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Al-Cu Alloy for Gas Panels

Abstract: The composition, phase formation, stress, resistivity, and, in particular, the oxidation and corrosion behavior of Cu-Al films with a variety of Cu:Al ratios have been determined. Their relevance to the gas panel is discussed.

Introduction

A metallic film suitable for gas panel use must adhere to dielectric substrates, seal well to glass, and resist both oxidation in air at elevated temperatures and corrosion during shelf life. In addition, it has to be a good conductor.

An obvious choice of a material is copper, since it is highly conductive, workable, and available. By itself, however, copper adheres poorly and has poor oxidation resistance. Its potential for this application would be improved if it were sandwiched between layers of other materials for both better adhesion and protection. However, the layers would then have to be etched in successive steps, and there is a possibility of copper undercutting. In addition, if left unprotected, the exposed sides of the etched metal might corrode.

Another way of stabilizing copper is by alloying. Bulk alloys with Be, Si, and Al are reported to have greatly improved corrosion resistance [1].

Because of our interest in thin film behavior, we have examined the Cu-Al system, one in which the components are easily obtained and handled. The very first experiment has shown that this film can be heated to temperatures of 700°C in oxygen with barely any loss of material to oxidation. The examination was extended to other properties of the alloy relevant to gas panel fabrication and use.

The paper examines several methods of film preparation in order to specify conditions leading to reproducible and reliable alloys. Attention is given to the effects of composition on stress, phase formation, grain size, conductivity, etchability, and oxidation resistance. Behavior of films at elevated temperatures, both in oxidizing atmosphere and in contact with seal glass, is studied with particular interest. Finally, corrosion resistance of the alloy in a hostile atmosphere and its galvanic compatibility with the ever-popular conductor, copper, are given.

Results have allowed a selection of an alloy with properties closely matching the requirements imposed on a metallization applicable to gas panels.

Film preparation

Films were prepared in several different ways, all of which eventually lead to the formation of an alloy of the desired composition.

• *Sequential evaporation*

Layers of Al/Cu/Al were deposited by successive e-beam evaporation of individual sources in a starting vacuum of about 1×10^{-5} Pa. In all cases the base aluminum was 30 nm thick; it was followed by 500 nm of copper, but the thickness of the upper aluminum layer ranged from 30 to 250 nm. The lower Al layer promoted adhesion, while the upper layer provided oxidation resistance.

Substrates, either Libby Owen Ford (LOF) plate glass or sapphire, were cleaned prior to evaporation by several techniques. The variations in substrate preparation were

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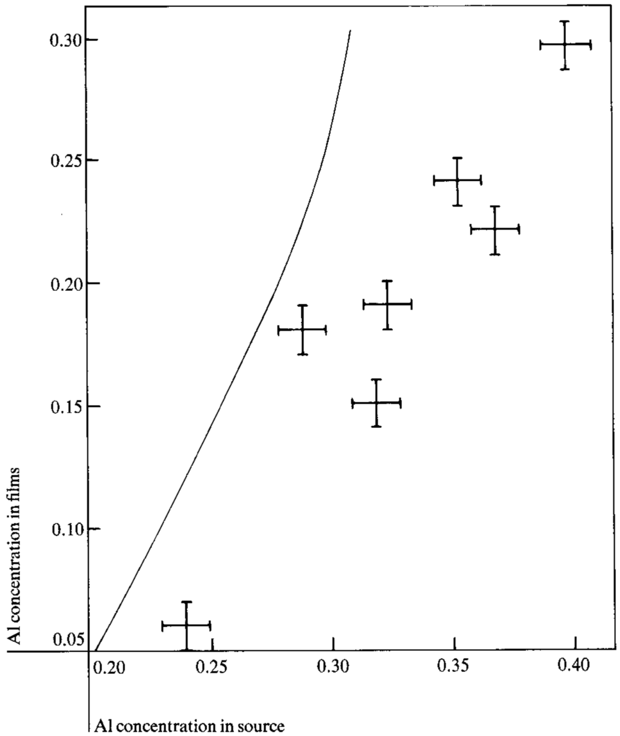


Figure 1 Theoretical and experimental variations of the average film composition as a function of the alloyed source material.

investigated primarily to determine their effects on adhesion. We found that all of the cleaning procedures were equally acceptable, with none by itself ensuring good adhesion. Instead it became evident that the substrate temperature during deposition was the most important factor governing adhesion. Substrate temperatures were either not controlled (referred to as "room temperature" but occasionally reaching 50–70°C) or kept at 100, 120, 130, 140, 150, and 200°C. All samples deposited at 130°C or higher adhered well.

Alloys were formed by subsequent heating of the layer structures. This was done outside the evaporator in furnaces with varying atmospheres at 450°C or higher.

- *Dual e-beam evaporation*

Alloy films were deposited by the simultaneous monitoring of two "e-guns" and sources. The substrates were kept either at room temperature or at 140 or 200°C. The film composition was a result of preselected evaporation rates of the individual components.

- *Evaporation from an alloy source*

Where practicable, the use of a single source offers the advantage of greater simplicity and reduced apparatus failures over dual source depositions. In the case at hand, Cu-Al, and for the range of compositions of interest for gas panel metallization, experimental results indicated that distillation is sufficiently limited to allow evaporation from single sources. Ingots were cast in the proper shape by arc melting Cu and Al in the desired proportions in an inert atmosphere. The substrates in this case were LOF panels, thinned LOF wafers, or oxidized Si wafers, heated to 200°C prior to and during depositions. The sources were outgassed prior to each deposition by overheating for about one minute to a monitored rate of 4 nm/s. The depositions were carried out at a film growth rate of 2 nm/s to a total film thickness of approximately 500 nm.

The composition of the first films obtained from different ingots is plotted in Fig. 1 against the composition of the ingots. The Al content of the films is reduced by a factor of 2 to 3 as compared to that of the source material. In Fig. 1 the plotted line represents the compositions of the films derived from the compositions of the source, and known thermodynamic [2] and vapor pressure data [3] for the Al-Cu system. The principles of this theoretical derivation of film compositions, as well as some practical limitations, are reported in detail elsewhere [4]. Agreement between theory and experiment is good in the lower range of Al concentrations, but is not as satisfactory for alloys with high Al content. For source materials containing less than 10 atomic percent Al, the film compositions tend rapidly towards 0% Al because of the extremely low activity coefficient, γ, of Al in liquid Cu-Al alloys of such compositions (at 1373 K, γ of Al is 0.002 in the limit of infinite dilution).

