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An *in situ* TEM study of phase formation in gold-aluminum couples

D. E. EAKINS, D. F. BAHR, M. G. NORTON
School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164-2920, USA
E-mail: deakins@mme.wsu.edu
E-mail: bahr@mme.wsu.edu
E-mail: norton@mme.wsu.edu

In the gold wire bonding of aluminum in microelectronic devices the presence of aluminum oxide on the metallization surface may be expected. Electron transparent couples containing an oxide layer at the interface were heated in a TEM to determine the effects of a passivation layer on intermetallic formation. Intermetallic phases were evidenced by changes in sample appearance and their structure was determined by electron diffraction. The presence of an oxide at the interface hindered second phase formation at temperatures at which they were usually expected to form. In aluminum rich couples, the formation of the $AuAl_2$ intermetallic was not observed to form until about 350°C with the oxide present. In a reverse configuration involving a gold rich couple, an amorphous oxide phase was observed between the Al and the advancing Au_2Al front. The movement of the reaction front appeared to be controlled by surface diffusion across this phase. © *2004 Kluwer Academic Publishers*

1. Introduction

The microelectronics industry is heavily dependent upon the bonding between gold and aluminum. Current integrated circuits may utilize 3000 gold to aluminum wire bonds to function [e.g., 1]. Failure at the Au/Al interface can occur in service, due in large part to the formation of intermetallics, specifically $AuAl_2$, which is known as the "purple plague". There are differing diffusivities between gold and aluminum in this phase, leading to the Kirkendall effect [2]. If the rate of atoms moving across the original interface is not equal in both directions when two materials interdiffuse, the result is a net flux of atoms in one direction and a net vacancy flux in the other. As diffusion continues, these vacancies will coalesce into microvoids, eventually forming cavities in the material. The presence of these voids in gold ball bonds weakens the interface and may result in failure. A further failure mechanism has been suggested arising from bond strength reduction associated with oxidation of the intermetallic compounds [3].

Over the past 40 years, much work has been done in an effort to gain a better understanding of the formation of intermetallics in the Au/Al system [e.g., 4, 5]. The crystal structures and lattice parameters of the intermetallic phases AuAl, Au_2Al, and Au_5Al_2 were determined by the evaporation of Au and Al thin films onto alkali halide crystal substrates pre-heated to temperatures between 350 and 450°C [6]. The thin samples were floated from the substrate and mounted onto gold or molybdenum grids for analysis using electron diffraction.

The phases formed during heating depend on the differences in thickness between the Au and Al in thin film samples [7]. In gold-rich couples, Au_2Al was found to form first, changing into Au_4Al after heating for 60 h at 150°C. Aluminum rich films yield initially Au_2Al, which transforms into $AuAl_2$ at temperatures as low as 100°C.

Other studies of the effect of film thickness on intermetallic formation were carried out using Rutherford backscattering spectrometry (RBS). Overlapping films were prepared by e-beam evaporation [8] and evaporation [9] to produce layers giving different thickness ratios. By examining samples with Au to Al thickness ratios of 2.55 and 2.04, it was shown that the preferential formation of Au_5Al_2 over Au_2Al was related to an increasing thickness ratio. RBS data from gold-rich samples revealed the presence of Au_5Al_2, which transformed into Au_4Al above 175°C. Samples containing thicker aluminum layers also revealed the presence of Au_2Al. This phase was shown to be stable up to 150°C, whereupon $AuAl_2$ would form at the Au_2Al/Al interface. Five possible end products were identified depending on the initial thickness ratios of gold to aluminum.

In situ transmission electron microscopy (TEM) studies of phase boundary migration in thin Au-Al couples have been performed [10]. Films of Al and Au were deposited sequentially by evaporation onto carbon-covered specimen grids at room temperature. Samples were placed into a heating stage for *in situ* analysis of phase formation and boundary migration in

