Diffusion-Related Behaviour of Gold in Thin Film Systems

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The process of diffusion in the solid state is one aspect of behaviour in gold thin film systems which has received increased attention as gold layers have had to be made significantly thinner without sacrificing their reliability. This article reviews the characteristics of this process for gold over the various one- and two-layer base metal systems which are in common use by the electronics industry. A number of interesting phenomena are described and related to the service problems which they may cause in various devices.

The electronics and telecommunications industries require high reliability in electrical connections. Thus, gold and gold alloys have long served as the standard for the contact or surface material in applications such as separable connectors, relays and lead frame metallization. Their low resistivity for electrical conduction, high chemical passivity for resistance to film formation, high bondability for ease of thermocompression and other forms of joining and their ease of application by standard manufacturing processes such as electroplating, sputtering, welding or cladding are ideally suited to the requirements of these devices.

Historically, gold was used in relatively thick layers deposited over the entire contact region, hence there was little concern over the substrate metal and its interaction with the gold or the environment. The surface region would remain as pure gold with its favourable properties through the device lifetime. However, the significant increases in the cost of gold and the concurrent economic pressures of this decade have stimulated appreciable efforts toward replacement of or reduction in gold usage per device. The more conservative use of gold has been the approach usually pursued. In this, a reduction from classically specified thicknesses had to be accomplished without any sacrifice in reliability. Thus, careful consideration had to be given to the behaviour of gold in thin film systems involving more than one metal.

Several potential mechanisms which can degrade the performance of a thin gold over base metal system are possible when the gold is thinned significantly. Thin gold films are more likely to be porous (1) and invite corrosion of the substrate metal despite the nobility of gold. They are subject to more rapid removal by wear (2), which exposes the base metal

substrate with its inherent unreliable performance. Thin gold films are also subject to penetration by the substrate materials by diffusion (3), which can place oxidizable base metals at the contacting surface and degrade performance due to increased electrical resistance. All of these potential hazards involving the interaction of gold and base metals in thin film systems have been the object of considerable attention over the last five to ten year period. This article will concentrate on a review of the diffusion behaviour of gold/substrate systems, in particular those where nickel and/or copper are the substrate materials.

Basic Diffusion Mechanisms

There are three mechanisms pertaining to diffusion behaviour which need to be considered and they are shown in a highly schematic form in Figure 1 for a typical gold over copper substrate layered structure. The first is classical **bulk** or **lattice diffusion** which involves vacancy-atom exchange (4). It is by this process that the atoms in the layers intermingle so that the latter become of increasingly similar composition while totally in the solid state. Bulk diffusion is highly temperature dependent, however, and temperatures approaching the melting point of the lower melting element are usually necessary for the reaction to near completion in a practically significant time. The rate constant which defines this process at a specific temperature is the lattice diffusion coefficient D . Bulk diffusion takes on importance in such fabrication steps as thermocompression bonding, which will be considered later.

As depicted in Figure 1, the lattice diffusion process is two-way. In the example shown, gold diffuses into copper as well as copper into gold. Although the latter step is the one most often considered, since one

Fig. 1 Schematic representation of the various diffusion-related reactions induced by thermal ageing of gold/copper structures. Bulk diffusion (coefficient D) corresponds to the transfer of copper into gold and gold into copper through the lattice. Defect path diffusion (coefficient D') involves transfer along lattice defects such as dislocations and twin or grain boundaries — only the latter is depicted here. Ordered Cu_3Au , CuAu and CuAu_3 phases form at stoichiometric positions along the concentration gradient. The Kirkendall porosity at the copper-gold interface illustrates the faster rate of diffusion of copper into gold as compared with that of gold into copper

is usually concerned with degradation of the reliability and properties of the gold by the inclusion of base metal in it, the fact that the reaction is two-way can have important consequences. If the rates of diffusion are unequal, as is often the case, excess vacancies are left behind in the layer of the faster diffusing element, which will coalesce into a line of porosity known as Kirkendall porosity (5). This can have an influence on the mechanical integrity of the system and has practical implications for the gold/copper system.

