Interface effects for very thin Al films deposited onto Cu, Si and SiO₂ substrates

D. Leinen*

Fisica Aplicada I, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain

Received 11 July 2003; Revised 3 December 2003; Accepted 5 December 2003

Al has been deposited by PVD in UHV onto Cu, Si and SiO₂ substrates. The film surfaces have been analysed quasi in-situ by XPS for increasing Al film thickness. At very low coverages, Al shows shifts in binding energy of Al 2p and the modified Auger parameter. These shifts are produced as an effect of the interaction with the substrate and depend on the amount of Al coverage and the type of substrate. They decrease with increasing conductivity of the substrate (SiO₂, Si and Cu) and with increasing Al coverage. For thicker Al films the modified Auger parameter tends to its bulk value. Auger parameter shifts are discussed in terms of chemical state plots and the relaxation energy of the photoholes. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: XPS; Auger parameter; Al; interface

INTRODUCTION

Since the fundamental work of Wagner it has been demonstrated that the modified Auger parameter α′ defined by α′ = photoelectron peak (BE) + Auger peak (KE), independent of the energy excitation source and sample charging shifts, is a powerful tool for the chemical characterization of material, in particular, when only small core-level ionization energy (chemical) shifts are present for different chemical states. As has been shown, the Auger parameter and its variation with respect to the pure metal are inherently related to the initial and final state effects, i.e. changes of the local environment potential and thus relaxation energy. The change of the modified Auger parameter can be used for charge transfer calculations since it can be accurately determined without concern for charging shifts. Recently, Auger parameter studies concerning charge redistribution phenomena have been carried out on various alloys. Furthermore, it has also been found that very low coverages of a metal or an oxide on another metal or oxide may affect the Auger parameter as the result of an interface effect where the local chemical environment, and by this, the polarizability due to extra-atomic relaxation, changes from one material to another. For our investigations Al has been selected since it shows large shifts in BE of the Al 2p photoelectron peak, in KE of the Al KLL Auger peak, and in the modified Auger parameter α′Al for different chemical states with respect to the pure Al metal. In this work, we investigate the variations of the modified Auger parameter α′Al for increasing amounts of Al coverage, starting at submonolayer coverages, on substrates of different charge screening capacity.

EXPERIMENTAL

Al has been evaporated from a W filament in UHV (p < 10⁻⁸ Pa). The filament was home-made of 0.173 mm diameter W wire of high purity (99.99%), formed to a coil of 15 mm length and 1 mm diameter. A piece of Al wire (15 mm length and 0.5 mm diameter) of high purity (99.99%) was put into the W coil and fused by 3 A filament current in order to overcoat the W filament with Al. The typical Al evaporation conditions have then been found empirically: 1.4 A filament current, 5 second evaporation time, 10 cm substrate to evaporation source distance. During evaporation the pressure increased to about 3 × 10⁻⁶ Pa. The delay time between evaporation performed in the UHV chamber attached to the spectrometer and the XPS measurement was less than 2 min, the XPS measurement itself took about 3 min. These times have been kept small in order to keep the surface contamination by gaseous residuals as low as possible.

The substrates were prepared as follows: (i) Cu substrate: a 10 mm × 10 mm piece of copper sheet of 0.4 mm thickness and high purity (99.99%) was sputtered for 45 min with Zalar rotation by 4 keV Ar⁺ ions (Ta₂O₅ equivalent sputter rate about 1 nm/min). On the freshly sputtered Cu surface only metallic Cu was found by XPS: Cu 2p₃/₂ at 932.7 eV, Cu NOO ions at 918.6 eV (KE) and αCu = 1851.3 eV; atomic concentration of O and C < 0.5 at%. (ii) Si substrate: a piece of standard boron-doped Si wafer has been used. It was first etched for 1 hour in fluoridic acid and then sputtered for 30 min with Zalar rotation by 4 keV Ar⁺ ions. XPS analysis of the Si surface showed Si 2p at 99.3 eV and atomic concentrations of O and C < 1 at%. (iii) SiO₂ substrate: a piece of standard boron-doped Si wafer was first etched for 15 min in fluoridic acid and then oxidized for 1 hour at 800 °C in a quartz tube under humid O₂ flow. In the spectrometer, 30 seconds of 4 keV Ar⁺ sputtering was sufficient to drop the C concentration below
The SiO$_2$ surface was confirmed with XPS by Si 2p at 103.7 eV, O 1s at 532.5 eV, Si KLL at 1607.8 eV (KE) and $\alpha'_{Si} = 1711.5$ eV.