In order to assess the practicality of the repeated usage of the same alloy source, a series of four films were successively deposited from an ingot initially weighing 37 g and containing 36 at% Al. The films contained increasing amounts of Al from about 24 to 29 at%. The weight loss in the ingot for each evaporation amounted to 2 g. Undoubtedly greater reproducibility would have been obtained if the ingot losses had been compensated by adding after each deposition the amount of material previously evaporated.

- *Sputtering*

A dc sputtering device manufactured by the Sloan Corporation was used to deposit alloys with a nominal composition of 22 at% Al. With an Ar pressure of 1 Pa, an acceleration voltage of about 400 V, and a total power dissipation of 1600 W, an average deposition rate of 50 nm/min was obtained. The uniformity of film thickness over any one panel was better than 20 percent. This could be improved, at the cost of a small loss in deposition rate, by locating the cathode somewhat eccentrically with respect to the axis of rotation of the five disks which serve as substrate holders.

The substrates were not heated, which resulted in occasional film failures due to poor adhesion. The factors that affect adhesion—substrate cleaning, vacuum conditions, pre-sputtering, and the nature of the vacuum system itself (e.g., oil diffusion pump vs vac-ion pumps)—were all given attention. Undoubtedly, heating of the substrates to a temperature in the range 150–200°C would eliminate any adhesion difficulty, which occasionally occurred.

Film treatment and analysis

In fabrication of gas panels, the metallization has to go through several thermal cycles. In order to determine the influence of temperature and ambient conditions on metal behavior, samples were exposed to different heat treatments and environments. Temperatures ranged from 300°C to 650°C in 50-degree steps. Atmospheres included purified helium, nitrogen, air, and oxygen. Exposure times varied from 0.5 to 6 hours. Some samples were in contact with a lead-rich sealing glass while heated at 300–500°C. A few samples were exposed for 24 hours to a corrosion chamber kept at 55°C and containing sulphur flowers at 80 percent relative humidity.

Films were examined before and after various stages of heat treatment. The average composition was determined by electron microprobe and Auger electron spectroscopy. Spectroscopic examination was also used for Cu:Al ratio evaluation as well as the oxygen, carbon, and impurity distributions at the surfaces and throughout the samples.

Surface changes caused by annealing and oxide growth were examined by ellipsometric techniques. Some experiments were carried out *in situ*.

X-ray diffraction provided information for the evaluation of phase formation (as a function of the average film composition) and of stresses. Reflection electron diffraction made possible the identification of the surface structure. The sample-to-beam tilt was about 1° and with an applied voltage of 50 kV the penetration depth was about 3–4 nm.

The apparent grain size and topography were evaluated with a SEM. A few samples were replicated and viewed by TEM.

Electrical resistance was determined with an in-line four-point probe and films of a known thickness.

Finally, several electrochemical methods were used to determine the corrosion characteristics of the alloys. Typical measurements consisted of the evaluation of the corrosion potential, the corrosion rate by Tafel extrapolation, the galvanic corrosion potential, and the galvanic corrosion rate in contact with copper, i.e., simulating use in a product. The details of these methods are described elsewhere [5].

Results

• *Film composition and phase formation*

The phase structure of the alloy films was determined mostly by x-ray diffraction, but supplementary information about surface oxides was obtained by electron diffraction. Obviously, for films deposited in layers the equilibrium structure was reached only after heat treatment. It was shown that a uniform Cu-Al distribution was attained in 30 minutes at 450°C or in less than 10 minutes at 650°C, regardless of the atmosphere (air, oxygen, or inert gas), with the only difference being a small amount of surface oxide (< 5 nm) formed in the presence of oxygen. These homogenization times are somewhat shorter than might be anticipated on the basis of bulk diffusion data. In the solid solution of Al in Cu, the average mutual (sometimes called chemical) diffusion coefficient is equal to 3 exp ($-48\,000/RT$), where R is the gas constant and T the temperature [6]. For films 500 to 600 nm thick, if lattice diffusion alone were responsible for homogenization, annealing times in excess of 60 minutes at 500°C would be required. Certainly in the cases at hand film uniformity is helped by the presence of short-circuit diffusion paths, mostly grain boundaries.

Table 1 Some properties of Cu-Al alloys.

at% Al in Cu	*Metal deposition*[a]	*Phase*	*Oxide thickness and composition after 1 hour at 500°C in* O_2
0	ℓ	αCu	fully oxidized, CuO
5	a	αCu-Al	fully oxidized, CuO
8	ℓ	αCu, Al_2O_3	<5 nm, Al_2O_3 (CuO in pits)
9	d	αCu	fully oxidized, CuO
13	a	αCu	40 nm, CuO, Cu_2O, Al_2O_3
14.9	ℓ	αCu	<5 nm, Al_2O_3 (CuO in pits)
15	d	αCu	40 nm, CuO, Cu_2O, Al_2O_3
21.6	ℓ	αCu,γAl_2O_3	<5 nm, Al_2O_3
22	a	αCu,γAl_2O_3	12 nm, Al_2O_3, Cu_2O (?)
22.8	d	αCu,γAl_2O_3	12 nm, Al_2O_3, CuO (?)
24.5	d	αCu,γAl_2O_3	12 nm, Al_2O_3 (?)

[a] ℓ—deposited in individual layers; a—evaporated from an alloy source; d—deposited by simultaneous monitoring of dual e-gun system.

For equal Al concentrations, the phase compositions of the films were identical, independent of their respective modes of preparation (Table 1). In accordance with the equilibrium diagram for the Cu-Al system [7], films with less than 20 at% Al displayed only one phase, the Cu α solid solution. X-ray diffraction yielded evidence for a single phase only, even in films containing somewhat more than 20 at% Al; however, as the almost universal presence of some degree of preferred orientation makes the detection of secondary phases particularly difficult and an accurate study on the limits of phase detectability was not conducted, it remains difficult to draw positive conclusions about the presence or absence of a second phase.