The second mechanism which must be considered is that of rapid **diffusion along defect paths**. This process has a lesser temperature dependence than lattice diffusion and usually becomes dominant at lower temperatures, and at room temperature for many systems. Defects like grain boundaries, dislocations and twin boundaries, which are common and practically unavoidable in metals, can serve as rapid transport pipes through a metallic layer. This factor is particularly relevant in thin gold films where the techniques of application such as electrodeposition (6,7,8), sputtering (9) and vapour deposition (6) all provide very fine grained structures of high defect density. The rate constant defining this process is usually given by the symbol D' and is called the defect path diffusion coefficient. D' has been found to be typically four to six orders of magnitude larger than the lattice diffusion coefficient D at half the melting temperature in kelvins and below (10,11). Defect path diffusion is of primary concern in relation to the formation on gold layers of surface films of base metal oxides which can degrade such properties as electrical contact resistance and bondability.

The third mechanism relating to interdiffusion is the possible formation of **ordered intermetallic phases** between gold and a substrate metal. These can take the form of layers growing at the original gold-base metal interface as depicted in Figure 1. Such is the case for the gold/copper system where three ordered phases, Cu_3Au , CuAu and CuAu_3 can form and are stable below about 400°C (12). The layer growth rate is relatively slow at these low temperatures and usually has no influence on the gold surface properties. However, ordered layers are often brittle and their formation can influence the mechanical integrity of the system. Susceptibility of the gold surface film to fracture and flaking off may result if mild bending stresses are applied under such conditions.

In the following sections, these basic mechanisms relating to diffusion will be highlighted in greater detail for particular gold/base metal systems of current widespread practical application.

The Gold Film/Copper Substrate System

A gold layer on copper or a copper alloy substrate has been a most common combination for electrical contacts and connectors for decades. Lattice diffusion in the gold-copper system at temperatures above the 400 to 500°C range was extensively evaluated as far back as the 1930's. These investigations (13 to 16) were carried out on fine (pure, unalloyed) gold and were aimed primarily at determining the lattice diffusion coefficient of gold in copper and that of copper in gold or the interdiffusion coefficient $\tilde{D}$, reflecting an average of the two-way diffusion process. The results

of these studies are summarized in Figure 2 and show good consistency among themselves and also with more recent data (17,18) acquired using more modern physical techniques such as electron probe microanalysis (EPMA) and Auger electron spectroscopy (AES) (18). These techniques permit the analysis of very small diffusion zones and data can be acquired in a much lower temperature range approaching that of practical interest where the diffusion rate is relatively slow. Actual operating temperatures for components such as connectors in circuit packs having a high density of power-dissipating devices currently exceed 80°C and are anticipated to become as high as 135°C . Also, some metallizations are exposed to temperatures near 300°C for hours in order to cure polymeric materials assembled within the same component. Thus, the importance of such data is in determining the time at temperature over which a given thickness of gold will survive before being penetrated by sufficient copper to alter its surface properties. As demonstrated in (17), one month exposure at 250°C is sufficient to allow copper to diffuse extensively through $2.5\text{ }\mu\text{m}$ of fine gold and at 500°C only three days is required for similar penetration of $25\text{ }\mu\text{m}$ of gold. Analogous determinations, based on the diffusion coefficients given in Figure 2, can be made for any combination of time, temperature and layer thickness.

Once copper has penetrated to the gold surface, its oxidation is unavoidable. At very high temperatures, copper oxidizes both as a surface layer and also as long stringers penetrating far back into the original gold layer (Figure 3). As can be observed from copper concentration EPMA profiles, the original copper-gold interface fades completely as in diffusion bonding and the original pure gold layer becomes a gold-copper alloy of varying composition as a result of high temperature lattice diffusion.

