On the Formation of the Ordered Phases CuAu and Cu₃Au at a Copper/Gold Planar Interface

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The formation of the ordered compounds, Cu_3Au and $CuAu$, has been observed in a study primarily aimed at determining the rate of interdiffusion in the gold-copper system. In the planar diffusion couples aged at temperatures from 50°C to 400°C and for times to 4 years, the compounds were observed to form as layers at the gold/copper interface for temperatures under 400°C. The layers were visible in the scanning electron microscope backscattered image of polished cross-sections, and their compositions were determined by the corresponding plateaus observed in the electron microprobe X-ray intensity profiles. Kirkendall type porosity was also observed to form in the copper-rich zone adjacent to the ordered compound layers. These results are compared and contrasted to the findings of several other studies which have considered this reaction and its practical implications to device performance.

THE crystallographic order-disorder transformations which occur over several composition ranges in gold-copper alloys[1] have been much studied classical reactions. Numerous references can be found dealing with the equilibrium structures, temperature and composition limits of stability, kinetics and thermodynamics of the order-disorder transformations, and arrangement of the ordered domains in the Cu_3Au, $CuAu$, and $CuAu_3$ superlattices. The differences in crystallographic structure and the transformations between the several superlattices which can form at the same composition, namely CuAu(I) and CuAu(II) and also Cu_3Au(I) and Cu_3Au(II), have also been thoroughly investigated. These studies are normally carried out on bulk or powder alloy samples of uniform composition which are fully homogenized at elevated temperature, quenched to a state of disorder, and then annealed at temperatures below about 400°C to study the ordering reaction.

Another mode whereby this reaction can occur and which has implications in current electronics technology is via diffusion in layered structures of copper and gold, which are present in connector components, hybrid circuit lead frames, and other metallizations. The occurrence of diffusion at low temperatures, primarily via defect paths,[2,3] and also at somewhat high temperatures, but still under 400°C, via vacancy-atom exchange through the crystal lattice[4,5] is an unavoidable process. During this diffusion process, regions, which are initially near the gold/copper interface, are going to develop which have the proper compositions to be able to form the ordered compounds.

Tu and Berry[6] were among the first to report the appearance of layers of Cu_3Au, $CuAu_3$ and, for longer annealing times, CuAu at the interface of copper-gold couples following diffusion anneals. They concluded that the ordered compounds form as sequential layers parallel to the original copper/bold interface with the Cu_3Au phase appearing first, followed by the $CuAu_3$

phase. The CuAu phase forms much later in the reaction and grows at the expense of the $CuAu_3$ phase. They also concluded that atomic transport for growth occurs by rapid boundary diffusion but that the rate limiting step in growth is the local atom movements that take place in the crystal lattice behind the advancing interface to secure order.

The findings of Borders[7] differ from those presented above. No evidence of a growing layer of any of the intermetallic compounds is reported. He suggests a model whereby the intermetallic phases grow into the parent grains of the gold and copper films from grain boundaries which serve as the diffusion paths. The result is patches of Cu_3Au in the copper film which are more dense near the original Cu/Au interface than within the parent copper film. This is in contrast to a distinct "layer" as advanced by Tu and Berry.[6] He also suggests that the $CuAu_3$ phase is distributed uniformly as patches in the grain boundary regions throughout the gold layer after annealing, thus giving a uniform composition of copper-enriched gold but not a complete layer of $CuAu_3$.

An example of the device related effects of these layers, regardless of their actual morphology, was reported by Hall, et al.[8] They reported a reduction in the pull strengths to fracture of the gold-plated copper lead frames which were thermocompression bonded to gold metallized thin film circuits, when aged for long times at 200 to 300°C. Analysis of the fracture faces revealed the presence of Cu_3Au in the fracture plane. Failure was ascribed to the formation of this limited ductility phase.

Feinstein and Snyder, in a more recent study evaluating bond failures in the copper-gold system, also observed intermetallic phase formation, but also observed the formation of extensive Kirkendall porosity.[9] They attributed the failures primarily to this latter factor.

During the course of a study on the interdiffusion of copper and gold in the low and intermediate temperature ranges for very long periods of time, part of which has been previously reported,[5] observations were made relating to the formation of these ordered

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compounds. Although not the designed intent of the study, the data do provide insight into the sequential growth of the phases, a qualitative feel for growth rate, an answer to the existing discrepancy on morphology, and a heretofore unreported effect of a third element addition, namely cobalt.