The lattice parameters of the Cu-Al films with compositions within the range of interest for gas panels are plotted

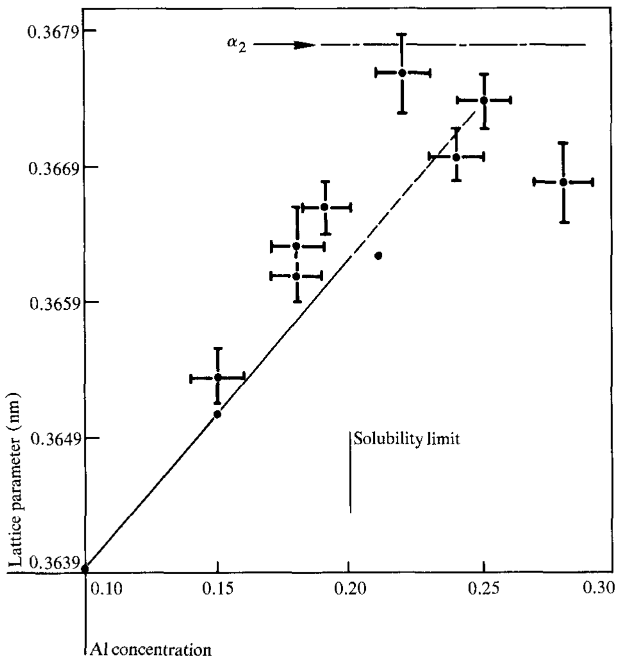


Figure 2 Average lattice parameters of Cu-Al films as a function of the Al concentration (the parameters were corrected for stress).

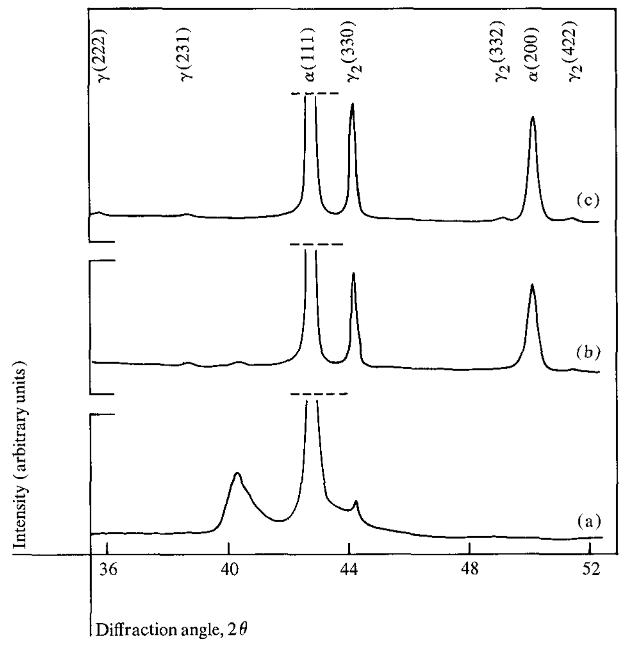


Figure 3 Portion of the diffraction pattern (CuKα) for a film containing 24 at% Al, (a) as deposited at a substrate temperature of 200°C, (b) after a 22-hour anneal at 325°C, and (c) after a one-hour anneal at 500°C followed by rapid cooling.

in Fig. 2 as a function of the Al concentration. The values, corrected for the effects of tensile stresses (for details see [4]), are in good agreement with the lattice parameters of bulk samples [8], confirming the validity of the chemical analysis. The lattice parameters of the films with more than 20 at% Al are larger than the value at the solid solubility limit of 0.36635 nm. This may indicate that in the as-deposited state the solid solubility would extend up to approximately 25 at% Al, with the film perhaps assuming a structure intermediate between the α solid solution and another face center cubic (f.c.c.) phase α_2. The latter, with a lattice parameter of 0.3678 nm with a composition of about 25 at% Al, had been reported previously [9].

The equilibrium structure of Cu-Al alloys with a concentration of 20 to 30 at% Al may not be definitely settled. In a relatively recent investigation [9] it was concluded that below 350°C there should exist three phases: the terminal α solid solution, another f.c.c. phase α_2 referred to above, and a complex cubic structure γ_2 for the high Al concentrations. Attempts to identify the α_2 phase in the films remained unsuccessful. However, one sees clearly the α(111) diffraction peak at about 43°, for a film containing 24 at% Al (Fig. 3); an unidentified peak appears at about 40°; and, after an anneal of 22 hours at 325°C, well formed γ_2 diffraction peaks are seen. An anneal at 500°C followed by rapid cooling caused the extra diffraction peak to disappear, which would indicate that the extra peak is associated with the rather complex temperature–composition phase diagram, which is characteristic of Cu alloys with an electron to atom ratio of the order of 1.5. The existence of the extra peak was verified from diffraction patterns obtained at a grazing angle on photographic films sensitive to x-rays. It was also observed on patterns from films deposited in layers and subsequently homogenized. Finally, one may note faint evidence of the extra peak on diffraction patterns shown in Fig. 4 for films analyzed as containing 18 and 19 at% Al. It is possible that the extra peak is the (220) diffraction of a phase Cu_4Al with a β-Mn structure and a lattice parameter of 0.626 nm which has been identified by one investigator [10].

As-deposited films exhibited a (111) preferred orientation regardless of their mode of deposition. The (111) texture may be somewhat weaker after annealing, as evidenced in Fig. 3 by the appearance of the (200) diffusion peak. However, it is rather difficult to express the change quantitatively since structure defects tend to hide the presence of weak diffraction peaks in the films analyzed directly after deposition.

- *Stress*

In order to study the state of stress in films produced by different means of deposition, and to determine the effect of annealing through the sealing cycle at 500°C, 2.5-cm diameter disks of very thin substrate/film combinations were examined by Newton ring observations [11–14] at

Table 2 Stresses in films.

