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 4f 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 5d 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.5 Similar splitting was observed on liquid as well as solid gold.6 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 ≤ 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 ≤ 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 (4f) level and valence band spectra of thin (t ≤ 30 Å) gold films and small clusters (dia. ≤ 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 5d electrons of gold and the substrate would be simple (gold on Al)5 or eliminated (gold on Al₂O₃). The vapor deposition of Au onto sapphire (Al₂O₃) is well characterized.9 Al₂O₃ is thermodynamically inert and does not react with gold under our experimental conditions. Gold also does not wet Al₂O₃, so that the gold deposited on Al₂O₃ 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 AuAl₂ phase grows at room temperature. A thin Au film can then be deposited on top of AuAl₂ 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(Kα) 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 = I₀ exp (−t/λ) with λ = 20 Å for 1.2 KeV photoelectrons.50

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(1s)/Al(2p) ~ 0.06). This small oxygen contamination
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 $25 \pm 5 \text{Å}$.

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 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 4f and Al 2p levels with the amount of Au deposited on aluminum.
of AuAl₂ formation, a transition from the AuAl₂ 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.

Fig. 3. Changes of the XPS valence band spectra of gold with the amount of Au deposited on sapphire.
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, Au₄Al, 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–Al³ 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 (Al₂O₃) are shown in Fig. 3. The same qualitative behavior is observed on Al₂O₃ as on AuAl₂. For spectrum (e) the average “thickness” is t = 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 Al₂O₃ case, that the Al₂O₃-Au 5d-band structure is quite clear and unambiguous. Recent XPS studies of Ag and Au on carbon observed similar behavior.

The similar observation of the change of the d-band of gold on AuAl₂ and Al₂O₃ 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(4f) levels of gold deposited on Al₂O₃ 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 SiO₂. The shift of Au(4f) level can cause “inconsistencies” when the deposited gold was used as an XPS energy reference.⁸ Recently, Kim and Winograd also observed a similar shift for Au implanted in SiO₂ 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 binding 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/2 and Al2p, and the full widths at half maximum intensities (FWHM) and the normalized binding energies (B.E.) of Au4f/2 levels (in eV) of gold deposited on Al₂O₃

<table>
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<th>Substrate</th>
<th>Intensity ratio</th>
<th>Au4f/2 B.E.</th>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.31</td>
<td>1.95</td>
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<tr>
<td></td>
<td>0.64</td>
<td>1.68</td>
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<td>1.44</td>
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</table>

* Normalized to the binding energy of Al2p (74.7 eV) of Al₂O₃.

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(4f) 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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REFERENCES