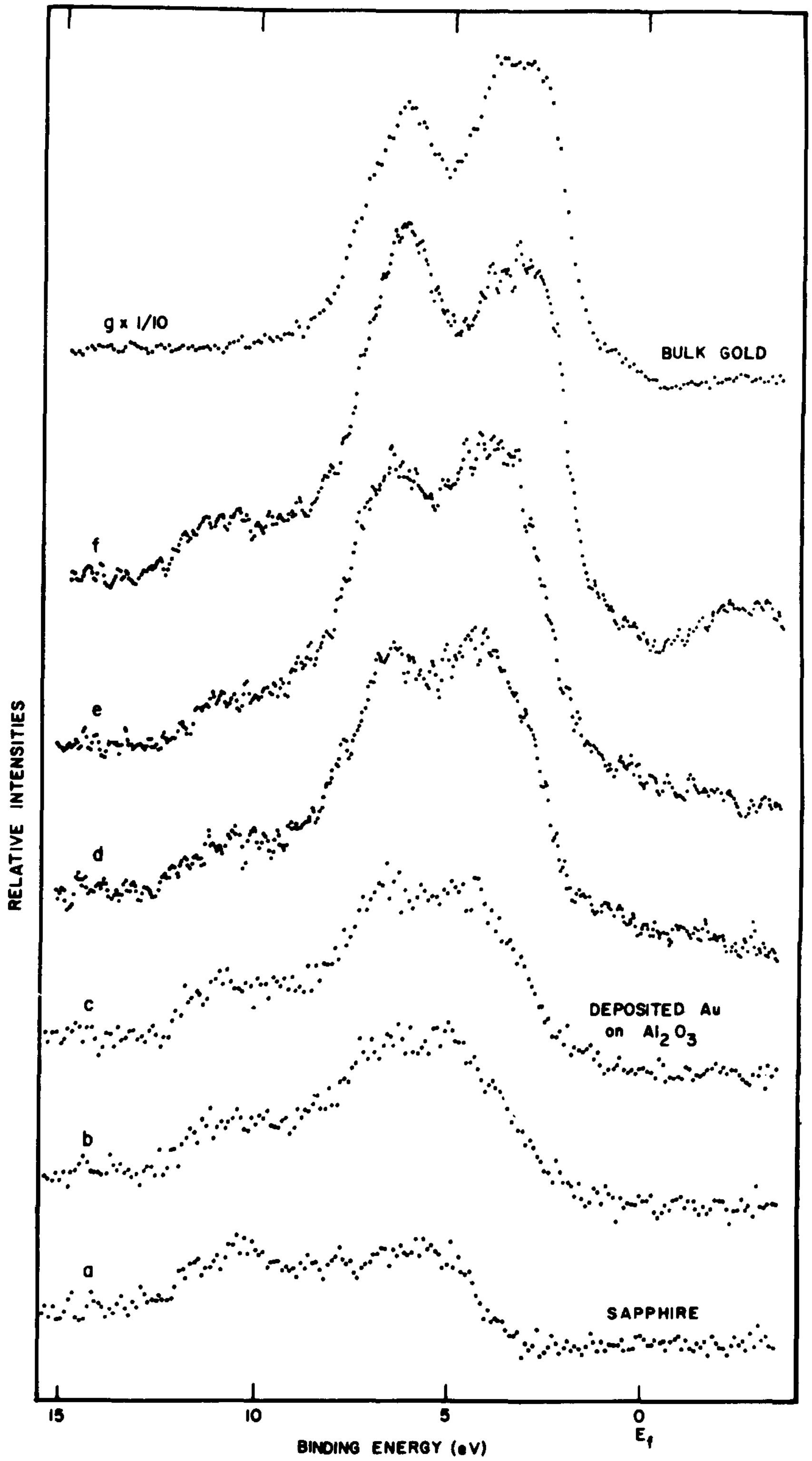

Fig. 3. Changes of the XPS valence band spectra of gold with the amount of Au deposited on sapphire.

of $AuAl_2$ formation, a transition from the $AuAl_2$ phase to a dilute Au(Al) alloy [spectrum (e)] is observed. Spectrum (d) shows this transition. From spectrum (e) of the Au layer to spectrum (h) of bulk gold, the splitting of the *d*-band increases from 1.9 eV to 2.5 eV. The width of the *d*-band changes from 4.4 eV to 5.7 eV. The center of the band shifts upward by about 1.5 eV. The core levels also shift toward the Fermi level by about 1.1 eV as shown on Fig. 2.

