Oxidation of Al–Au intermetallics and its consequences studied by x-ray photoelectron spectroscopy

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Three common Al–Au intermetallics, Al 2Au, AlAu 2, and AlAu 4, were oxidized in the air and characterized using x-ray photoelectron spectroscopy in terms of the elemental chemical state. It was found that there is an increasing trend of oxidation in these intermetallics as the Au content increases. AlAu 4 shows the greatest tendency to oxidize with two extra peaks appearing on the Au 4f spectra after long exposure time in air. The surface of AlAu 2, although fully oxidized, reveals only one Au 4f peak shift as depth increases. Al 2Au was the least oxidizing compound, and the oxide is thin. The binding energies of Al 2p and Au 4f peaks were measured and reported. The Au atoms trapped in the oxide layers exhibit higher binding energy emissions compared to those of elemental Au.

I. INTRODUCTION

Au wire ball bonding to Al pads is a common interconnection method used in the microelectronics industry. A good Al–Au bond inevitably contains intermetallics at the interface whose composition, thickness, and stability play a key role in the reliability of the joint. Many researchers have studied the formation and growth of intermetallics at Al–Au interfaces for decades; the works by Campisano et al.1 and Majni et al.2 are frequently cited. The Al–Au alloy system shows many possible intermetallic phases but only some have been detected in each study and, even then, the reports are not in agreement. One phase that forms initially was found to transform to other phases on continued diffusion-driven reaction. Such interface transformation has been a fascinating topic for scientific investigation, and experimentalists have predominantly used scanning electron microscopy (SEM) and x-ray diffraction (XRD) to examine them. Transmission electron microscopy (TEM) has been adopted in some recent reports.3–6 The intermetallics observed at the interface vary with the relative amounts of Au and Al available and also on the growth conditions. The phases Al 2Au, AlAu, AlAu 2, Al 2Au 5, and AlAu 4 are reported to form in different combinations by various studies.

The bond reliability in these joints is thought to be controlled by Kerkendall void formation,7–9 resulting from unbalanced interdiffusion during the annealing or due to volume shrinkage that accompanies intermetallic formation and growth.7,10,11 Recently, Karpel et al.5,6 have reported that voids exist even in the as-formed bonds, which was attributed to solidification shrinkage that occurs when the molten Au ball solidifies. With increasing integration and miniaturization, the wire diameter and the metallization thickness have become extremely small, and consequently, it has become even more critical to understand the connection between interface quality and microstructure. Besides those

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failure mechanisms reported in the literature, one mechanism that could purportedly cause failure is oxidation/corrosion of the intermetallic phases at the joint interface. The oxidation characteristics of Al–Au intermetallics have not been examined. Recently, Piao et al. studied the room-temperature oxidation behavior of Al–Au thin films containing Al$_2$Au and AlAu$_2$ at the interface. They report that oxidation of these phases occurs by Al$_2$O$_3$ formation with consequent Au enrichment associated with phase transformation from Al-rich to Au-rich phases. A accelerated oxidation could occur when wire bonds are subjected to high temperatures in the range 175–200 °C during the packaging process, particularly at the bond periphery where the intermetallics are exposed to the ambient until encapsulation. Although, such phase transformations may be harmless by themselves, they are accompanied by volume changes and interdiffusion, which could produce harmful internal stresses or voids. Therefore, characterization of the intermetallic oxidation at elevated temperatures will be beneficial to assess joint reliability.

The study of oxidation of intermetallics at the actual Al–Au interfaces in wire bonds could be extremely difficult. Because information on the oxidation behavior of even the bulk Al–Au intermetallics is very limited, it was decided to examine some common phases reported in wire bonds, in single phase form, in a systematic manner. This report details the results obtained in a study of three intermetallic phases, synthesized and oxidized under controlled conditions, at temperatures typically encountered in an electronics packaging process, and investigated by x-ray photoelectron spectroscopy (XPS).