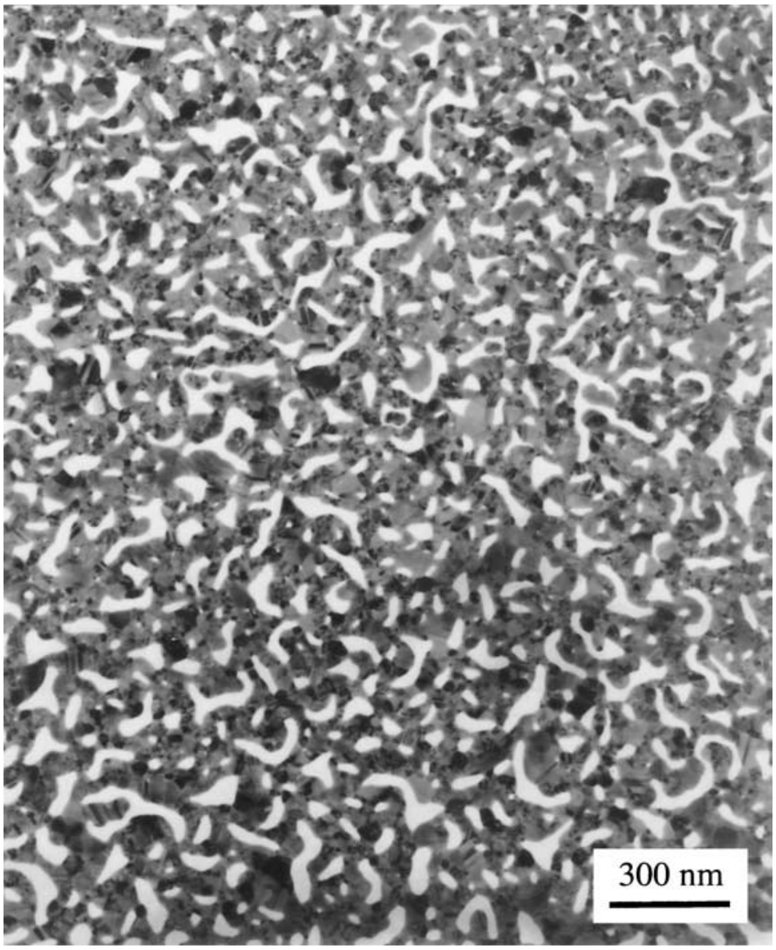

Figure 1 BF image of Au film over Al substrate at 100°C.

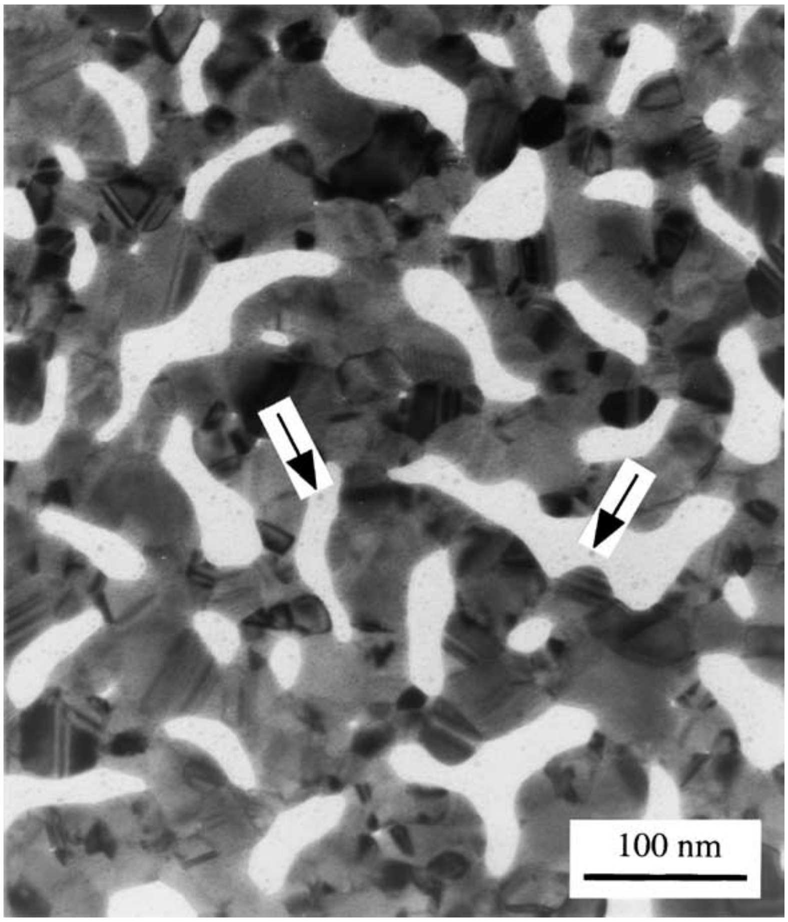

Figure 2 BF image taken at 350°C showing the formation of a second phase in the regions between Au grains.