Reference	*Film composition*	*Substrate temperature*
	I Layers	
a	Al 40 nm—Cu 500 nm—Al 90 nm	150°C
	II Alloy Source	
b	18 at% Al	200°C
c	19 at% Al	200°C
d	24 at% Al	200°C
	III Sputtering	
e	18 at% Al	25°C
	σ in 10^{-5}N/cm^2 *before annealing*	*after annealing*
a	1.9×10^{9} [a]	5×10^9
b	2.6	5×10^9
c	2.7	5×10^9
d	2.9	5×10^9
e	3.5×10^8	7×10^9

[a]Averaged through the three different layers.

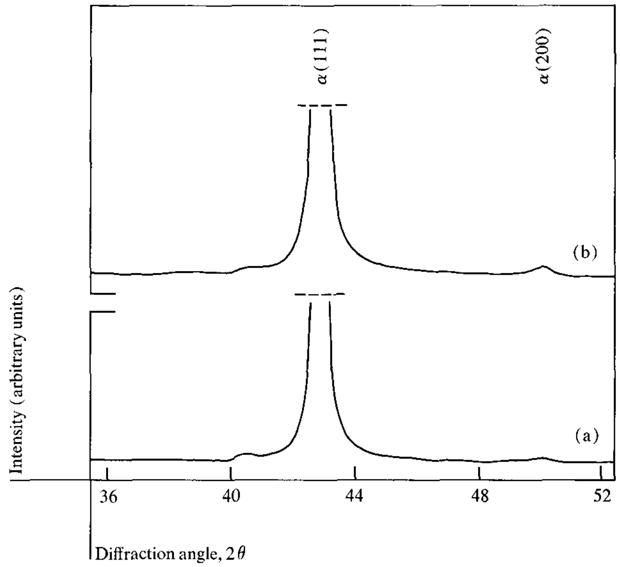


Figure 4 Portion of the diffraction patterns for two films with presumed compositions of 18 and 19 at% Al, as deposited at a substrate temperature of 200°C.

various process stages. Details of the stress (and strain) calculation are given in [4]. The results are listed in Table 2.

It should be noted that in all films the stresses are tensile. In films obtained from an alloyed source, the stress level can be entirely accounted for by the difference in thermal expansion between Cu-Al (18×10^6/°C) [15] and the LOF glass substrate (8.8×10^6/°C) over the range of temperature from 200°C (substrate temperature) to room temperature. This immediately indicates two things: 1) the intrinsic stresses in the films resulting from the nucleation and growth process were vanishingly small, and 2) the temperature at which Cu-Al becomes sufficiently soft to be unable to sustain stresses exceeds 200°C. This last observation is confirmed by the stress level in the films after annealing. These results indicate that the films were soft and stress-free at the maximum temperature of 500°C and remained so during the initial cooling down to a temperature in the vicinity of 350–400°C. From there down to room temperature, tensile stresses developed. The small level of stresses in the films obtained by sputtering corroborates the expectation that in the particular device used for film deposition, substrate heating should be negligible.

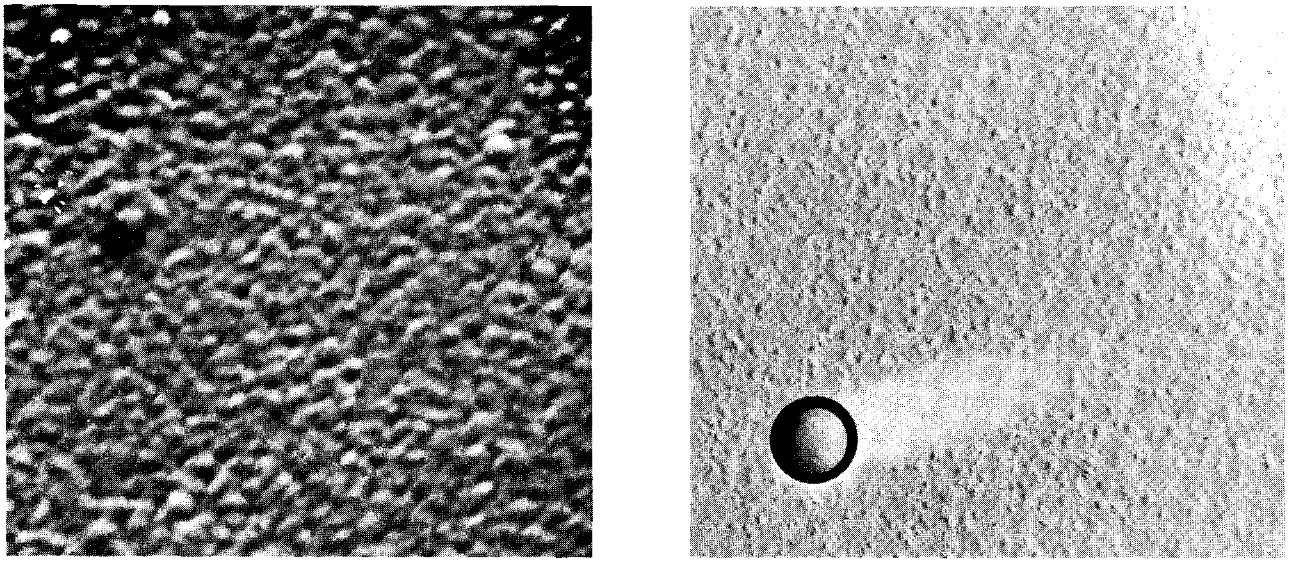
Table 3 Apparent grain size on as-deposited films.

Films deposited in layers			
Grain size (GS) as a function of substrate temperature T_s; Al/Cu/Al = 30/500/30 nm		*Grain size as a function of upper Al thickness L_{Al}; deposition temperature 140°C*	
T_s (° C)	*GS* (nm)	L_{Al} (nm)	*GS* (nm)
room temperature	35	60	60
100	35	100	60
120	35–40	150	60–150
130	35–50	1500	100–200
140	35–60		
150	35–90		
200	>600		
Films deposited from alloy or dual sources and by sputtering			
Grain size about 35 nm for all films irrespective of T_s and average composition.			

• *Apparent grain size and surface morphology*

The fact that surface appearance depends on the manner of film preparation is illustrated by Table 3 and by Figs. 5 and 6. All of the films viewed by SEM and by TEM replicas show very smooth, uniform surfaces whose "grains," and thus their grain size, cannot be clearly defined.