EXPERIMENTAL PROCEDURES

Materials and Heat Treatments

The base material used for all samples was 1.55 mm thick, commercial OFHC, annealed copper sheet. The sheet had an ASTM grain size of 9. Rectangles (2.5 cm by 1.25 cm) were cut from the sheet and given the following pretreatment prior to plating: a) electro-cleaned in an alkaline cleaning solution; b) rinsed in a 50 percent aqueous solution of hydrochloric acid to neutralize the surface; c) dipped in a nitric acid-sulfuric acid-water bright dip to final clean and lightly etch the surface to be plated. Gold from three different plating baths was used in preparing the various coupon samples. Samples designated series A and B were electroplated with pure gold from an acid citrate bath to nominal thicknesses of 100 μm and 25 μm, respectively, on the copper substrate. Samples designated series D and F were electroplated from an Autronex CI bath, which produces a hardened gold layer containing approximately 0.3 wt pct codeposited cobalt, to nominal thicknesses of 25 μm and 5 μm, respectively. Finally, samples designated series H were electroplated from an Autronex C bath, which produces a hardened gold layer with nearly 1.0 wt pct codeposited cobalt, to a nominal thickness of 5 μm. Subsequent to plating the rectangles were cut into squares, 6.25 mm on a side, for the various thermal exposures.

Details of the annealing treatments and furnaces were described in a previous publication.[5] The specific annealing conditions for these experiments were temperatures of 50, 100, 150, 200, 250, 300 and 400°C for times ranging from as short as two hours at the highest temperature to as long as 48 months at the lowest temperature. All anneals were carried out in laboratory air.

Concentration-Distance Profiles

The heat treated samples were mounted in aluminum-lucite conductive potting compound in preparation for X-ray analysis. The mounted couples were ground perpendicular to the gold/copper interface to a region in the central portion of each sample. This was done to avoid probing edge regions where extraneous diffusion effects may have occurred. Final preparation of the surface to be probed consisted of abrasive polishing through 1 μm diamond paste.

X-ray intensity vs position data (penetration curves) were measured with an electron microprobe. A continuous X-ray intensity-distance profile was obtained by line-scanning the incident electron beam along a line perpendicular to the interface. The line-scanning
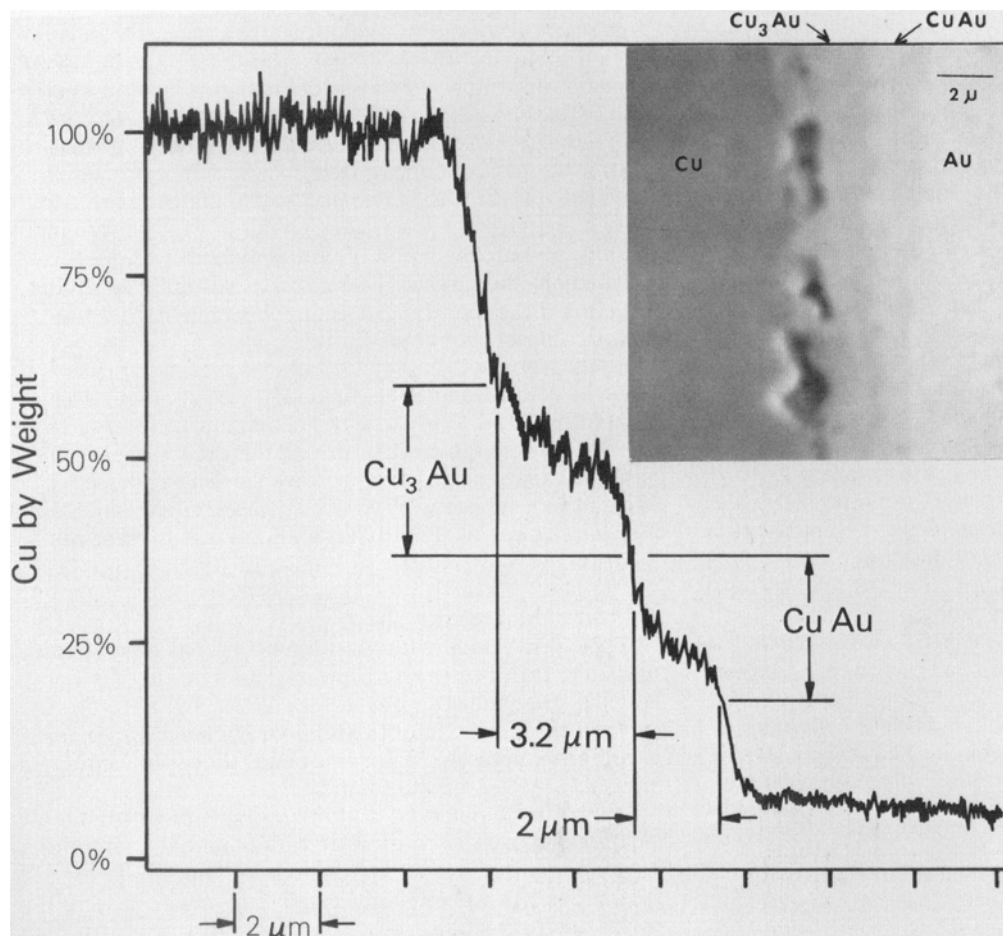