II. EXPERIMENTAL DETAILS

Approximately 1.5 g of the intermetallics Al$_2$Au, AlAu$_2$, and AlAu$_4$ were produced by arc melting stoichiometric amounts of 99.99% pure Au and Al granules in an argon atmosphere. The samples were repeatedly flipped over and remelted to ensure homogeneity. Parts of the final samples were ground to powder, and XRD was used to confirm that the phases obtained are indeed the intended intermetallic without any residuals or impurities. In addition, the melting points of the Al$_2$Au, AlAu$_2$, and AlAu$_4$ samples measured by a differential scanning calorimeter are 1055, 627, and 526 °C, respectively, which also match values quoted in the literature. Hence, the samples are indeed pure intermetallics. The mass change of solid intermetallics was measured with a thermogravimetric analyzer (Mettler Toledo TGA/SDTA, Switzerland).

Nine specimens of size 4 mm x 2 mm were cut from each intermetallic, and one convenient face was polished down to 1-μm diamond paste surface finish and ultrasonically cleaned. The polished samples were heated at 175 °C in an oven in air for durations of 0.25, 0.5, 1, 2, 4, 8, 16, and 24 h with care to avoid contamination and contact with the polished surface. XPS measurements were conducted in a Kratos AXIS Ultra spectrometer (UK) with a monochromatized Al K$_\alpha$ x-ray source (1486.71 eV) operated at a reduced power of 150 W (15 kV and 10 mA). The base pressure in the analysis chamber was $2.66 \times 10^{-7}$ Pa. The core-level spectra were obtained in Al 2p and Au 4f regions at a photoelectron take-off angle of 90° measured with respect to the sample surface and were recorded in 0.1 eV steps with a pass energy of 40 eV. The binding energy scale of the XPS spectrum was calibrated with the C 1s peak (neutral C–C peak at 284.5 eV). The depth profiling chemical states were analyzed on the same equipment for the 24 h oxidized samples only. An argon ion gun with accelerated voltage of 4 kV and filament current of 15 mA was used to etch the samples at a gas pressure of $6.65 \times 10^{-6}$ Pa. Ion bombardment was performed at an incident angle of 45° to the surface normal. The Al 2p and Au 4f spectra were collected after each etching cycle of 3 min. Depth profiling was done until the oxygen peak reached undetectable level.

III. RESULTS

A. Al$_2$Au

The Al 2p and Au 4f spectra obtained on Al$_2$Au sample surfaces oxidized for different times, up to 24 h, are shown in Figs. 1(a) and 1(b), respectively. The data in Fig. 1(a) can be resolved into two component peaks at binding energies (b.e.) of 75.8 and 73.5 eV. The reported b.e. of oxidic Al peak matches well with 75.8 eV, and thus this could be assigned to Al$_2$O$_3$. The other component at 73.5 eV is near to that of Al species in Al$_2$Au, and its intensity gradually reduces to a weak tail as oxidation is prolonged. Since the oxidic peak is the dominant one even in the as-polished sample, Al$_2$Au is oxidized even in the as-polished state.

In the Au 4f spectra shown in Fig. 1(b), two spin-orbit split components of the Au peak are clearly visible in all samples at b.e. values of 89.1 and 85.4 eV, which correspond to the Au 4f$_{5/2}$ and Au 4f$_{7/2}$ values of 89.4 and 85.7 eV reported in Al$_2$Au by Fuggle et al. The b.e. and the intensity of the component peaks do not seem to change with increasing oxidation time, and no additional component peaks are required to achieve a good fit to the experimental data. This implies that a strong signal is received from Al$_2$Au phase in all samples although clear evidence of oxidation is also detected in Fig. 1(a).

The depth profiling curves (not shown) of Au in Al$_2$Au at different oxidation durations confirm that there is no change in binding energy indicating that the oxidation...
The treatment does not influence the valence of Au. The depth profiling information obtained in the 24 h oxidized \( \text{Al}_2\text{Au} \) sample is shown in Fig. 2 for Al 2p peaks. A shoulder is clear at the surface (0 min), at the low b.e. end in Fig. 2, indicating that two component peaks are overlapping. The smaller peak with lower b.e. gradually becomes dominant as the depth increases while the peak dominating on the surface diminishes. A good fit to
experimental data could be obtained in the deconvolution with two component peaks at 75.8 and 73.5 eV, as shown in Fig. 2. These peaks were observed in Fig. 1(a), too, and were assigned to Al 2p in Al$_2$O$_3$ and Al$_2$Au, respectively. The evolution of the relative intensities of the component peaks is in good agreement with the presence of an Al$_2$O$_3$ layer on Al$_2$Au whereby the oxidic peak is dominant at the surface, and the Al$_2$Au peak increases in dominance with increase in depth.