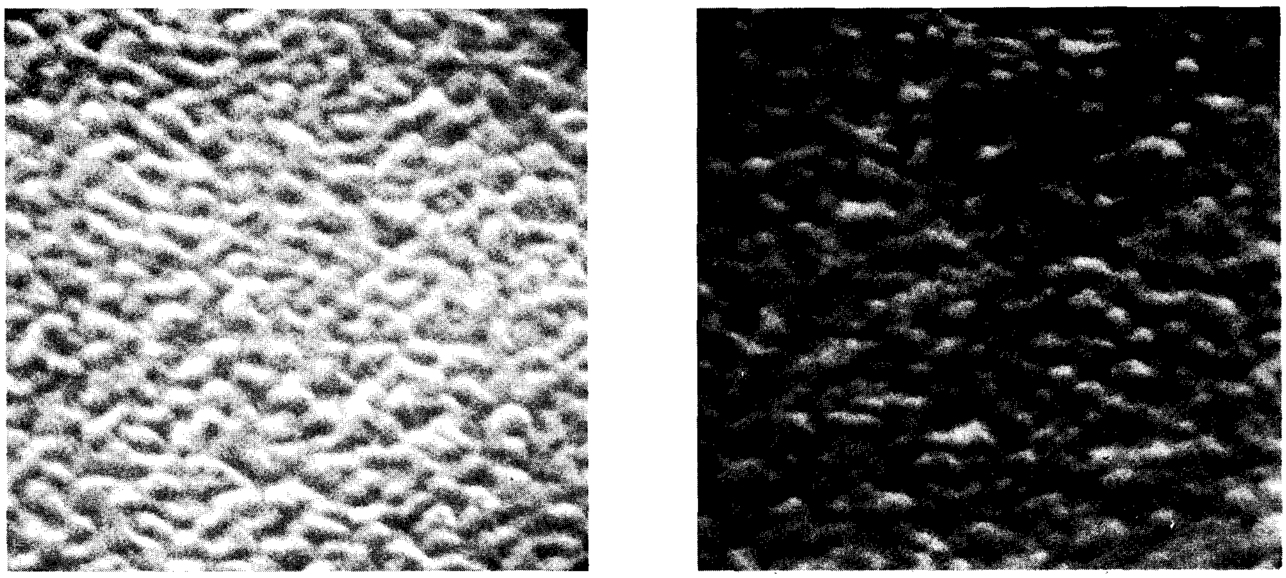
Films deposited as layers exhibit apparent "grains" of approximately 35 nm, increasing in size with the film thickness and the substrate temperature during deposition (Table 3). The best films, i.e., the most adherent (as discussed earlier) and miscible, were produced between 130°C and 150°C. Subsequent heating of these films to temperatures up to 600°C in either inert or oxidizing atmospheres did not change the surface topography (Fig. 6). The growth of grains, characteristic of pure aluminum and, in particular, of pure copper when heated above



25 000 × (a)

20 000 × (b)

Figure 5 Surface morphology of the Cu at% Al deposited by evaporation of the alloyed source viewed by (a) SEM, magnification 25 000 × and by (b) TEM of the sample replica, magnification 20 000 ×.



30 000 × (a)

30 000 × (b)

Figure 6 Surface of the three-layered film of Al/Cu/Al (with 30/500/30 nm) (a) as deposited at 140°C and (b) after 1 hour oxidation at 500°C as viewed by SEM, magnification 30 000 ×.

200°C, is not observed. Deep grain boundary grooves formed on pure copper are, in an oxidizing atmosphere, loci for the initial oxide nucleation (Fig. 7). Such an inhomogeneous oxidation is not observed on Cu-Al films where a thin aluminum oxide uniformly covers the entire surface, interrupted only by an occasional whisker of CuO. The latter most likely grows through pits in the original layer of the upper aluminum and its occurrence is reduced to much less than 1 percent of the area if the aluminum thickness is 90 nm or more.