Fig. 1—CuK$_\alpha$ X-ray probe profile of 25 μm, 0.3 pct cobalt-gold layer on Cu aged 250°C for 4 months.

voltage signal was applied to the Y-scale of the plotter. This provided a continuous trace of X-ray intensity *vs.* position across the diffusion zone. Profiles were obtained monitoring the Au-Mα X-radiation and also the Cu-Kα X-radiation. A typical X-ray intensity profile is given in Fig. 1 for the Cu-Kα X-rays on a sample aged at 250°C for 4 months.

Data Analysis

The cross sections were also photographed in the SEM using the backscattered electron image. The ordered layers were readily imaged in this mode as can be observed on the photographic insert of Fig. 1. The median layer thickness was determined both from measurements on the photographs as well as measurements of the concentration plateau widths on the X-ray scans. These latter measurements were made by first converting the X-ray intensity-position curves to chemical composition-position curves using the MAGIC (Microprobe Analysis General Intensity Corrections) computer program.[10]

No correction was implemented to account for the small false gradient caused by the fact that the electron beam of the microprobe has a finite diameter (about 1.2 μm). As shown by Lo and Schuele,[11] this
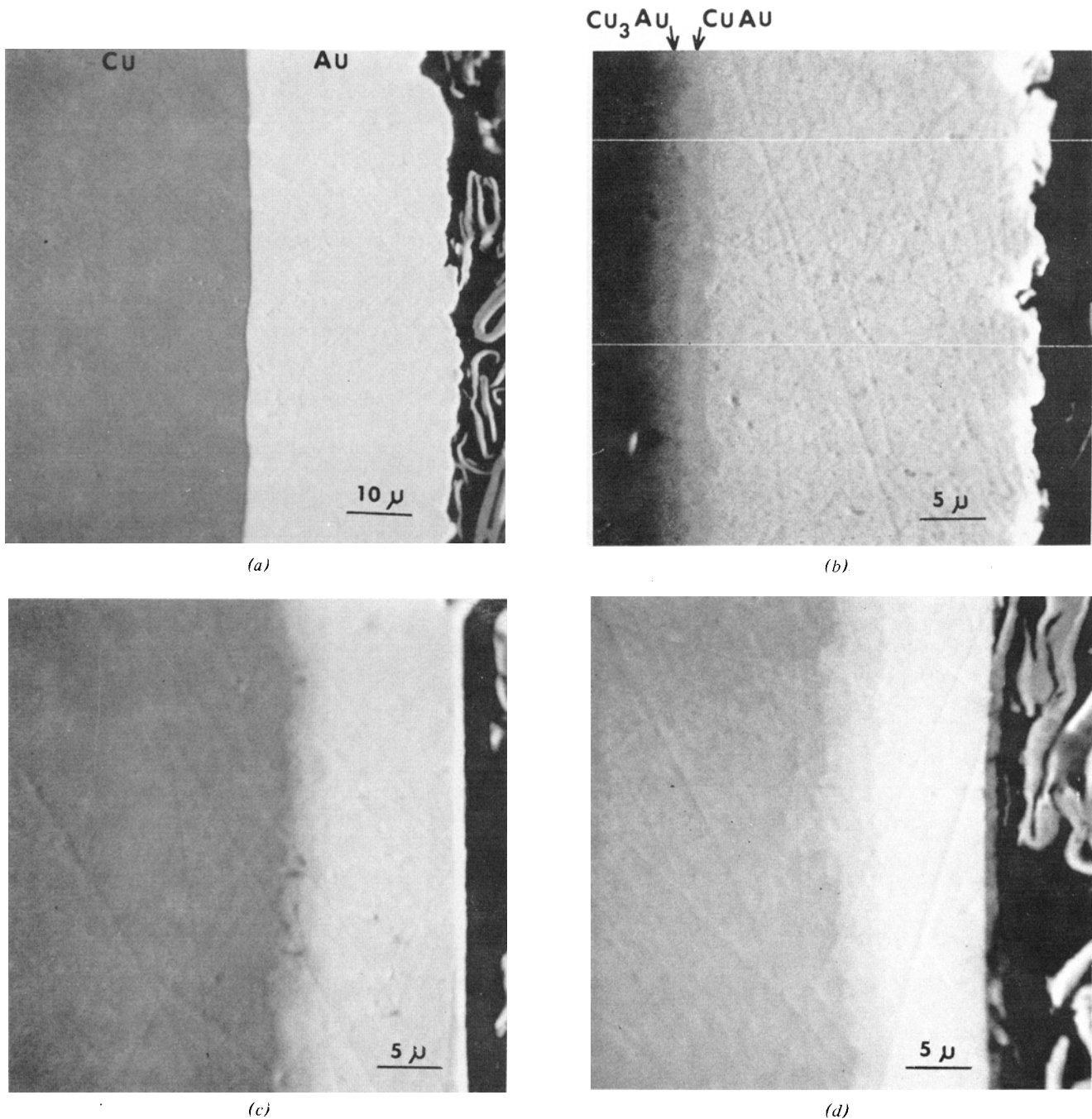