Under these conditions, it is possible to estimate the remaining oxide layer thickness from the ratio of the intensities of the peaks using the Strohmeier equation\(^\text{18}\):

\[
d\ (\text{nm}) = 2.8 \ln\left(1.4 \frac{I_o}{I_m} + 1\right),
\]

where \(I_o\) and \(I_m\) are the intensities (peak areas) of the oxide and metal photoelectron peaks, respectively, which can be readily obtained from the quantification parameters list when deconvoluting the peaks using the CasaXPS software (version 2.2.99, Casa Software Ltd., UK). The oxide layer thickness calculated using Eq. (1) at each point in the depth profiling is also indicated in Fig. 2. Accordingly, Al$_2$Au forms an oxide layer of thickness 10.8 nm approximately when heated in air for 24 h at 175°C.

In contrast, the two spin-orbital split Au 4f peaks do not change with depth, implying that the Al$_2$O$_3$ layer of 10.8 nm does not significantly change the electronic environment of the Au atoms or absorb the Au photoelectrons, because the surface and subsurface signals are identical.

\section*{B. AlAu$_2$}

The Al 2p and Au 4f spectra for AlAu$_2$ samples oxidized for up to 24 h are shown in Figs. 3(a) and 3(b), respectively. For all oxidation times, the data could be fitted well with a single peak at the b.e. of 75.8 eV, which could be attributed to the oxidic Al peak. This is in contrast to the observation in Fig. 1(a) for Al$_2$Au where the experimental data could be resolved into two component peaks corresponding to the oxide and the intermetallic. The absence of the Al 2p component of AlAu$_2$ on the surface implies a thicker oxide layer in comparison to Al$_2$Au. The Au 4f spectra in Fig. 3(b) show that two peaks at the positions of 88.7 eV and 85.0 eV generate a perfect deconvolution to the data for all oxidation times without any shift in b.e. This implies that the Au 4f signal of AlAu$_2$ is received clearly in all samples despite the presence of a thicker oxide layer here.

The spectra obtained in depth profiling are shown in Figs. 4(a) and 4(b) for Al 2p and Au 4f, respectively. The scan on the surface (0 min) in Fig. 4(a) generates a single peak which can be assigned to the oxidic component of
Al at 75.8 eV after deconvolution. A small tail appears at the low b.e. side in 3 min of etching, which evolves into a significant peak at 73.9 eV after 15 min etching. This new peak could be assigned to Al in AlAu₂. The oxide peak is weakened with increase of depth but is still detectable even after 90 min of etching, while the AlAu₂ Al 2p peak strengthens, signifying penetration through the oxide layer and reach of the underlying intermetallic. The
remaining oxide layer thickness computed using Eq. (1) is also shown in the figure, except for the spectrum on the original surface as the AlAu$_2$ component is not detected. Hence, the full thickness of the oxide could not be computed but is probably higher than in Al$_2$Au since the alloy peak was obscured.

The evolution of Au 4f spectra shown in Fig. 4(b) manifests a chemical shift for the two peaks with increase

FIG. 4. Deconvolution of (a) Al 2p and (b) Au 4f depth profiling spectra of 24 h oxidized AlAu$_2$. Note the shift in the peaks in (b) at the surface.
in depth. The b.e. decreases from 88.8 to 88.2 eV for Au $4f_{5/2}$ and 85.1 to 84.5 eV for Au $4f_{7/2}$. Note that the shift in b.e. is systematic and is higher than the resolution of the technique, which is typically ±0.2 eV. Piao\textsuperscript{12-15} reported the b.e. of the two Au 4f peaks in AlAu$_2$ as 88.6 and 84.9 eV, which are in good agreement with the b.e. values obtained in this study on the initial surface of AlAu$_2$. However, the surface is oxidized, and our results clearly show a shift in b.e. to higher values at the surface. Therefore, the lower b.e. values obtained after depth profiling should give a better estimate of the true b.e. in AlAu$_2$. Consequently, we attribute 88.2 and 84.5 eV Au 4f emissions in AlAu$_2$. The increase in b.e. near the surface signifies that the electronic environment around Au atoms is changed because of the thicker oxide layer on AlAu$_2$.