No comparable data are available for the commonly used cobalt- or nickel-hardened golds. This is a consequence of the instability of these films at elevated temperatures. It has been pointed out (19) that the pronounced blistering and porosity which develop in such electrodeposited golds when heated above about 400°C are probably due to thermal decomposition of incorporated organic contaminants. A typical example is shown in Figure 4 of a 0.3 per cent cobalt-hardened gold after exposure at 500°C for 24 hours. The extensive porosity throughout the gold is obvious. However, the fact that much of this porosity is concentrated at the original gold-copper interface, so as almost to cause delamination, reduces diffusion across this boundary to near zero and precludes detailed study of the diffusion process at such elevated temperatures.

At less elevated temperatures, between room temperature and 250 to 300°C, where defect path diffusion becomes the predominant process, porosity of hard gold does not develop to any appreciable degree. Thus, defect path diffusion does take place and can be measured. This observation is highly relevant for several reasons. Hard golds are commonly used in devices on account of their superior wear properties and resistance to cold-welding in comparison to fine gold. Increased hardness is mostly attributable to refined grain size (20) and consequent increased defect density (7,8). This has obvious effects on the amount of copper (or other base metal) which can be transported via these paths to the surface region within a given time. Diffusion-related behaviour of hard gold/copper systems and of fine gold/copper systems should therefore not be considered as identical in terms of either of the two different processes: defect path diffusion and lattice diffusion.

Some of the available data on the diffusion rate of copper along defect paths in hard or pure gold are shown in Figure 5. These results were all obtained using AES on cobalt-hardened gold (21,23) or on pure gold (22,24). The greatly enhanced rate of defect path diffusion over that of lattice diffusion is apparent. The former process occurs with surprising rapidity even at room temperature as shown by the data of (22) or by the extrapolation of the other data to 25°C assuming no change in the process mechanism. These

Fig. 4 SEM micrograph showing the thermal degradation of a 25 μm thick 0.3 per cent cobalt-hardened gold electrodeposit on copper after 24 hours exposure at 500°C in air. Note the virtually continuous Kirkendall porosity near the original gold-copper interface

Fig. 5 Summary of the values measured by various authors in determinations of the defect path diffusion coefficient D' in the gold-copper system. Some of the lattice interdiffusion data of Figure 2 are also indicated for comparison purposes

Table I
Approximate Thicknesses of Cu_3Au and CuAu_3 in Thermally Aged 3 000 Å Gold/4 500 Å Copper Couples. After (29)

Ageing temperature °C	Ageing time hours	Cu_3Au thickness Å	CuAu_3 thickness Å
160	1 200	1 350	2 700
180	50	325	850
180	200	1 300	3 500
200	20	450	1 050
200	50	1 100	2 700
220	5	525	950
220	20	1 800	3 500

results would predict the arrival of appreciable amounts of copper at the gold surface in normal device lifetimes. However, it is also clear that there is wide scatter in the data. In addition to the potential differences in the measured apparent diffusion rate resulting from differences between hard and fine gold microstructures, other factors can produce such variation. These have been discussed in detail (21,25) and they include the sample boundary conditions, the method of extracting a diffusion coefficient (from first arrival time as opposed to surface accumulation measurements) and the surface sinking reaction.

Surface sinking is particularly relevant. Gold does not participate in the reaction at the surface. However, oxidation or any other film-forming reaction of the base metal can have a direct effect on the course of diffusion. If the reaction at the surface, which essentially removes copper from the diffusion process, is slower than the diffusion step, the gold diffusion paths will become clogged with base metal and diffusion will slow down to the rate of removal at the surface rather than proceed at its intrinsic rate. In the absence of an environment, as is the case in vacuum, this surface removal step is surface diffusion. It has been shown (21) that in the system discussed here, surface diffusion is least effective and corrosion in contaminated air (such as with chlorine) one of the processes most effective in removing copper from the surface. Oxidation in relatively clean air falls between these extremes. The nature of these surface reactions has been examined in detail (26) and is of high relevance to gold/copper devices in electronic apparatus, since the formation of surface films leading to an increase in resistance is a primary mode of failure. Thus, a number of factors, including both the diffusion rate and oxidation rate, must be considered in determining whether these processes are a potential hazard for a particular device application.