Fig. 2—Typical SEM backscattered images showing gold/copper couple cross sections after various annealing times and temperatures. For very long times at 150°C (*a*) no ordered compounds are detectable, but after anneals at 250°C for 3 or 4 months (*b-d*) all the types of golds used show ordered layers. (*a*) Pure gold; aged 150°C for 24 months, (*b*) pure gold; aged 250°C for 3 months, (*c*) 0.3 pct Co-gold; aged 250°C for 4 months, and (*d*) 1.0 pct Co-gold; aged 250°C for 4 months.

has only a minor effect for the larger diffusion zones of this study. The primary influence of the beam diameter appears to be that the plateaus in concentration across the ordered layers have a gradient rather than a fixed composition. However, as shown in Fig. 1, the inflection points, which mark a perceptible change in slope, fix the boundaries of the ordered layers with reasonable accuracy. The concentration gradients across the ordered layers may also be partly produced by the fact that the ordered compounds are stable over a rather wide composition range[12] and thus the layers in these couples may, in fact, include a range of compositions. The inflection points correspond rather closely to the compositions of the ordered phase boundaries for the several experimental temperatures evaluated. Furthermore, the ordered phase layer widths determined from both the microprobe traces and the SEM images showed excellent correlation.

RESULTS

At temperatures of 150°C and below and for aging times as long as 3 years at 150°C and 4 years at 50°C, no ordered layers were detected in either the X-ray traces or scanning electron microscope images. A typical example of this case is shown in Fig. 2(a) for a pure gold on copper couple. However, for times in excess of about one year at 200°C or for shorter times at the other temperatures investigated between 200°C and 400°C, well resolved layers of two of the ordered phases in the gold-copper system were detected. Typical examples of such layers for the three different plated golds observed in this study are shown in Fig. 2(b) thru (d). The thickness of the layers can be seen to vary as a function of the type of gold plating for these anneals at 250°C over a time span of 3 to 4 months. This effect will be highlighted more fully with the microprobe results.

The microprobe profiles, when corrected from X-ray intensity to composition, showed the compositional "plateauing" was centered about 50 wt pct copper and 25 wt pct copper in all cases. The nature of these plateaus is shown quite clearly in the profile of Fig. 1 and their correspondence to the layers revealed in the SEM images is evident. It is concluded that these
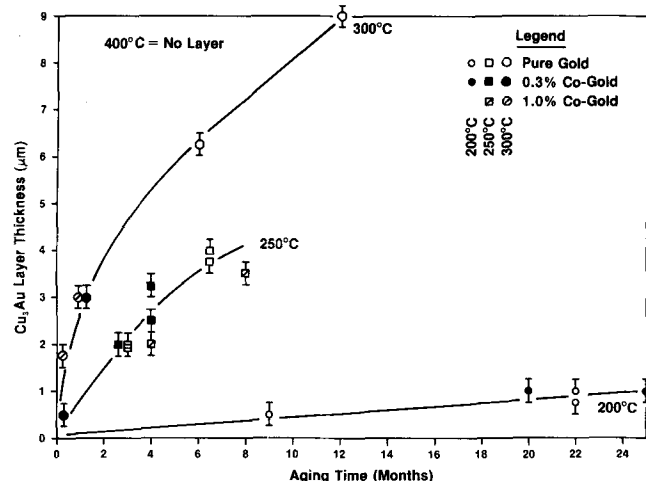