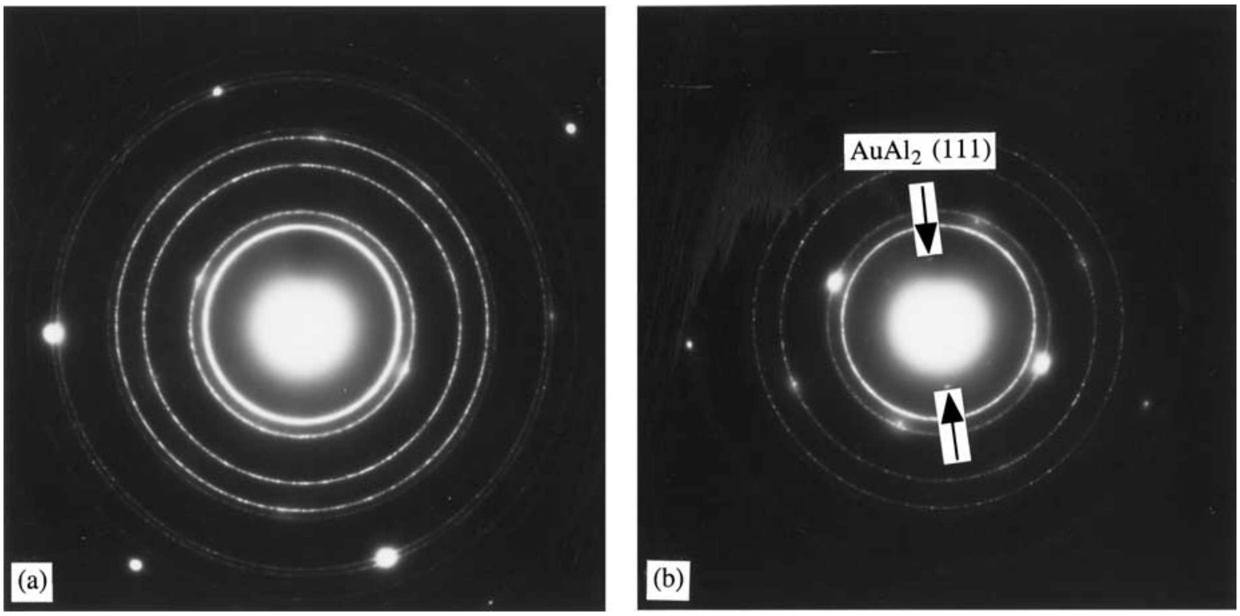

Figure 3 (a) Electron diffraction pattern taken before the heating experiment showing rings from the Au film and spots belonging to the Al substrate. (b) At 400°C additional reflections corresponding to the {111} planes of AuAl$_2$ can be seen.