XPS measurements were carried out with a PHI 5700 spectrometer. Spectra were recorded at 45° take-off-angle with a concentric hemispherical energy electron analyser operating in the constant pass energy mode at 29.35 eV, using a 720 $\mu$m diameter analysis area. Under these conditions, the Au 4f$_{7/2}$ line was recorded with 1.16 eV FWHM at a binding energy of 84.0 eV. The spectrometer energy scale was calibrated using Cu 2p$_{3/2}$, Ag 3d$_{5/2}$ and Au 4f$_{7/2}$ photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. Atomic concentrations have been determined from Al 2p, Cu 2p, Si 2p, O 1s and C 1s photoelectron peaks. For all measurements the Mg $K_a$ source has been used working at 15 keV and 300 W. The bremsstrahlung produced at the Mg anode was used by Al 1s excitation for the measurement of the Al KLL peak.

**RESULTS AND DISCUSSION**

Figure 1 shows the binding energy values of Al 2p photoelectrons, the kinetic energy values of Al KLL Auger electrons together with the values calculated for the modified Auger parameters $\alpha'_{Al} = Al$ 2p (BE) + Al KLL (KE) for increasing amounts of Al coverage represented as Al/X atomic ratio (X = Cu, Si, SiO$_2$). In Fig. 1 we observe a shift in Al 2p, Al KLL and $\alpha'_{Al}$ for low coverages, i.e. until about Al/X = 0.2, tending for higher coverages (Al/X > 0.2) to constant values corresponding to the Al bulk. Comparing the situation for the different substrates, we find very little variation for Al deposited on Cu. When Al is deposited on Si and SiO$_2$, we observe for Al/X < 0.2 a decrease of Al 2p of about 0.2 eV and 0.3 eV and a considerable increase in KE of Al KLL of about 0.8 eV and 2 eV. Owing to the latter $\alpha'_{Al}$ changes similarly. In any case, the variation of values for Al deposited on Cu, which is very small and in the magnitude of the experimental error, goes in the opposite direction, i.e. a slight increase of Al 2p and decrease of Al KLL for Al/Cu < 0.2. In order to relate the observed shifts in Al 2p (BE), Al KLL (KE) and $\alpha'_{Al}$ with initial and final state effects we use the simple approximation introduced by Wagner$^2$ and Thomas,$^{16}$

\[
\Delta BE = \Delta \varepsilon - \Delta RE \quad (1)
\]
\[
\Delta \alpha' = 2 \Delta RE \quad (2)
\]

where $\varepsilon$ is a term related to the eigenvalue of the level undergoing photoemission that accounts for the initial state charge distribution and $RE$ is the extra-atomic relaxation energy of the photoholes. From Eqns (1) and (2) we can calculate the values of $\Delta RE$ and $\Delta \varepsilon$ with respect to Al bulk for the situations of evaporation of Al onto Cu, Si and SiO$_2$. The magnitude of shifts (small Al coverage—high Al coverage) together with the $\Delta RE$ and $\Delta \varepsilon$ values are summarized in Table 1. The most remarkable feature of these data is the decrease of $\Delta RE$ from Cu over Si to SiO$_2$ reflecting the electrical character of the support, i.e. the charge screening capacity. The magnitude of $\Delta RE$ is more negative for more insulating substrates. This is in accordance with other results where oxides have been deposited at very low coverage on insulating support; positive $\Delta RE$ values have been obtained for thin oxide films on metal substrates.$^{12}$ In our study, $\Delta RE$ and $\Delta \varepsilon$ values of Al evaporated on the Cu substrate are practically zero and within the experimental error. The $\Delta \varepsilon$ value is small for Al evaporated onto Si which means that the shift in the position of the Al 2p peak is dominated by the final state effect rather than by changes in the electron density and the Madelung potential. However, for Al on SiO$_2$, $\Delta \varepsilon$ is about $-0.5$ eV which shows a considerable contribution in initial state variation, i.e. charge transfer from the substrate to the Al atom when deposited onto the SiO$_2$ surface.