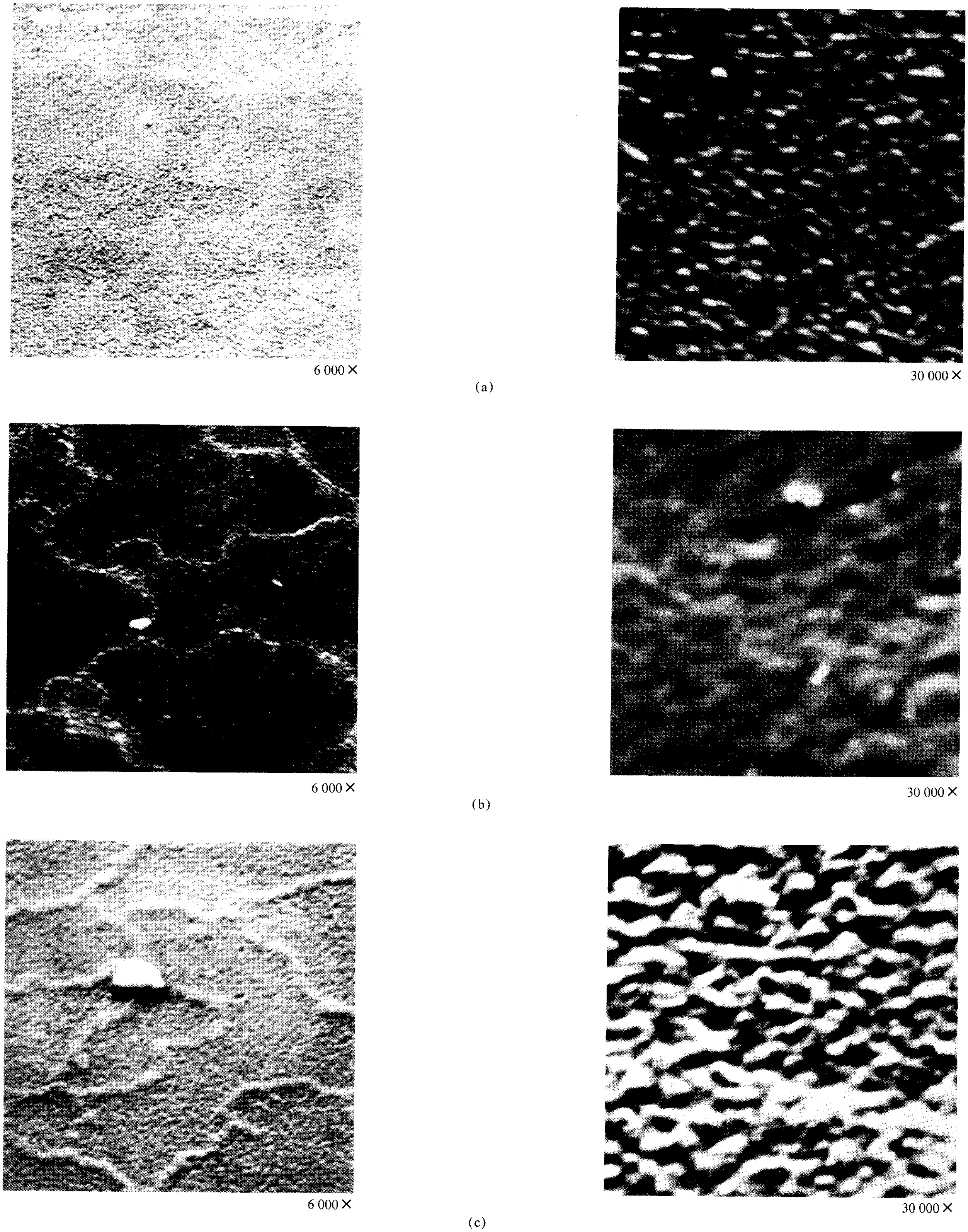


Figure 7 Copper films (a) after deposition, (b) after 3 hours of heating in helium at 500°C and (c) after 2 hours of heating in oxygen at 200°C. Magnification was 6000 and 30 000 ×.

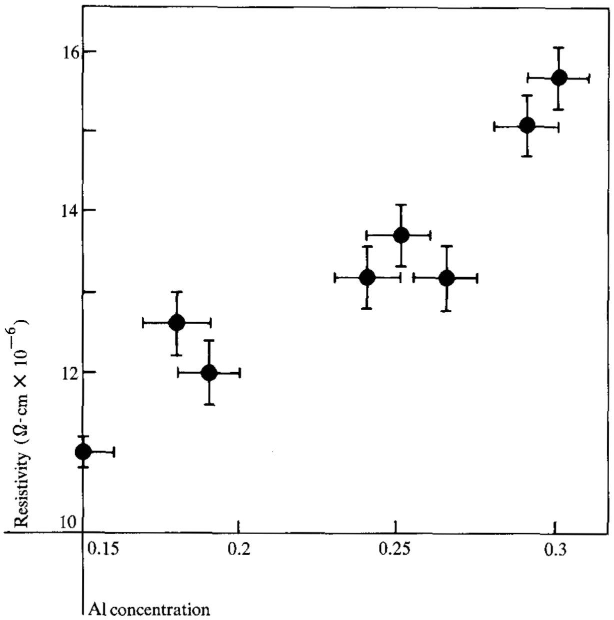


Figure 8 Electrical resistivity as a function of film composition.

Films deposited from alloyed and dual sources or by sputtering exhibit apparent "grains" of 35 nm independently of the substrate deposition temperature and of the film thickness. When alloys with a composition of 13–20 at% Al are heated in inert atmospheres, the surface morphology is not altered. However, when exposed to oxygen, these alloys form a surface oxide composed of both copper and aluminum oxides which change the appearance of the films but not the size of the "grains."

• *Etching*

Normally, pattern definition on panel plates is done after film deposition, prior to any thermal treatment. It should be noted that all films, irrespective of the manner of preparation, can be etched as a single layer. One of the suitable etchants is the "TIL" solution recommended by Texas Instruments Co. as an etchant for aluminum. Its composition is: 20 cc of H_2O, 300 cc of H_3PO_4, 12 cc of HNO_3, and 60 cc of glacial acetic acid. At the recommended temperature of 50°C, the etching rate of Cu 18% Al obtained by evaporation from an alloy source was determined to be 1 μm per minute. Layer structures have an apparent etching rate of 400 nm/min, on the average. The "TIL" solution was also used at room temperature where the etching is somewhat slower but still uniform; the three-layer film, Al/Cu/Al with a thickness of 30/1000/250 nm, was fully etched in four minutes. Measurements of the dissolution time and potential of Cu and Al alone and of Al/Cu/Al layers indicate that the etching process is basically under cathodic control for both metals, particularly copper, which also etches somewhat faster than aluminum. When aluminum is in layers, its dissolution is greatly increased, which is a likely reason for the average etching rate of the Al/Cu/Al at room temperature being about the same as that of Al at 50°C. The latter is 0.5 to 1 μm per minute, depending on grain structure, impurities, etc.

Another suitable etchant, particularly for laboratory use, is a mixture of $(NH_4)_2S_2O_8$, NH_4OH, and H_2O with a resulting pH of 10.4.

Films forming the α-Cu phase, i.e., with at% Al < 20%, can be etched as pure Cu, in $(NH_4)_2S_2O_8$, pH 1. The average etching rate is 3 nm/s, close to 2.7 nm/s determined as the dissolution rate of copper alone.

• *Electrical resistivity*

The film resistivity of the Cu-Al alloys (irrespective of the manner of their preparation) increases with an increase of the aluminum concentration (Fig. 8). The sputtered films, however, show the highest resistivity. For example, films with a composition of approximately 18 at% Al after deposition at room temperature have a high resistivity of 16–17 $\mu\Omega$-cm, characteristic of a material with a high degree of disorder, in comparison with 12–12.5 $\mu\Omega$-cm determined on annealed films of similar composition. After annealing as well as heating in an oxidizing atmosphere, the resistivity of all of the films decreased below the original values, and for the reported composition range it is 5–8 times higher than the resistivity of the pure copper films.

The resistivities of the films are roughly equal to those of "bulk" samples of similar compositions as found in the literature [16]—10.2, 11.9, and 13.6 $\mu\Omega$-cm for respective compositions of 11, 17, and 21 at% Al.