Fig. 3—Cu₃Au layer thickness vs aging time at 200, 250 and 300°C for the various gold and Co-gold layers.
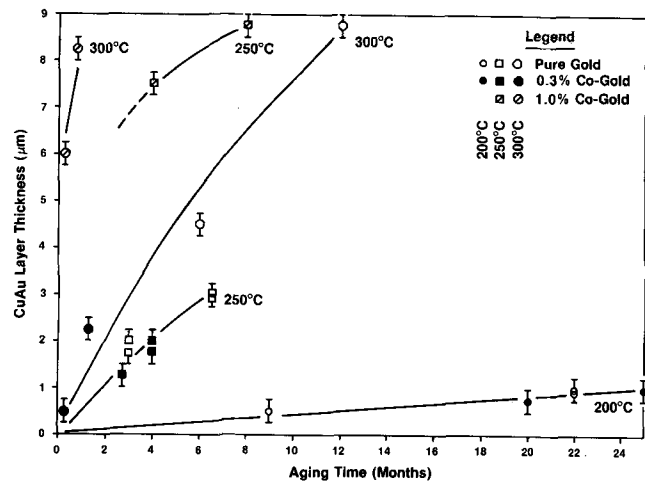

Fig. 4—CuAu layer thickness vs aging time at 200, 250 and 300°C for the various gold and Co-gold layers.

plateaus correspond to the formation of zones of the ordered compounds Cu₃Au (50 wt pct copper) and CuAu (24 wt pct copper). The range of compositions observed across the plateau may be partly attributable to the resolution limits of the microprobe, but also to the fact that the ordered compounds are stable over a rather broad range of compositions which increase with decreasing temperature.[11] This latter fact was utilized to establish the approximate width of the ordered compound layers on the X-ray intensity traces. The compositions corresponding to the limits of stability of both the Cu₃Au and CuAu phases at the given temperature, as taken from the equilibrium diagram, were used to define the boundaries of the ordered phase layers as shown in Fig. 1. As pointed out previously, this procedure gave layer widths which correlated quite closely with those measured on the corresponding SEM images.

Plots of the thickness measurements for the Cu₃Au and CuAu layers as a function of time at the various temperatures of exposure for the pure gold, 0.3 pct Co-gold, and 1.0 pct Co-gold are given in Figs. 3 and 4, respectively. Each thickness value is the average of 3 to 5 measurements on the microprobe traces and the error bars represent the estimated accuracy of this measurement of ±0.25 μm. Layer thicknesses ranging from under 1 μm to as large as 9.0 μm can be observed, with the thicknesses of both the Cu₃Au and CuAu layers increasing with time and temperature as would be expected. Where comparable times and temperatures and original gold layer thicknesses exist, the layer growth rates in both the pure gold-copper and 0.3 pct Co gold-copper are found to be similar. In most all cases for these two systems, the Cu₃Au layer is equal to or slightly greater in thickness than the CuAu layer after a given anneal.

The more Co-rich gold-copper system, however, shows a striking difference. Although the Cu₃Au layer growth is similar to the other systems, the growth rate of the CuAu layer is greatly accelerated in this Co-enriched gold-copper structure (see Fig. 4, 250°C and 300°C curves). The results for 5 μm thick Co-gold layers demonstrate that in times as short as 4 months at 250°C and one to 3 weeks at 300°C the entire original Co-gold region is converted to a thin layer of Cu₃Au
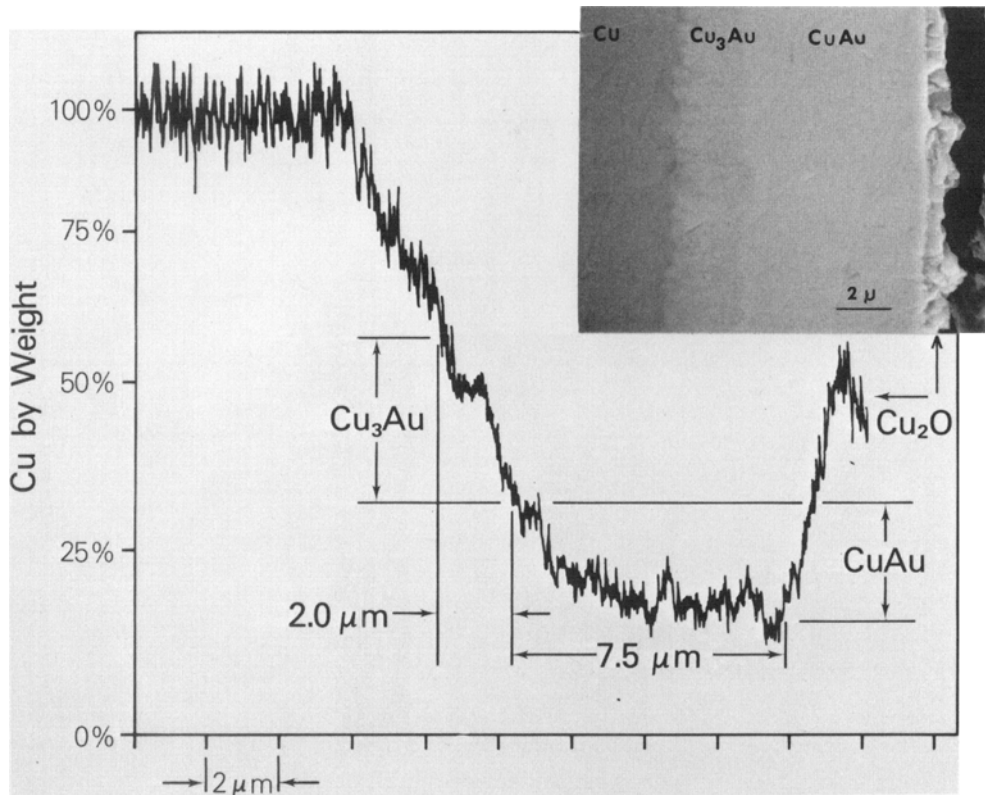
Fig. 5—CuK$_\alpha$ X-ray probe profile of 5 μm, 1 pct cobalt-gold layer on Cu aged 250°C for 4 months.