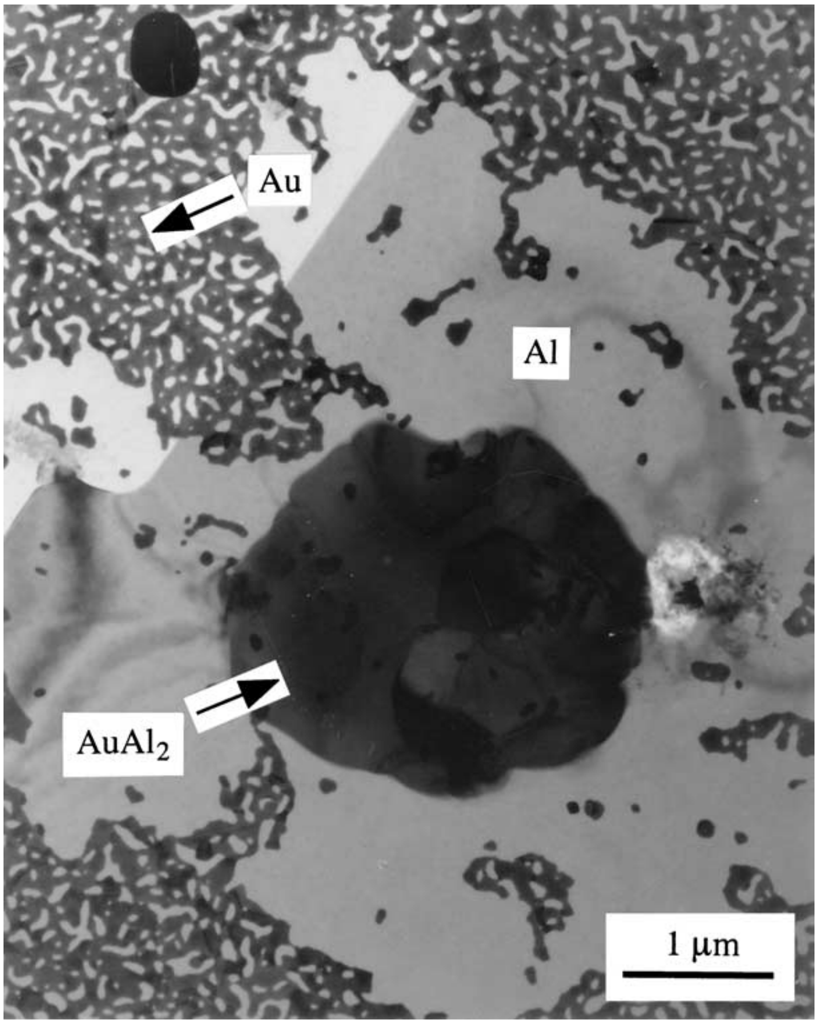

Figure 4 BF image of newly formed AuAl$_2$ grains several hundred nanometers in diameter at 500°C. The region immediately surrounding the intermetallic is depleted of Au, which was consumed in the reaction.

the temperature range 120 to 280°C. As soon as the annealing temperature was reached, a phase boundary formed at the aluminum/gold plus aluminum regions could be observed moving towards the aluminum region. The movement consisted of rapid advancement followed by brief periods of arrest at aluminum grain boundaries. Regions of the sample behind the moving front gradually became transparent to the electron

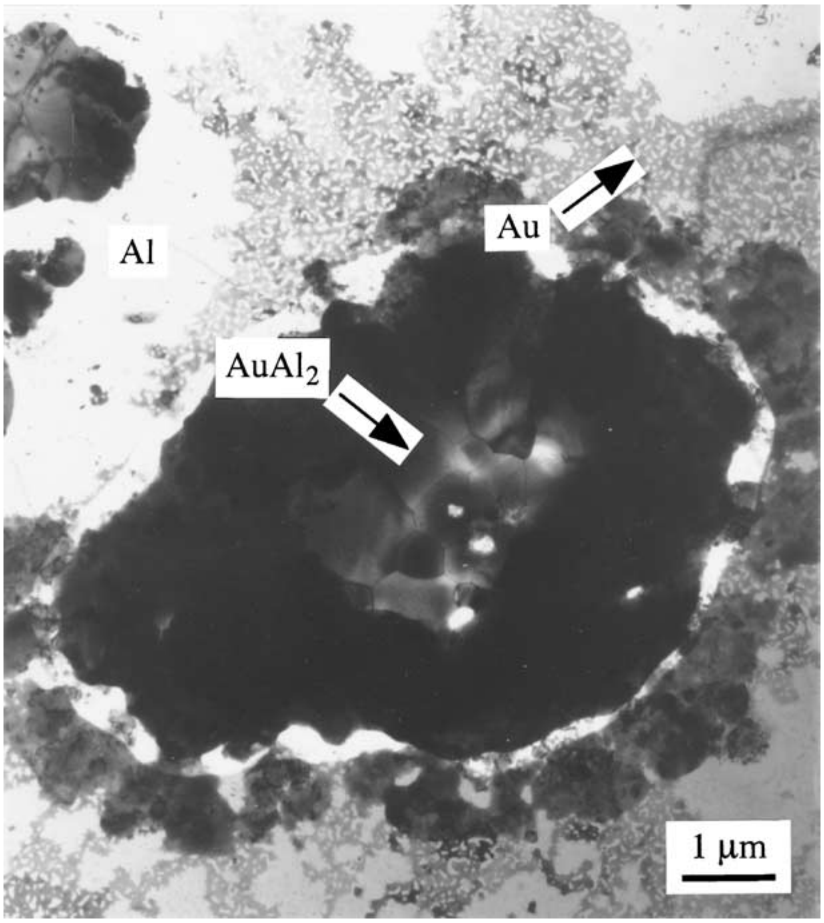

Figure 5 BF image showing the formation of AuAl$_2$ grains at 525°C. Reflections from AuAl and Au$_2$Al were also observed, resulting from reactions between AuAl$_2$ and the Au film.

beam, associated with the formation of Au$_2$Al. Observation of the intermetallic phase showed a well-defined advancing boundary. This suggested the diffusion to be through the Al film, and not restricted to the surface. Analysis performed on several films of varying Al grain size demonstrated the lack of any significant grain boundary diffusion, and that migration of the phase boundary was more rapid through the larger grains.