• *Oxidation resistance at elevated temperatures*

Oxidizing atmosphere

Films deposited in layers show interesting behavior when exposed to an oxygen-containing atmosphere at temperatures of 450°C or more; their surfaces oxidize forming a continuous aluminum oxide, while, simultaneously, fast interdiffusion of the three layer components forms an alloy. Even films with an aluminum upper layer of only 30 nm, with about 8 at% Al, show a high degree of oxidation resistance. After 7 h at 650°C, they stay metallically bright with less than 10 nm of aluminum oxide on the surface.

The behavior of the films deposited from alloyed and dual sources is more concentration dependent. 1) Films with less than 9 at% Al tend to oxidize fast, as pure Cu does (Table 1). A 600-nm film can be, in minutes, transformed into black CuO. 2) Films with less than about 20 at% Al show limited surface oxidation with less than a hundred nanometers of the oxides, CuO and Cu_2O. Al_2O_3 is also present, most likely as a layer underneath the copper oxides.

It has to be noted that the oxidation resistance of these samples is much improved if they are annealed in an "inert atmosphere" prior to oxidation. In this case only aluminum oxide is formed. Qualitative and quantitative differences on nonannealed and annealed samples are reflected in the ellipsometric parameters [17] Δ and ψ recorded *in situ* during oxidation in air at 500°C. Figures 9 and 10 show the changes of Δ (proportional to the oxide thickness) under both sets of conditions for Cu 15 at% Al samples deposited by dual e-beam evaporation. When copper oxides form (nonannealed sample), they form rapidly in the first few minutes of the oxidation. Their combined thickness may reach about 35 nm in 15 minutes (using $n^* = 2.7–0.4i$ as the best index of refraction). At later times only small additional changes of Δ were observed. This stage of growth of the reaction product can be described by a linear relationship between both Δ (i.e., thickness) and $1/\Delta$ (inverse thickness) with the logarithm of time. There are several mechanisms which may result in the observed law of oxide growth, involving, for example, the place exchange of oxygen and metal ions, or electron tunneling. They are not, however, easily acceptable, as the former would require a high activation energy and the latter might play a role only if the film thickness were smaller. A better explanation of the data may be as follows: The growth of the inner oxide film, i.e., aluminum oxide, practically nonmeasurable during the first fifteen minutes of the process, starts to play a role beyond that time. In a few minutes, although thin, this oxide may uniformly cover the entire metallic surface and further growth of Cu oxide can become limited by a field-assisted migration of Cu ions through the inner (aluminum) oxide. This may result in the inverse logarithmic law of growth which was observed.

The thicknesses of the individual oxide layers were not determined separately. However, the growth of Al_2O_3 alone was measured on an annealed sample and is visible in Fig. 10; a measurable change in Δ appears at comparatively later times, just about at the beginning of the logarithmic stage, Fig. 9. After initial nucleation, the oxide thickness changes exponentially with time, indicating that the new oxide fully covers the surface and that further growth is diffusion-limited. Such a growth proceeds for days. The thickness of the newly formed oxide is small, reaching 2.5 nm after 4 h. When the oxide becomes about 12 nm thick, the growth law changes into a slow logarithmic relationship, limited either by electron tunneling through an imperfect film (direct logarithmic law) or by a field-assisted ionic migration (indirect logarithmic law).

The difference in behavior of a nonannealed and an annealed alloy is probably the result of the formation of a very thin aluminum oxide during the initial annealing. Although a purified inert gas was used for annealing, the residual or backstreamed oxygen partial pressure is sufficient to form 0.3 to 1.8 nm of the new oxide. This was evaluated from the changes in ellipsometric data (on a number of annealed samples) assuming that these changes are entirely a function of the oxide growth. At low oxygen pressures, below the dissociation pressure of

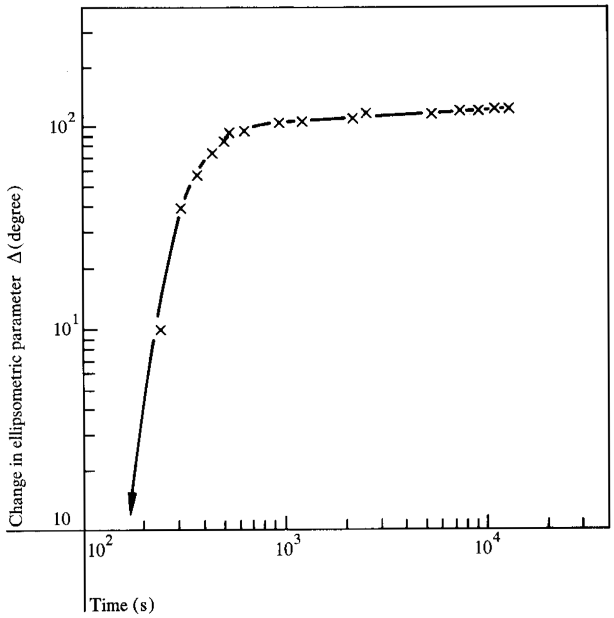


Figure 9 Change in the ellipsometric angle Δ for Cu-15 at% Al oxidized in air at 500°C.

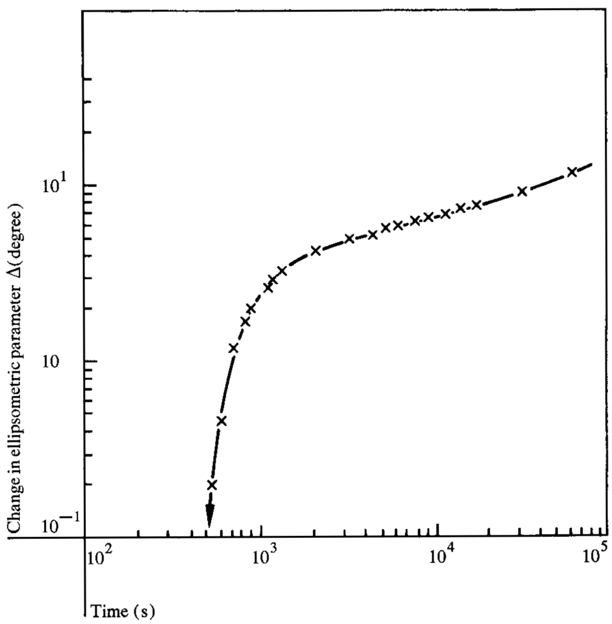


Figure 10 Change in the ellipsometric angle Δ for Cu-15 at% Al during oxidation in air at 500°C, following a previous anneal in He.