The single exception to the statement that the gold layer does not participate in the surface reaction is for hard electrodeposits which include base metals such as cobalt or nickel. Part of these additions exist as free atoms in gold-based solid solution and can diffuse to the surface, like the substrate material does. Indeed, the formation of layers of cobalt oxide (23,27) and potassium oxide (28) has been observed and can be deleterious to the properties of the gold surface.

The last diffusion-related mechanism to be discussed for the gold/copper system is the reaction which takes place at the gold-copper interface. During exposure, even for short times, to temperatures below about 400°C, the three ordered gold-copper phases are in equilibrium and can develop since the stoichiometric compositions are attained in specific ranges across the diffusion profiles. In very thin films of fine gold on copper it has been demonstrated (29) that the Cu_3Au phase is formed initially and followed by the CuAu_3 phase at temperatures as low as 160 to 220°C and in times as short as hours. The CuAu phase does not appear in the early stages of the process. It is first observed after 60 hours at 200°C and thereafter continues to grow at the expense of the CuAu_3 phase. Metallographic observations showed that these phases formed as layers parallel to the original gold-copper interface. Typical thicknesses of the layers formed at various times and temperatures (29) are given in Table I. It is clear that even though the Cu_3Au layer appeared first and continued to grow with time at temperature, the CuAu_3 layer was thicker by at least a factor of two for almost all time and temperature conditions measured.

Fig. 6 This $\text{CuK}\alpha$ X-ray emission scan reveals the presence of Cu_3Au and CuAu only at the diffusion interface between a 25 μm thick 0.3 per cent cobalt-hardened gold electrodeposit and the copper substrate. The sample was aged 4 months at 250°C

Fig. 7 SEM back-scattered images showing the effects of ageing time and temperature on the respective formation of layers of ordered phases and of Kirkendall porosity in cobalt-hardened or fine gold/copper systems. Ordering is slow below 250°C and not possible at or above about 400°C. The formation of Kirkendall voids is greatly accelerated by increased diffusion temperature and time

Other studies involving thicker layers (25 μm) of fine and cobalt-hardened gold, aged up to 3 years at temperatures ranging from 150 to 400°C, showed consistent behaviour (30). In these cases, ageing times were sufficiently long for the CuAu layer to totally consume the Cu₃Au layer and only Cu₃Au and CuAu remained. In some instances, the layer thicknesses exceeded 5 μm as determined by X-ray profiling with a wavelength dispersive spectrometer in a scanning electron microscope (SEM) on specimen cross sections. A profile of the CuK α X-ray line for a sample aged four months at 250°C exhibits the above mentioned features (Figure 6). The layers have a composition range consistent with the equilibrium diagram (12). They are also readily distinguished in the SEM backscattered images shown in Figure 7 for samples aged at 250 and 300°C. The ordered phases are not discerned after ageing at 400°C as CuAu is barely stable at this temperature and the upper limit of stability of Cu₃Au is about 390°C (12).

Another important feature visible in Figure 7 is the development of Kirkendall porosity along the copper-rich side of the couple, which increases in abundance with the time and temperature and hence the extent of diffusion. The formation of this porosity reflects the more rapid transport of copper into gold than vice versa (17). It is apparent that such a line of porosity could lead to delamination of the gold layer. This was found to be the case in the evaluation of thermocompression bonds between gold plated copper lead frames and gold metallized thin film circuits (31). The pull strengths of the leads decreased measurably

(in many instances to zero) when aged between 200 and 300°C for times to only 2000 hours. Analysis of the fracture surfaces by X-ray and SEM techniques revealed the presence of Cu₃Au. The development of this layer of limited ductility together with Kirkendall porosity probably caused the degradation of this particular system.