**Table 1.** Shifts observed for (small Al coverage — high Al coverage) in Al 2p (BE) and Al KLL (KE), and calculated values of $\alpha'_{Al}$, $\Delta RE$ and $\Delta \varepsilon$. All values are in eV

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta BE$</th>
<th>$\Delta KE$</th>
<th>$\Delta \alpha'_{Al}$</th>
<th>$\Delta RE$</th>
<th>$\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Cu</td>
<td>-0.05</td>
<td>+0.05</td>
<td>0</td>
<td>0</td>
<td>-0.05</td>
</tr>
<tr>
<td>Al/Si</td>
<td>+0.15</td>
<td>-0.80</td>
<td>-0.6</td>
<td>-0.3</td>
<td>-0.15</td>
</tr>
<tr>
<td>Al/SiO$_2$</td>
<td>+0.30</td>
<td>-2.00</td>
<td>-1.70</td>
<td>-0.85</td>
<td>-0.55</td>
</tr>
</tbody>
</table>
An important contribution to the relaxation energy of photoholes of the adsorbed species is the polarization of the substrate.\cite{17,18} This has been shown by Moretti and co-workers\cite{19} for bulk oxides and relates the Auger parameter of the cations with the magnitude of the polarizability of the anions to which they are bonded. Thus, the different contributions to the relaxation energy of the polarization of Si and SiO\textsubscript{2} substrates are the reason for the observed differences in $\Delta \alpha$. The photoholes created in Al for low coverage relax more easily on Si than on SiO\textsubscript{2}. Within this argumentation and the data presented in Table 1, it seems reasonable that Al 2p increases somewhat for Al on Si and Al on SiO\textsubscript{2} with respect to the value for Al bulk, being first a semiconductor and second an insulator. The small decrease of Al 2p for Al on Cu may be due to the relatively higher free charge electron density in Cu compared to Al bulk. As already mentioned, the shift in $\alpha$ is an effect of extra-atomic relaxation. The extra-atomic relaxation changes with increasing Al coverage from the situation where it is determined by the substrate ($\text{Cu}$, Si, SiO\textsubscript{2}), i.e. by its screening response, to the one where relaxation occurs in the Al bulk. This can be seen in Table 1 which shows the shift of $\alpha_{\text{Al}}$ with respect to the Al bulk situation of about $-0.6$ eV for Al on Si and $-1.7$ eV for Al on SiO\textsubscript{2}. This is the direct response of less polarizability, i.e. less local charge compensation for the photoholes in the vicinity of Si bulk with covalent ligand bonds, and, even more pronounced, for photoholes in the vicinity of SiO\textsubscript{2}, an insulating material, with more ionic bonds and higher bond strength. As can be seen in Fig. 1, the main shifts are found for Al/X $< 0.2$. Taking into account the inelastic mean free path $\lambda \approx 21$ Å of Si 2p photoelectrons in the Al metal,\cite{20} we can roughly estimate the thickness $x$ of Al coverage where the main shifts in $\alpha_{\text{Al}}$ are observed. The Si 2p signal decreases with increasing Al coverage according to $\exp(-x/\lambda)$. By this we obtain an $x$ value of about 5 Å, which means that the observed shift of $\alpha_{\text{Al}}$ corresponds to an Al film thickness of the order of one monolayer. This shows that the observed shifts are an interface effect. Al at the interface in the vicinity of Cu, Si or SiO\textsubscript{2} is very differently screened, i.e. different extra-atomic relaxation energies for the Al photoholes are involved.

We would like to mention that no particle size effect is taken into account in the approximation that we have used for $\Delta \alpha$, given by Eqn (2). It was found that in the case of metal clusters supported on weakly conducting substrates $\Delta \alpha$ depends on both type of substrate and cluster size.\cite{21,22} However in our evaporation experiment, the adhesion of Al atoms to the different substrates is strong enough to prevent major cluster formation during the initial stages of substrate coverage. Hence, we consider the particle size effect of poor importance compared to the substrate effect for the shifts observed in $\alpha$.

Figure 2 represents in terms of a chemical state plot\cite{23} the series of Al evaporation experiments onto Cu, Si and SiO\textsubscript{2} substrates. The arrows indicate the direction of variation for increasing Al coverage. The chemical state plot of Fig. 2 shows that a simple inspection of $\alpha_{\text{Al}}$ may lead to misinterpretation of the chemical state of Al in cases of very low coverage. This is in particular the case if Al is deposited on insulating material. For higher coverages, $\alpha_{\text{Al}}$ moves for all three series of evaporation experiments to the Al bulk value. The data of Fig. 2 stress the necessity of knowing the type of support and the dispersion degree of the deposited metal in order to prove the oxidation state of Al by measuring the BE of Al 2p or the magnitude of the modified Auger parameter.

The implication of these results for practical work in catalysis and related fields where a metal is dispersed on the surface of a carrier is obvious. In these cases the assessment of the stoichiometry by XPS has to be evaluated very carefully. Thus, it is likely that shifts in BE and $\alpha$ due to the effects discussed above may contribute to an apparent lack of reproducibility of experimental results.

Acknowledgements

The author is grateful to J. P. Espinós for discussions and to the University of Málaga for the analytical techniques.

REFERENCES