Table 4 Corrosion behavior of Cu-Al and Al oxidized after 1 hour at 500°C prior to the electrochemical measurements under a droplet of solutions of various pH.

		Cu-Al		
pH	3.2	5.4	7.2	9.1
$V_{corr,AlCu}$(mV,NHE)	+238	233	186	325
$V_{corr,Cu}$(mV,NHE)	+213	228	208	122
$V_{galv,corr}$(mV,NHE)	222	218	208	103
$i_{galv,corr}$(A/cm^2)	1×10^{-8}	-1×10^{-9}	$\pm 10^{-10}$	-3×10^{-9}
$i_{corr,AlCu}$(A/cm^2)	6.4×10^{-8}	9×10^{-8}	6×10^{-8}	6×10^{-8}
$i_{corr,Cu}$(A/cm^2)	1.4×10^{-4}	5.2×10^{-6}	9×10^{-7}	7×10^{-7}
$i_{corr,AlCu}$[a]	3.8×10^{-8}	7×10^{-9}	7×10^{-9}	4×10^{-9}
		Al		
pH	3.2	5.4	7.2	9.1
$V_{corr,Al}$(mV,NHE)	−249	−161	−121	−400
$V_{corr,Cu}$(mV,NHE)	218	234	201	128
$V_{galv,corr}$(mV,NHE)	+221	225	198	113
$i_{galv,corr}$(A/cm^2)	$+2.2 \times 10^{-6}$	2.5×10^{-7}	1×10^{-7}	1.3×10^{-7}
$i_{corr,Al}$(A/cm^2)	1×10^{-8}	8×10^{-8}	5×10^{-9}	8×10^{-9}
$i_{corr,Cu}$(A/cm^2)	4.5×10^{-5}	5.1×10^{-6}	9×10^{-7}	7×10^{-7}

[a]Values obtained on sample annealed in nitrogen at 500°C for 1 hour.

copper oxide, the growth of copper oxides is not expected; thus an initial anneal results in a selective surface oxidation of aluminum and thereby increases oxidation resistance.

When there is an increase of Al concentration from 20 to 25%, the combined surface oxide is thinner and becomes preferentially Al_2O_3 with some CuO detectable as an occasional hillock or whisker on the surface. Annealed samples show much the same oxide growth as described earlier (Fig. 10).

It is evident that the Cu-Al alloy with 13–25 at% Al (possibly 8% for films deposited in layers) shows very impressive oxidation resistance at elevated temperatures. While Cu alone becomes fully oxidized at temperatures of 350°C or more and Al alone cannot sustain temperatures above about 600°C (films with a thickness of 500 nm on LOF glass disintegrate in 2 hours at 600°C), Cu-Al alloys on suitable substrates have been brought up to 700°C without any appreciable losses due to oxidation.

Effects of sealing glass

The presence of a sealing glass on the metallic surface at 500°C causes a discoloration of the area under the glass. The effect depends on the sealing atmosphere and decreases as the environment changes from He to N_2, air, and O_2. The most likely reaction involved is the extraction of Al from the Cu-Al alloy via Cu-Al $\rightarrow$ Al_2O_3 $\rightarrow$ dissolved in glass. The reaction is speeded up by the presence of CuO and slowed down by the presence of Al_2O_3 in the sealing glass. The rate of this reaction was not determined, but it was experimentally evaluated that the effect due to IBM glass SG67 decreases with an increase of the upper Al thickness and is barely noticeable for films with more than 15 at% Al and thicker than 90 nm.

- *Corrosion resistance*

The corrosion resistance of the alloys with 8 to 25 at% Al, mostly prepared by layer deposition and annealing, was examined more closely.

S-containing atmosphere

Judging by the amount of the corrosion product formed, the corrosion resistance of Cu-Al is at least an order of magnitude higher than the resistance of Cu alone.

Comparison of the corrosion rates of Cu-Al and Cu

Corrosion rates evaluated under droplets of solutions of different pH on Cu-Al alloys are smaller than the dissolution rates of Cu determined under the same conditions (Table 4, lines 6, 7, and 8). The differences, depending on pH, are one to four orders of magnitude.

Galvanic compatibility of Cu-Al and Al with Cu

Simple electrochemical examination of the two galvanic couples indicates that Cu-Al is much less attacked than Al in the presence of Cu. In fact, the alloy exposed to oxidation at 500°C prior to contact with Cu is galvanically protected by copper (Table 4). The corrosion rate of aluminum, fairly low without galvanic coupling, is always increased by coupling to copper. The difference in the rates of galvanic corrosion of the two metallizations, Cu-Al and Al, coupled with Cu, is at least two orders of magnitude, favoring greatly Cu-Al.

Concluding remarks

Cu-Al alloys with 13–25 at% Al always show a hindrance of both grain growth and oxidation rate under all of the thermal cycles relevant to gas panel fabrication. The films adhere well. Even if deposited in several layers, they can be etched by a single etchant. Moreover, the films are fairly conductive. The degree of the oxidation resistance depends on the manner of film preparation; however, as long as the Al content of the films exceeds $\approx$13%, they can be exposed to air and sealing glass at high temperatures without considerable oxidation hazard. Their corrosion resistance promises a long shelf life, and their galvanic compatibility with Cu makes them particularly applicable for panel fabrication.

Acknowledgments

The authors are greatly indebted to many colleagues who provided their help in the course of this study. S. Ruffini and N. Bojarczuk supplied all of the layered films, and D. Irmischer prepared the alloys for the single source depositions. G. Spencer made the dual source depositions, C. Aliotta made most of the electron probe analyses, J. Karasinski carried out many of the x-ray film diffraction experiments, and J. Baglin and W. Hammer followed the progress of film homogenization with α particle backscattering.

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Received July 22, 1977; revised February 24, 1978

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