The Gold Film/Nickel Substrate System

Lattice diffusion in the gold-nickel system has also been studied (32), but primarily above 812°C where complete solid solubility exists (33). It was found that the rate of interdiffusion is two orders of magnitude greater in gold-rich solutions than in nickel-rich solutions, which is certainly the direction unfavourable to the properties of the gold surface layer as was already described for copper in gold. Fortunately, these elevated temperatures are outside the realm of practical interest for common devices incorporating a gold layer over nickel and at lower temperatures the circumstances change appreciably. A broad miscibility gap occurs in the gold-nickel system which at 300°C, for instance, limits the solubility of nickel in gold to less than 8 atomic per cent and that of gold in nickel to less than 2 atomic per cent (33). Phase separation greatly restricts lattice diffusion and by comparison makes it a much slower process than in the copper-gold system. This is presumably the reason why no bulk diffusion has been observed in the lower temperature range and why nickel enjoys its reputation as an outstanding diffusion resistant substrate under gold.

Table II
Comparative Thicknesses of Copper and Nickel Measured at the Free Surface of a 2.5 μm Coating of Cobalt-Hardened Gold After Ageing at 150°C

Ageing time days	Equivalent copper thickness Å	Equivalent nickel thickness Å
0.17	18 ± 4	—
5	206 ± 40	—
10	461 ± 90	—
18	—	None*
40	—	8 ± 2
80	—	38 ± 8

*Less than the detection limit of about 0.1 monolayer

If defect path diffusion is considered, however, the restrictive nature of the miscibility gap is not so clear. Available data (25) for exposure to temperatures under 250°C indicate that such diffusion does occur and at a rate nearly equal to or only moderately slower than that of copper through gold. As a result, nickel oxide or other nickel-based corrosion products can form on the surface of gold deposits and thereby degrade the properties related to resistivity and bondability. A comparison of the rate at which this process takes place, relative to copper and in terms of surface accumulation of base metal, is given in Table II. In this instance, the nickel defect path diffusion and surface oxidation rates are moderately slower than those for copper, but still rapid enough to warrant consideration in some gold over nickel applications.

To degrade the surface properties of gold, nickel must react with the environment to form a resistive film. It has been shown in a study of nickel oxidation out of gold solution (34) that the gold does not participate in this film formation, which was to be expected due to its nobility. The nickel was found to

form a limiting film thickness (34,35,36), which is a function of temperature, relative humidity and atmospheric contaminants, but which for comparable conditions is substantially thinner than the continuously growing film of copper compounds. In this sense, the gold/nickel system may be considered as superior to the gold/copper system.

The gold-nickel metallurgical system does not have the potential for ordered phase formation and thus no low temperature mechanical degradation of the layer-substrate bond is expected.

The Gold Film/Nickel Underlayer/Copper Substrate System

Frequently, both copper and nickel are present under a gold or gold alloy surface layer in electronic components and other products. The copper or a copper alloy serves as the primary inexpensive substrate with good mechanical spring properties, solderability and formability. A layer of electrodeposited (or with newer techniques also sputtered, vapour deposited, etc.) nickel is then applied to provide improved wear resistance, due to its hardness, and also as a diffusion barrier to inhibit the penetration of copper to the gold surface (3) as discussed in an earlier section of this review. Common wisdom prescribed nickel as a reasonably effective barrier to copper diffusion and some accelerated ageing studies supported this belief (37). Results showed that fine gold over copper devices failed more rapidly than similar samples with a nickel barrier when aged up to 1000 hours at 125°C (Figure 8). While the reputation of nickel as an effective barrier is well founded with respect to lattice diffusion, recent AES results on defect path diffusion through gold (25) are only marginally in favour of nickel when compared to copper.