In Au/Al interfaces formed by wire bonding, the situation may often be even more complicated than these cited studies of intermetallic formation indicate. Bonding between Au wires and Al pads is rarely done before an oxide has the opportunity to form. Because of the bifurcation of device and component fabrication, metallized die may wait several weeks, in some cases months, before bonding and packaging is completed. During this time oxidation of the metallization may be expected to occur [11]. Investigating the role that this oxide layer has on intermetallic formation is of importance to the microelectronics industry. In this present study, *in situ* TEM heating experiments were conducted to study intermetallic formation in Au/Al couples possessing a native oxide on the aluminum.

2. Experimental

Diffusion couples of Au/Al for *in situ* heating studies using TEM were prepared by deposition of a thin film onto pre-thinned electron transparent substrates. Aluminum sample substrates, with grain size $>10\ \mu$m, were prepared by mechanically thinning and dimpling 3mm discs cored from 99.999% pure Al sheet. Perforation of the samples was done by jet electropolishing using a solution of 50% methanol, 48% nitric acid, and 2% hydrochloric acid. Once TEM preparation was complete, samples were aged at room temperature to allow oxide formation to occur. The oxide film thickness under these conditions is approximately 4–5 nm [12]. A Au layer approximately 30 nm in thickness was then deposited on the pre-thinned substrate by DC sputtering.

Gold sample substrates, with grain size $>10\ \mu$m, were mechanically prepared in a similar fashion from 99.987% purity slugs, the final thinning to electron transparency was done by ion milling using 4 kV Ar$^+$. Approximately 75 nm of Al was then deposited onto the samples by RF sputtering. The samples were kept at room temperature prior to heating.

The couples were heated from 25 to 500°C using a Gatan heating holder in a Philips CM200 transmission electron microscope operated at 200 kV. *In situ* heating of the samples allowed direct observation of changes in sample appearance during formation of the intermetallics. Electron diffraction was used to identify the phases present and energy dispersive spectrometry (EDS) was used for qualitative chemical analysis of the samples. The temperatures of intermetallic formation were measured for each sample and compared to results in the literature.

3. Results and discussion

The first set of heating experiments were conducted on samples consisting of a Au film deposited on an oxidized Al substrate. The average grain size of the as-deposited Au film was ~20 nm. As the temperature was increased to 100°C, coalescence of the Au grains occurred. The microstructure of the Au film at this temperature is shown in Fig. 1. In pristine interfaces, i.e., without an interfacial oxide layer, previous studies demonstrated that the aluminum-rich intermetallic, $AuAl_2$, would form at temperatures as low as 100°C [7]. The first indication of second phase formation in the present study occurred at 350°C, diffusion between the aluminum and gold apparently being hindered by the presence of the oxide at the interface. Images of samples at this temperature revealed the formation of new grains, several nanometers in diameter, which had nucleated in regions between the Au grains (Fig. 2). At 400°C electron diffraction patterns from these regions contained reflections that could be indexed as arising from the {111} and {222} type planes of $AuAl_2$. Fig. 3a and b are electron diffraction patterns taken at 100 and 400°C, respectively, showing the additional {111} reflections present at the higher temperature. Formation of the intermetallic $AuAl_2$ is consistent with aluminum rich thickness ratios [9]. It was not until sample temperatures of 500°C that large intermetallic grains, several hundred nanometers in diameter, were formed. Fig. 4 shows a cluster of newly formed grains of $AuAl_2$ surrounded by a region of the sample depleted in Au after heating to 500°C. The reaction occurred instantaneously, ceasing only when the local Au source was exhausted. When the temperature was increased to 525°C the reactions continued leading to the formation of several intermetallic phases (Fig. 5). These regions consisted primarily of $AuAl_2$, though reflections belonging to AuAl and Au_2Al were also observed in the diffraction patterns. The presence of these more gold rich intermetallics is the result of reactions between the $AuAl_2$ phase and the Au film.