The origin of the *d*-band narrowing during stages (e) through (g) is of particular interest. From the core-level intensities, the effective amount of aluminum observed at stage (e) is estimated to be about 8%. Since the last Au–Al compound phase,[12] Au_4Al, contains 20% aluminum, the spectra (e) ~ (g) can not be simply associated with an Au–Al compound phase. This also agrees with the comparison of our *d*-band spectra with those obtained from bulk gold alloys, Au–Al[3] and Au–Cd.[4] The spectrum (e) of Fig. 1 would be equivalent to a gold alloy of 35–50 at.% aluminum, rather than 8% as observed, if the spectrum was associated with an Au–Al alloy. Therefore, the change of the *d*-band during stages (e) ~ (g) of deposition is mainly associated with the thickness increase of the Au layer, ~ 30 Å at (e) and ~ 100 Å at (g). Although the dilute amount (< 8%) of dissolved aluminum may have additional effects on the *d*-band narrowing, their contribution should be negligible as compared with the thickness effect.

The XPS spectra of the valence band of Au islands on sapphire (Al_2O_3) are shown in Fig. 3. The same qualitative behavior is observed on Al_2O_3 as on $AuAl_2$. For spectrum (e) the average "thickness" is $t \sim 10$ Å, from $t = \lambda \ln (I_0/I)$, which corresponds to an average island diameter of ~ 30 Å. The valence spectrum of the substrate is smooth enough, in the Al_2O_3 case, that the Au 5*d*-band structure is quite clear and unambiguous. Recent XPS studies of Ag and Au on carbon[13] showed similar behavior.

The similar observation of the change of the *d*-band of gold on $AuAl_2$ and Al_2O_3 can be attributed to the increased fraction of surface atoms to bulk atoms in the thin film or small cluster structure. The observed narrowing of the *d*-band is due to the reduction of Au nearest neighbors (and thus the reduction of spin–orbit splitting) of the surface atoms.

The binding energies of Au(4*f*) levels of gold deposited on Al_2O_3 were also measured. Their values are listed in Table 1. Similar to gold on aluminum, Au levels were all shifted to higher binding energies at low deposition and shifted back to the values of bulk gold as deposition progressed. Similar results were also observed on gold deposited on SiO_2. The shift of Au(4*f*) level can cause "inconsistencies" when the deposited gold was used as an XPS energy reference.[8] Recently, Kim and Winograd[14] also observed a similar shift for Au implanted in SiO_2 and attributed it to the matrix effect of the host material. From our study, however, the observed correlation between the valence band structure and the core-level shift suggests that the difference between the core-level linding energies of deposited gold and those of the bulk gold may, at least partially, be attributed to intrinsic difference of the electronic structure, rather than simply to a matrix effect.

Table 1. The measured intensity ratio between $Au4f_{7/2}$ *and* Al2p, *and the full widths at half maximum intensities (FWHM) and the normalized binding energies (B.E.) of* $Au4f_{7/2}$ *levels (in eV) of gold deposited on* Al_2O_3

Substrate	Intensity ratio	~~Au4$f_{7/2}$~~	
		FWHM	B.E.[a]
Al_2O_3	0.31	1.95	84.95
	0.64	1.68	84.70
	0.96	1.57	84.74
	1.24	1.53	84.60
	2.01	1.42	84.52
	2.46	1.44	84.50

[a] Normalized to the binding energy of Al2*p* (74.7 eV) of Al_2O_3.

4. CONCLUSION

Through a careful choice of substrates and sample preparation techniques, we have observed the XPS valence band spectra and core-level spectra of ultra thin Au-films and small Au-clusters. We observe a change in the *d*-band structure, and a shift of the *d*-band relative to the Fermi level when sample thicknesses (or diameters) are about 30 Å or less. The Au(4*f*) core-levels exhibit an overall shift due to the different electronic structural effects associated with the small dimensions. A practical consequence of this phenomena is when the gold-dressing techniques are utilized in the calibration of XPS spectra, errors on the order of one eV may be encountered.

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