A number of intriguing aspects were uncovered in a detailed study (38) of diffusion-related behaviour in the fine or cobalt-hardened gold/nickel/copper tri-layer systems between 150 and 750°C. Nickel layers 20 μm thick under 20 μm of fine gold and also 5 μm thick under 5 μm of cobalt-hardened gold were investigated. Ageing times were extended to as long as three years at the lowest temperatures. Interdiffusion of the elements was followed by EPMA profiling in a SEM on metallographically polished cross sections. The high temperature results exhibited the expected behaviour and are depicted in Figure 9. Copper and nickel being mutually soluble in all proportions, a gradual concentration gradient reflecting interdiffusion has built up across the copper-nickel interface. Kirkendall porosity now appears at the copper-nickel interface reflecting the more rapid penetration of copper into nickel than vice versa (39,40). Nickel and gold show very limited mutual solubility, due to the broad miscibility gap previously mentioned, hence

Fig. 8 Reliability vs. ageing time at 125°C of electrical contacts consisting of 0.5 μm pure gold on copper with or without a nickel intermediate layer. The acceptance criterion was a contact resistance lower than 1.0 m Ω . After (37)

Fig. 9 Typical concentration vs. distance profiles on a gold/nickel/copper system after 6 hours ageing at 750°C. The profiles were produced from X-ray emissions induced in a SEM

Fig. 10 Typical concentration vs. distance profiles on a gold/nickel/copper system after ageing at 500°C or below. The sample shown here was annealed 80 days at 400°C

the very abrupt concentration discontinuity at their interface. The concentration of nickel in gold remains very low but this has not prevented sufficient nickel from diffusing to the surface to form an oxide layer.

At 500°C and below, the nature and results of interdiffusion are found to change significantly. As illustrated by Figure 10, copper and nickel no longer exhibit mutual solubility, but instead the copper-nickel and nickel-gold interfaces show similar features. The nickel appears to be unaffected by the diffusion process with little penetration of it into copper or gold detectable by the experimental technique used. AES analysis of the gold surface detected the presence of some nickel, transported there by defect path diffusion through gold. However, the nickel seems to serve as a transport medium for gold through to the copper substrate. As a consequence, gold has accumulated at the copper-nickel interface and has gradually diffused into the copper as shown by the gold concentration gradient. Identical behaviour can be noted for the copper which accumulated at the nickel-gold interface. This copper will eventually diffuse to the gold surface in spite of the nickel 'barrier' and oxidize. The intermediate layer will extend the life of the system by at least the time required by copper to diffuse across it but not indefinitely. The rate of transport across the nickel layer for both copper and gold must be fairly similar due to the absence of any visible Kirkendall porosity (Figure 10) which is so clearly evident after diffusion at higher temperature (Figure 9). Diffusion behaviour of this type has been observed down to 250°C and is likely to take place down to room temperature as no change in mechanism is foreseen over this

extrapolated range. However, ageing at 200°C and below for times as long as three years has not resulted in sufficient diffusion to be detected by EPMA.

This unusual behaviour has been attributed to the deep penetration of the miscibility gap in the gold-nickel binary system into the gold-nickel-copper ternary system (41). The rapid defect path diffusion of gold through nickel and into the copper near the copper-nickel interface limits the solubility of nickel in this 'alloyed' region compared to that in pure copper and restricts copper-nickel interdiffusion. At 300°C and below, the distribution of copper in gold and that of gold in copper at the opposing nickel interfaces become very patchy. This is taken as supporting evidence of the defect path mode of diffusion of copper and gold through the nickel because significant bulk diffusion would lead to even distribution of these metals in each other parallel to the nickel underlayer. The lack of detectable concentrations of copper and gold in the nickel (Figure 10) further supports this interpretation.