### C. AlAu$_4$

Al 2p spectra for AlAu$_4$ samples oxidized up to 24 h (not shown here), are similar to those of AlAu$_2$ in Fig. 3(a). Only the oxidic Al component at b.e. of 75.7 eV could be detected at the surface of the samples indicating a thick oxide layer. The emission from the Al species in AlAu$_4$ was obscured totally, indicating that the oxide on this compound is thick even at the as-polished state.

The Au 4f spectra obtained on the surface are shown in Fig. 5. In the as-polished state, two distinct peaks at 87.8 and 84.2 eV, corresponding to Au 4$f_{5/2}$ and Au 4$f_{7/2}$, respectively, fit the experimental data very well. Because values of b.e. in AlAu$_4$ are not reported in the literature for comparison and because the Al 2p spectrum clearly indicates a thick oxide layer on these samples, we cannot attribute these b.e. values to those of Au 4f doublet in AlAu$_4$. With increasing oxidation duration, it is clear that additional overlapping peaks become necessary to deconvolute the data. Each of the Au 4f doublets could be resolved into two overlapping components; one pair at 88.8 and 87.8 eV and another pair at 85.2 and 84.2 eV. Thus, with increasing oxidation, the two additional peaks appear at the higher energy side of the Au 4f doublet observed in the as-polished sample. There is no evidence for a similar high b.e. component in the as-polished Al 2p spectra and hence these additional peaks are not artifacts of differential charging at surface regions. This additional Au 4f doublet appears to represent an Au 4f emission coming from a different chemical environment to that in the as-polished sample.\textsuperscript{19} Since the presence of a thick oxide layer is confirmed by the Al 2p spectra, the new peaks at 88.8 and 85.2 eV must be emitted by Au atoms trapped in Al$_2$O$_3$, as was observed for the case of AlAu$_2$.

Depth profiling shows that the unetched surface scan shows only the oxidic Al 2p peak at 75.7 eV after deconvolution, as evident in Fig. 6(a). With increasing

**FIG. 5.** Curve-fitted experimental data and the deconvolution of Au 4f XPS spectra of AlAu$_4$ oxidized for 24 h. Note the appearance and strengthening of new extra peaks as the depth increases.
depth, a second peak appears as a shoulder at 15 min etching time and subsequently as a doublet at 33 min. After 15 min etching, the remaining oxide layer thickness, calculated using Eq. (1), is 5.1 nm. Comparison with the Al₂Au ion etching suggests that the initial oxide layer is more than 10.8 nm thick. In 108 min, the oxidic peak is still evident as a minor peak while the second peak is predominant. Deconvolution shows that the
second peak should be at the b.e. of 73.7 eV for good fitting to the data. Since this second peak was not detected at all at the surface, all surface Al atoms have been oxidized to Al$_2$O$_3$. After 108 min etching, the photoelectron signal from the subsurface AlAu$_4$ is received clearly, and thus the b.e. of Al 2$p$ peak in AlAu$_4$ can be taken as that of the second peak of 73.7 eV.

The Au 4$f$ spectra during depth profiling and their deconvolution are shown in Fig. 6(b). Each peak at the surface could be resolved into two components; an overlapping pair with b.e. of 88.8 and 87.8 eV and another overlapping pair with values 85.2 and 84.2 eV. This is similar to the spectra in Fig. 5(b) obtained at the surface. It is clear that the intensities of the two high energy peaks at 88.8 and 85.2 eV rapidly diminish in a short etching time of only 6 min. In the spectra for 33 and 108 min etched samples, deconvolution shows that single peaks at 87.8 and 84.2 eV are adequate to fit the data. Having the additional high energy pair with a small intensity would not make any noticeable difference to the fit. Thus, the peaks at 87.8 and 84.2 eV could be attributed to the Au 4$f$ doublet in AlAu$_4$ while the additional peaks at the binding energy of 88.8 and 85.2 eV could be attributed to a new emission from Au atoms trapped in the thick Al$_2$O$_3$ layer.