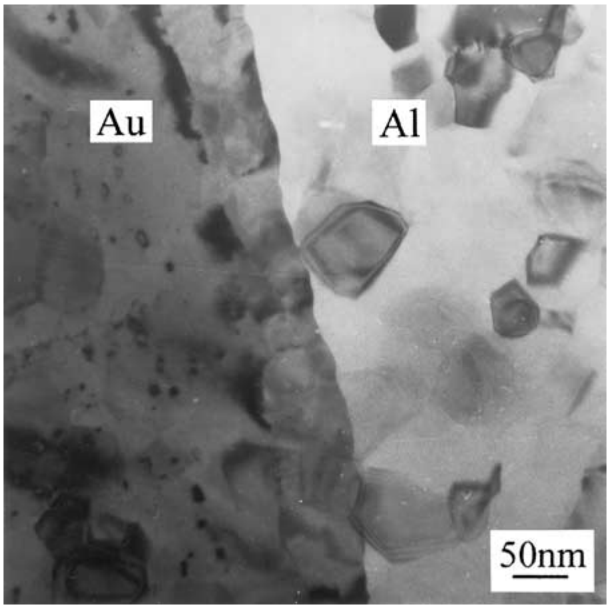

Figure 6 BF image of Au substrate/Al film couple prior to heating.

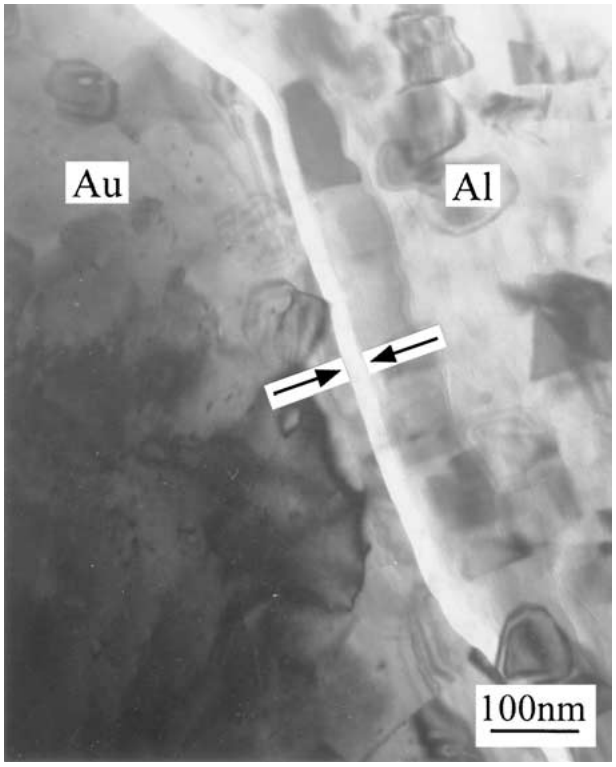

Figure 7 Image taken at 150°C showing an intermediate layer formed at the Au_2Al/Al boundary. In the Au side of the couple, indicated in the image, unreacted Au is the predominant phase at this temperature.

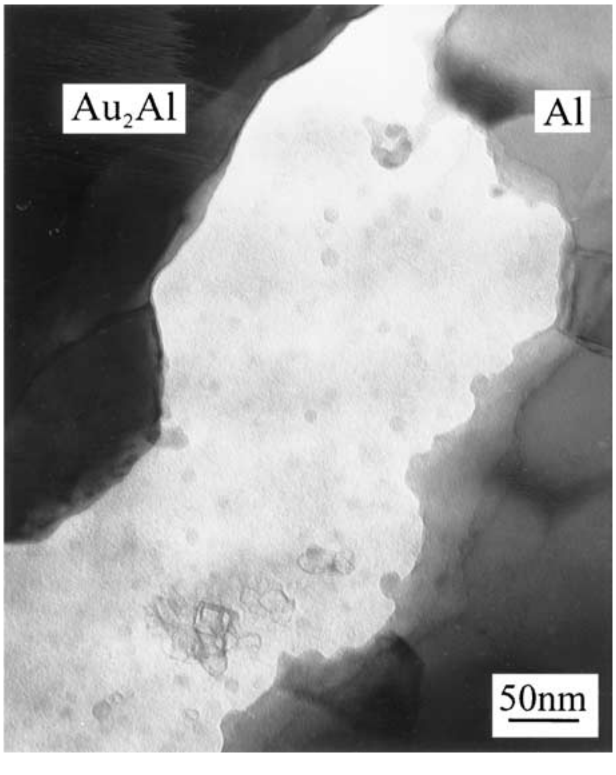

Figure 8 BF image of the phase boundary after the formation of Au_2Al at 189°C.