The benefit of nickel in at least retarding the outwards diffusion of copper is apparent from the work described here (38). Another study (42) supports the conclusion that nickel does have such an effect but disagrees with the intuitive feeling that increasing the nickel thickness will increase the time for copper to eventually reach the gold surface. An additional benefit of the nickel layer at lower temperatures is its ability to retard the formation of the ordered gold-copper phases at the interface as well as that of Kirkendall porosity. This prevents the loss of bonding strength that is observed in the gold/copper system when aged at 200°C and above (31).

The Gold Film/Tin-Nickel Underlayer/ Copper Substrate System

An equiatomic alloy of tin and nickel which can be electrodeposited has been advocated as a substitute or as an underplating for gold on copper in applications such as printed circuit boards (43,44). Its attractive features include high hardness and strong corrosion resistance, making it of interest under thin gold films which are usually porous. This alloy has already found application under gold layers as thin as $0.05\text{ }\mu\text{m}$.

The behaviour of a tin-nickel layer between copper and gold at temperatures where diffusion related effects come into play is also of interest and a curiosity. In one study, tin-nickel deposits $12.5\text{ }\mu\text{m}$ and $2.5\text{ }\mu\text{m}$ thick, plated between $60\text{ }\mu\text{m}$ fine gold and copper, were aged at up to 500°C . It is clear from the results depicted in Figure 11 that tin-nickel underlayers are unsuitable at temperatures toward the upper end of this range. After only 50 hours exposure at 500°C , the initially continuous layer has begun to decompose

Fig. 11 SEM micrographs showing the decomposition and general behaviour of a $12.5\text{ }\mu\text{m}$ thick tin-nickel layer, deposited between a copper substrate and a gold coating, when thermally aged. At 500°C , SnNi decomposes while at 250°C only partial decomposition and migration of some tin towards the gold surface are visible

Fig. 12 SEM micrographs showing the decomposition and general behaviour of a $2.5\text{ }\mu\text{m}$ thick tin-nickel layer, deposited between a copper substrate and a gold coating, when thermally aged. The same effects as those depicted in Figure 11 are observed after shorter ageing times

into discrete particles. Gold and copper have completely penetrated the layer, as if it were not even present. AES analysis of the gold surface revealed the presence of both tin and copper — over 60 μm away from their initial position! Thus, both copper from below the layer and tin from the decomposed layer diffused through the 60 μm gold layer (again probably by defect path diffusion) and altered its surface properties.

The decomposition of the tin-nickel alloy is probably related to the modification of the metastable electrodeposited SnNi phase into the elevated temperature equilibrium two-phase structure consisting of Ni_3Sn_2 and Ni_3Sn_4 (45). This phase change, together with intermixing of the four elements by diffusion, may possibly explain the apparent disintegration of the interlayer. At lower temperatures, where the modification of the layer is less dramatic (for example, 1 year at 250°C), tin is already being released and is reforming as stringers of tin-rich phase in the gold surface region (Figure 11). Even these milder conditions are deleterious to the surface electrical properties of the gold film/tin-nickel underlayer/copper substrate system.

Thinner tin-nickel electrodeposits, such as the initially 2.5 μm thick layers shown in Figure 12, exhibit

similar behaviour except that they are nearly totally dissolved much more quickly. After 5 hours at 500°C, only a few remnants of the original layer are visible and the tin or tin-rich phase can be observed to be flowing toward the gold surface in 'waves'. After 30 days at 300°C, decomposition is incomplete but already the tin-rich stringers form a network in the surface region of the gold.

Conclusions

Gold when plated over base metals such as copper or nickel will be subject to interdiffusion. This will occur with surprising rapidity even at room temperature by the process of defect path diffusion. The typical result is the accumulation of base metal or base metal oxide in the surface region, which can alter electrical properties such as contact resistance. In addition to surface phenomena, other characteristics of the diffusion process, which occur near the gold-base metal interface, such as Kirkendall porosity or intermediate phase formation can also alter the behaviour of gold layers in thin film systems by mechanical strength degradation. Thus, diffusion and its potential consequences must be carefully considered when designing devices using gold/base metal thin film systems.

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