and the balance entirely to a layer with a reasonably uniform composition corresponding to CuAu. The original Co-gold layer, which had a thickness of about 5 μm, now has a total thickness exceeding 10 μm with the inclusion of sufficient copper to make these two alloy layers. This result is shown graphically in Fig. 5 and may be contrasted to Fig. 1, which shows the result for the identical time and temperature in the 0.3 pct Co gold-copper system. Figure 5 also shows that the copper diffusion, which is necessary to form these layers, was also extensive enough to have enabled a thick layer of copper oxide to form on the CuAu surface.

Figure 6 shows the 1.0 pct Co gold-copper system after annealing at 250°C for 8 months. Comparing to Fig. 5, it is seen that doubling the annealing time has
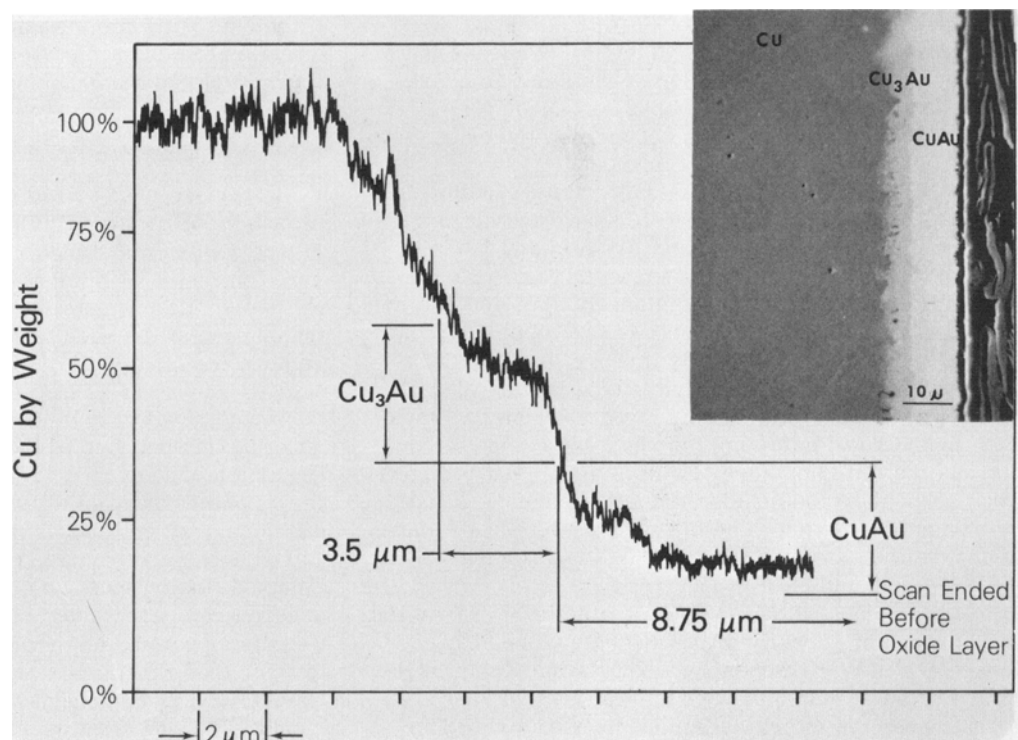

Fig. 6—CuK$_\alpha$ X-ray probe profile of 5 μm, 1 pct cobalt-gold layer on Cu aged 250°C for 8 months.