A second set of heating experiments involved Al films deposited on electron-transparent Au substrates. Fig. 6 shows the initial state of one of the Au/Al couples where the Al film extends over the edge of the Au foil substrate. The size of the Al grains in the sputter-deposited layer is in the range of 50–100 nm. Samples

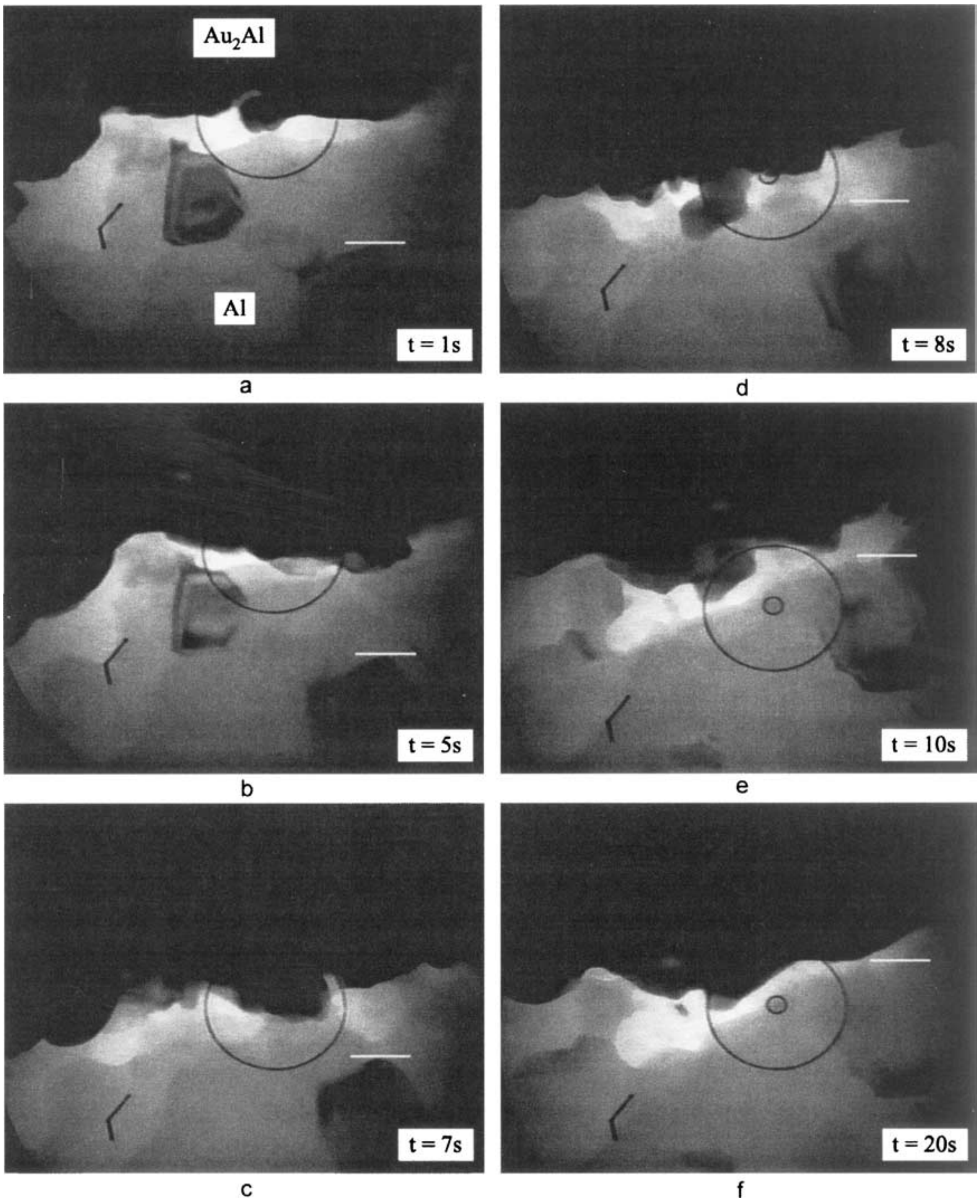

Figure 9 Video stills of the phase boundary movement. A reference point has been indicated by a white line. The intermediate phase is visible when the boundary is at rest (a, e, f). While the boundary is in motion, the intermediate layer recedes (b–d). Shown sequence lasted 20 s.

left at room temperature for several weeks were found to contain the intermetallic compound Au_5Al_2. This observation is consistent with those of other groups, which showed the formation of Au_5Al_2 in Au/Al thin film samples after one month of aging at room temperature [9]. During each heating experiment, it was noticed that the overlapping Au plus Al regions of the sample became increasingly opaque to the electron beam in the temperature range of 100–200°C. Diffraction data revealed that this coincided with the formation of Au_2Al.