D. Oxidation rate constant

Oxidation rate constant $k_p$ was calculated from Eq. (2)\textsuperscript{20}:

$$\left( \frac{\Delta W}{A} \right)^2 = k_p t,$$  

where $\Delta W/A$ is the mass increase per unit surface area measured by TGA, and $t$ is time. The values obtained for the three intermetallics at three temperatures are shown in Table I along with that for pure Al for comparison. Note an increase in $k_p$ of all intermetallics compared to Al. The higher Au containing intermetallics show higher $k_p$ values, which implies faster oxidation.

IV. DISCUSSION

A. Binding energies of Al 2$p$ and Au 4$f$ peaks

Table II summarizes the b.e. values measured in this study and compares it with those reported in the literature. Our measurements are in good agreement with reported values in Al$_2$Au and in Al$_2$O$_3$. In AlAu$_2$, on the other hand, the Au 4$f$ b.e. determined in this study is lower by about 0.4 eV than the values reported by Piao et al.\textsuperscript{12–15} This could be attributed to some interference from the oxide layer as we indeed obtained the same values at the surface, but on depth profiling, the lower values were obtained, which must be the native emissions from the intermetallic phase. The effect of the oxide layer in increasing the b.e. was more apparent in AlAu$_4$ where distinct new peaks were required to fit the experimental data. These new peaks were at the higher b.e. side of the peaks attributed to Au 4$f$ in AlAu$_4$, as tabulated in Table II. No reports are available on measurement of b.e. in AlAu$_4$, and thus we are not in a position to authenticate our results, but the depth profiling study is able to distinguish the native peaks of the intermetallic from the additional emissions, which are believed to be from the Au atoms trapped in the oxide layer. It is thought that a similar phenomenon also occurs in AlAu$_4$, which causes a shift in b.e. values of the Au 4$f$ peaks when measured at the oxidized surface. Since its oxide layer is thicker, it was possible to distinguish this effect as clearly as in AlAu$_4$. In Al$_2$Au, however, the oxide layer is very thin for any embedded Au atoms to cause a shift in the native Au 4$f$ peaks of the phase, and, consequently, measurements made at the surface give an accurate value for the b.e. representative of the phase.

### Table I. List of oxidation rate constant $k_p$.\textsuperscript{20}

<table>
<thead>
<tr>
<th>Material</th>
<th>200 °C</th>
<th>300 °C</th>
<th>400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>$6.60 \times 10^{-10}$</td>
<td>$1.60 \times 10^{-9}$</td>
<td>$5.60 \times 10^{-9}$</td>
</tr>
<tr>
<td>Al$_2$Au</td>
<td>$9.90 \times 10^{-10}$</td>
<td>$4.50 \times 10^{-9}$</td>
<td>$8.10 \times 10^{-9}$</td>
</tr>
<tr>
<td>AlAu$_2$</td>
<td>$1.49 \times 10^{-9}$</td>
<td>$5.17 \times 10^{-9}$</td>
<td>$1.11 \times 10^{-8}$</td>
</tr>
<tr>
<td>AlAu$_4$</td>
<td>$2.97 \times 10^{-9}$</td>
<td>$1.33 \times 10^{-8}$</td>
<td>$3.93 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