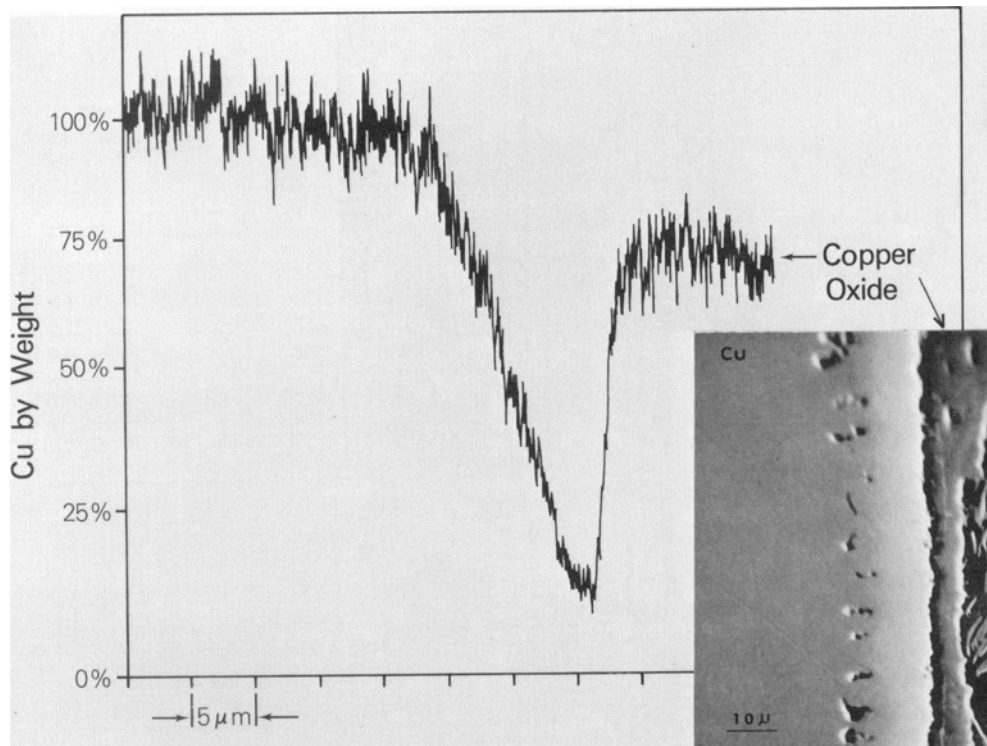Fig. 7—CuK$_\alpha$ X-ray probe profile of 5 μm, 1 pct cobalt-gold layer on Cu aged 400°C for 4 days.

nearly doubled the thickness of the Cu$_3$Au layer but the CuAu layer, which makes up the balance of the original gold layer, has not changed appreciably in thickness or composition. The oxide on the surface has continued to grow, however, indicating that copper continues to be transported via diffusion through these ordered layers to the surface, where it can react with the air environment.

Identical behavior was observed at 300°C as was described above for anneals at 250°C. In only 3 weeks at temperature for the 1.0 pct Co gold, the entire layer is converted to about 3 μm of Cu$_3$Au and the balance (8.25 μm) to CuAu (see Figs. 3 and 4). Whereas the 0.3 pct Co gold, when annealed at the same temperature for a longer time of 5 weeks, produces a similar Cu$_3$Au layer of about 3.0 μm but forms a layer of CuAu only a little over 2.0 μm in thickness.

At 400°C, which is near the upper limit of stability for the ordered phases, ordered layers are no longer observed for pure gold, 0.3 pct Co-gold and 1.0 pct Co-gold/copper couples. As shown in Fig. 7 for the 1.0 pct Co gold-copper system annealed at 400°C for four days, the composition profile for copper decreases continually and monotonically through the diffusion zone without evidence of a plateau. Likewise the SEM microprobe insert reveals no layers but only a gradation in contrast indicating the changing composition across the diffusion zone. Increasing time at temperature at or above 400°C also did not produce any ordered compound formation. The behavior at 400°C and above also was the same for the pure gold and 0.3 pct Co gold layer samples.