Fig. 7 is a bright field image recorded at 149°C showing an intermediate phase with lower mass-thickness contrast at the Au_2Al/Al boundary. EDS analysis indicates that this intermediate phase is aluminum oxide. Tilting the sample did not induce contrast changes in this region and diffraction patterns contained no sharp diffraction maxima. These observations suggest that this intermediate phase between the Al and Au_2Al is amorphous. Its origin is most likely oxidation of the Al film in air prior to insertion of the sample into the electron microscope. In several locations, Al grains can be seen across the intermediate layer, indicating that the film is discontinuous at the wedge tip. The width of the intermediate phase is about 20 nm, and it became increasingly wider as the temperature was increased. At 189°C the width of the intermediate layer was nearly 250 nm in some regions, as shown in Fig. 8.

Because of the wedge-shaped geometry of the initial Au foil substrate the oxide layer actually straddles the Au_2Al and Al regions. For further reactions to occur there must be surface diffusion along the oxide film. From a study of the micrographs it appears that the Al film is consumed by the advancing intermetallic phase at the tip of the sample forming a series of Au-rich phases. The movement of the phase boundary was first apparent at 340°C. This temperature is very similar to that needed for Au diffusion through the aluminum oxide layer in the first set of samples used in this study.

Fig. 9 shows a montage of images taken from a videotaped heating sequence. The amorphous intermediate phase is clearly visible as a region of lighter contrast between the Au_2Al and Al. After 5 s the intermetallic can be seen to diffuse towards the Al region. The movement occurs in a series of advances followed by short periods of arrest. Boundary motion appeared to be accelerated through the larger Al grains, but was frequently pinned at the boundaries between large grains.

Aluminum grains ahead of the advancing phase boundary were in a state of stress, as evidenced by the constant motion of the bend contours. Further movement of the pinned boundary could be instigated by either an increase in heater temperature or by localized heating using a focused electron beam. As the phase boundary advanced, the apparent width of the amorphous layer decreased. As soon as movement slowed or arrested, the width would increase until a uniform boundary between the intermetallic and Al grains was formed. This may be due to surface tension effects that temporarily dominate when boundary motion is pinned. Since the Au_2Al intermetallic is of higher gold concentration than the amorphous intermediate phase, it is the first to migrate. The speed at which the front moves is dependent on the grain size of the Al ahead of the boundary, and the temperature at which the reaction takes place. The velocity of the front was estimated from several videotaped sequences to be $\sim 20\ \text{nm} \cdot \text{s}^{-1}$. Behind the reaction front the newly formed intermetallic appeared to form nano-crystallites that were 50–100 nm in diameter. Diffraction data identified these grains to be Au_2Al.

At 350°C the end reaction products were a mixture of Au_2Al, Au_5Al_2 and Au_4Al. These products are consistent with Au-rich thickness ratios [9]. Due to the wedge shape geometry of the samples, the thickness ratios along the sample length were variable. Areas closest to the perforation would be Al rich, whilst further from the hole the sample would be increasingly gold rich. Because only 75 nm of Al was deposited, the regions in which the Al layer was thicker than the Au were quite limited, and most probably consumed by Au-rich intermetallics. Frequently, two intermetallic phases (e.g., Au_2Al and Au_4Al) were present at the conclusion of the heating experiments, confirming the existence of variable thickness ratios.

4. Conclusion

The use of electron transparent samples as substrates for the *in situ* study of solid-state reactions has been demonstrated. The presence of an oxide layer on Al foil substrates inhibits diffusion in Au/Al couples, increasing the temperature required for intermetallic formation. For example, the formation of $AuAl_2$ did not occur until 350°C, more than 200°C above the temperature found when an interfacial oxide layer is not present. In diffusion couples formed by depositing Al onto Au foil substrates intermetallic formation occurred within the expected temperature ranges. The composition of these phases was consistent with thickness ratios where Au $>$ Al. Several of the samples contained multiple end products arising from the wedge-shaped nature of the samples. The presence of an amorphous aluminum oxide layer bridging the Al and Au_2Al phases controls the extent of subsequent reactions because surface diffusion of the intermetallic is required for the reactions to continue. This study indicates that interdiffusion and intermetallic formation in Au/Al couples is complicated by the presence of native oxide formation on the Al—a situation that may be encountered in Au ball bonding to Al.

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