### Table II. Binding energy values measured in this study and compared with those reported in the literature.

<table>
<thead>
<tr>
<th>Intermetallic</th>
<th>2p b.e. (eV)</th>
<th>4f b.e. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This study</td>
<td>Literature</td>
</tr>
<tr>
<td>Al$_2$Au</td>
<td>73.5</td>
<td>73.7\textsuperscript{12–15}</td>
</tr>
<tr>
<td>AlAu$_2$</td>
<td>73.9</td>
<td>88.2, 84.5</td>
</tr>
<tr>
<td>AlAu$_4$</td>
<td>73.7</td>
<td>87.8, 84.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>surface layer</td>
<td>75.7 to 75.8</td>
</tr>
<tr>
<td>Au in AlAu$_4$</td>
<td>surface oxide</td>
<td>88.8, 85.2</td>
</tr>
</tbody>
</table>
gold-richest phase in Al–Au phase diagram, oxidation of \( \text{AlAu}_4 \) to \( \text{Al}_2 \text{O}_3 \) will result in the emergence of a significant amount of elemental Au. The reported binding energies of elemental Au 4f peaks are 87.5 and 83.8 eV.\(^{27,28}\) The new peaks observed at 88.8 and 85.2 eV in this investigation are significantly higher than the binding energy of elemental Au 4f peaks and thus must be emitted from a different, strongly electron-withdrawing chemical environment. As a thick Al oxide is present on the surface, this binding energy shift may result from isolated Au atoms or nanoclusters of Au surrounded by oxygen defects in the oxidized layer. Such impurity atom-vacancy combinations are now offered as a possible reason for the emergence of strong magnetic response in Co- or Fe-doped TiO\(_2\) dilute magnetic semiconductors.\(^{29,30}\) Hence, this phenomenon may be a common occurrence in oxides containing alien cations as substitutional defects leading to shifts in the b.e. of the cation.

The b.e. shifts are characteristic of the physical and chemical environment of the analyzed species while the electronegativity determines the type of interaction between the various atoms in the system. The interaction of Au with alumina has been investigated elsewhere.\(^{31-36}\) Serrano et al. observed the formation of \( \text{Al}_2 \text{Au} \) at the \( \text{Au}–\text{Al}_2 \text{O}_3 \) interface at room temperature when Au is sputtered onto an alumina substrate. Upon heating, this \( \text{Al}_2 \text{Au} \) disintegrated and the emerging elemental Au was incorporated into \( \text{Al}_2 \text{O}_3 \), resulting in a solid solution of Au in \( \text{Al}_2 \text{O}_3 \). Serrano theorized that the Au atoms could cluster into nanoparticles in the oxide matrix.\(^{37}\) Nguyen et al. coated thin gold films on \( \text{Al}_2 \text{O}_3 \) ceramic substrate and reported the initial formation of \( \text{AlAu}_2 \) as well as subsequent appearance of \( \text{Al}_2 \text{Au} \) upon heating at 500 °C for 3 h.\(^{38}\) Furthermore, Atsuko et al. proved that Au diffused through \( \text{Al}_2 \text{O}_3 \) in an \( \text{Au}–\text{Al}_2 \text{O}_3–\text{Al} \) sandwich to form \( \text{Al}_2 \text{Au} \) intermetallic at the Al interface.\(^{39}\) Thus, dissolution of Au in \( \text{Al}_2 \text{O}_3 \) has been suspected in some studies, but its characteristic XPS emissions have not been reported. This study, while giving a strong indication of dissolution of Au in \( \text{Al}_2 \text{O}_3 \), also measures the Au 4f b.e. of such dissolved species. This value will be affected by electronic interaction between Au and the neighboring atoms or vacancies. The b.e. of Au 4f in \( \text{Al}_2 \text{O}_3 \) determined in this study is higher than that reported for elemental Au, and that attributed here for \( \text{AlAu}_4 \). This implies that Au, under these circumstances, has a tendency to donate electrons to the neighboring atomic sites, implying the presence of O vacancies. Some Au–O bonds may exist to stabilize the Au atoms, although no explicit evidence is available for any specific Au oxide species in our investigations. The Au 4f\(_{7/2}\) binding energy of 85.2 eV is less than the reported value of 85.7 eV for \( \text{Au}_2 \text{O}_3 \)\(^{40}\) suggesting that any such bonds are not as ionic as the bulk \( \text{Au}_2 \text{O}_3 \) oxide.