A final point, which is demonstrated in Fig. 7, is the appearance of porosity in the diffusion zone. This is concluded to be Kirkendall porosity attributable to the more rapid diffusion of copper into the gold zone than gold across the interface into the copper zone. The

resulting excess vacancies left behind in the copper region coalesce into voids or porosity along a line within the copper-rich region. The density of these voids increased with time and temperature, hence amount of diffusion, as would be anticipated. Similar porosity was also observed at temperatures as low as 250°C, where the ordered layers were concurrently formed. This porosity appeared at the interface between the copper-rich region and the Cu$_3$Au layer as can be clearly observed in Fig. 1 for the 250°C anneal. It presumably will occur at even lower temperatures, if the annealing time is sufficiently long for enough diffusion to occur. The porosity was observed in all 3 types of plated gold-copper couples.

DISCUSSION AND CONCLUSIONS

At temperatures of 150°C and below, no ordered phases were observed. This is expected since the total lattice diffusion distance in copper-gold is only measured in tenths of micrometers for several year anneals over this temperature range.[5] As shown by extrapolation of the results of Tu and Berry,[6] ordered regions less than 0.15 μm wide might be expected for anneals of 4 to 12 months duration near 150°C. This is below the resolution limit of the electron microprobe scan (beam spot size of the order of 1 μm) to distinguish a band of near constant composition representing a zone of ordered phase or phases within a total diffusion gradient profile of less than 0.5 μm.[5] These expectations are based primarily on the condition that lattice diffusion must be strongly involved in the ordered compound layer formation. Clearly penetration distances via defect path diffusion are much greater than those cited above.[2,3] However, in order to form layers or zones of ordered phase, diffusion must carry sufficient quantities of copper into the

grain interiors to attain the proper composition to make ordering possible. This stage of the process should be controlled by the lattice diffusion rate.

For the times observed at 200°C and above, ordered layers exceeding 1.0 μm in width, which are readily resolved via this technique, were found. Their appearance in the SEM images and the corresponding distinct plateaus in the X-ray profiles, such as given in Fig. 1, support the model for growth expressed by Tu and Berry[6] and thus are not in accord with the hypothesis of Borders.[7] The ordered zones do indeed appear to grow as layers parallel to the original copper/gold interface with relatively sharp steps in composition between the different phases, as advanced by the former authors.[6] A model[7] given by rapid diffusion along boundaries followed by formation of patches of ordered phases in the boundary region, which would decrease in density with increasing distance from the original interface, is not supported by these observations.

Tu and Berry[6] observed that the Cu_3Au and $CuAu_3$ phases form initially, but that after long times, e.g., 60 h at 200°C, the CuAu phase appears and then grows at the expense of $CuAu_3$. They observed that after 210 h at 200°C only Cu_3Au and CuAu(I) remained. The present results are entirely consistent with this picture also as only Cu_3Au and CuAu were observed for annealing times measured in weeks, months, and years.

No explanation can be offered for the apparent accelerating influence of the higher cobalt concentration on the formation of CuAu, but the results for the anneals at 250°C and at 300°C clearly show it to be so (see Fig. 4). It is likely that the cobalt content somehow affects the diffusion rate to provide the amount of copper necessary to form the much larger layer of CuAu in the same time frame. The general impression from the data was that the amount of Kirkendall type porosity was greater in comparably aged samples for the higher cobalt content alloy. This is also consistent with the proposed acceleration of the copper diffusion into the gold. However, this point is advanced with a word of caution, since this increased porosity at the interface may also be influenced or contributed to by the decomposition of organics in electrodeposited hardened gold, which is known to occur at these elevated temperatures.[13]

Hall, et al,[8] in their evaluation of loss of bonding strength in lead frames bonded to thin film circuits, attributed this failure to the formation of the Cu_3Au ordered phase at the interface, which was detected by X-ray diffraction on the fracture faces. It is not clear why either $CuAu_3$ or CuAu, which one depending on aging time and temperature, was not observed in ad-

dition to Cu_3Au, since the combined results of Tu and Berry[6] and this study suggest one of these two additional phases should be present. Nevertheless, the authors concur with their conclusion that the presence of an ordered compound, formed via diffusion at the interface, was primarily responsible for loss of strength. Hall, et al,[8] also considered oxidation and pore formation as potential causes, but ruled out the former and considered the latter less likely to be effective in creating failure than the ordered phase formation. The present results suggest, however, that pore formation does occur as a necessary part of the process creating the ordered layers and contributes to decreased strength. In fact, the results of Feinstein and Snyder[9] demonstrate that in cases where the gold is very thin and effective sinking of the copper exists to maintain the rapid diffusion of copper, pore formation after one to four exposures at 350°C is so extensive as to clearly be the cause of lost bond strength.

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