### C. Oxidation reaction in Al–Au intermetallics

Two processes could take place in oxidation of Al–Au intermetallics: the oxidation of Al and the phase transformation due to depletion of Al. As indicated in previous XPS studies on Al–Au thin film alloys,\(^{12-15}\) \( \text{Al}_2 \text{Au} \) transforms to \( \text{AlIAu}_2 \) during exposure to atmosphere even at room temperature. This process could be expressed by,

\[
8\text{Al}_2\text{Au} + 9\text{O}_2 \rightarrow 6\text{Al}_2\text{O}_3 + 4\text{AlIAu}_2.
\]

Such transformation was however not observed in the present study of \( \text{Al}_2 \text{Au} \). In Fig. 1(a), only \( \text{Al}_2 \text{O}_3 \) is detected on the surface of \( \text{Al}_2 \text{Au} \) sample without any sign of \( \text{AlIAu}_2 \). Then, the oxidation reaction of Eq. (3) has to be re-written as

\[
2\text{Al}_2\text{Au} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 2\text{Au}.
\]

The presence of elemental Au also could not be detected as no corresponding peak shift in Au 4f was observed for up to 24 h oxidation. Figure 2(a) shows that the oxide on \( \text{Al}_2 \text{Au} \) is very thin (about 10 nm), thus any Au that is formed might be in minute amount below the sensitivity of the technique. The \( \text{AlIAu}_2 \) oxidation reaction may lead to the formation of more Au-rich phases such as \( \text{AlIAu}_4 \) or \( \text{Al}_2 \text{Au}_5 \), but again such phases were not detected according to the b.e. of the Au 4f peaks observed. The observed binding energy shift in Au spectra upon depth profiling in Fig. 4(b) suggests there is only a change of chemical environment around the atoms due to oxide thickening instead of the formation of new phases. The oxide thickness on \( \text{AlIAu}_4 \) is the largest among the intermetallics studied here, causing considerable depletion of Al and the appearance of extra Au peaks attributed to elemental Au trapped in the oxide. Hence, the reaction of \( \text{AlIAu}_4 \) oxidation could be given as

\[
4\text{AlIAu}_4 + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 16\text{Au}.
\]

This reaction implies that 16 mol Au is produced for 2 mol \( \text{Al}_2 \text{O}_3 \). Hence, a significant amount of Au could remain trapped in the oxide when \( \text{AlIAu}_4 \) oxidizes, compared to the other two intermetallics. In addition, the thicker oxide layer in this phase also obscures photoelectron emission from the pure \( \text{AlIAu}_4 \) beneath, making photoelectron emission from Au in the oxide layer easier to detect.

### D. Oxidation tendency of Al–Au intermetallics

Note that the k\(_p\) of \( \text{AlIAu}_4 \) is the largest among the intermetallics at every temperature, and the effect of increasing Au content is to increase k\(_p\). This implies that higher Au containing intermetallics oxidize more readily. These results are in agreement with XPS investigations.
V. CONCLUSIONS
The following can be concluded from this detailed XPS study of oxidation of the three bulk intermetallic phases: $\text{Al}_2\text{Au}$, $\text{AlAu}_2$, and $\text{AlA u}_4$.

The degree of oxidation increases in the order $\text{Al}_2\text{Au} < \text{AlAu}_2 < \text{AlA u}_4$. The oxide layer thickness in $\text{Al}_2\text{Au}$ is estimated to be 10 nm. $\text{AlA u}_4$ has the greatest tendency to be oxidized among the intermetallics tested, suggesting that the oxidation of $\text{AlA u}_4$ in wire bond could be a serious reliability problem.

The binding energies were measured for the $\text{Al}$ and $\text{Au}$ species in the intermetallic phases and are shown in Table II. A binding energy shift was observed in the $\text{Au}$ 4f peak of $\text{Al Au}_4$ on its oxidized surface, while at higher binding energy, additional peaks were discovered on the oxidized surface of $\text{AlAu}_2$. These were attributed to emissions from $\text{Au}$ atoms dissolved in the oxide layer, which were at a higher binding energy than elemental $\text{Au}$. Such abnormality was not noted in $\text{Al}_2\text{Au}$.

The binding energy of the two spin-orbit split components of $\text{Au}$ 4f in $\text{Al Au}_2$ are determined as 88.2 and 84.5 eV, which are slightly lower than previously reported values. It is proposed that measuring the binding energy on the oxidized surface leads to erroneously higher values because of emission from $\text{Au}$ atoms entrapped in the oxide layer.

The binding energies of the two spin-orbit split components of $\text{Au}$ 4f in $\text{AlA u}_4$ are determined as 88.8 and 85.2 eV. Binding energies of these peaks are reported for the first time in the literature.

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