M. C. Shine
F. M. d'Heurle

Activation Energy for Electromigration in Aluminum Films Alloyed with Copper

Abstract: The rate of electromigration in thin films of aluminum and aluminum alloyed with copper has been determined by measuring the changes in resistance of stripes subjected to a current density of 4×10^6 A/cm^2. At temperatures in the range from 100 to 200°C the activation energy for electromigration has been found to have the same value for both the pure and the copper-alloyed samples, namely, 0.6 eV. However, the rate of migration is much smaller, by a factor as large as 100, in the copper-bearing samples. These results are discussed in terms of grain boundary diffusion and the effect of alloying additions on diffusion mechanisms.

Introduction

The flow of direct electric currents with densities of the order of 10^5 to 10^6 A/cm^2 has been shown[1] to cause failure in thin-film aluminum conductors. Recent work indicates that, under given conditions of temperature and current density, the lifetime of aluminum stripes can be increased by a factor of approximately 50 by alloying with two to four percent copper[2,3]. In pure aluminum at standard test temperatures it has been established that the transport of matter, which is responsible for the failure, occurs through grain boundary diffusion[4–6].

The effect of alloying on the rate of damage formation in current-stressed samples can be determined by measuring for pure aluminum some convenient parameter, such as the rate of change of resistance with time, and comparing this characteristic with those for alloyed films. The rate of resistance change is assumed to be proportional to the rate of material transport and to the rate of damage formation resulting therefrom. Studies made on bulk materials[7,8], as well as theoretical considerations[8,9], indicate that the rate of transport should obey a diffusion law of the type $A\exp(\Delta S/k)\exp(-\Delta H/kT)$. Whether the activation energy ΔH is increased or the coefficient A and the entropy ΔS are decreased by alloying can be determined from a measurement of ΔH, which can be obtained from the temperature dependence of the rate of change of resistance with time.

Experimental considerations

• *Method*

The activation energy for electromigration was determined by the resistometric technique[4]. At a given current density J and temperature T_1, the resistance R of the sample is monitored as a function of time. The temperature is then suddenly changed to T_2. If the transition from T_1 to T_2 is rapid enough that the concentration n_d of defects (the accumulation of which results in an increased sample resistance) remains constant, the slopes (see Fig. 1)

$$\dot{R}_1 = \frac{1}{R}\frac{dR}{dt}\bigg|_{T_1} \text{ and } \dot{R}_2 = \frac{1}{R}\frac{dR}{dt}\bigg|_{T_2} \tag{1}$$

are related by the expression

$$\ln(\dot{R}_1/\dot{R}_2) = \Delta H(1/T_2 - 1/T_1)/k. \tag{2}$$

In the case of measurements on alloyed films, care was taken to ascertain that the resistance changes measured were associated with electromigration-caused damage and not with precipitation phenomena. Under the experimental conditions resistance changes due to precipitation were found to be negligible and not significantly affected by electric current. All determinations of ΔH were carried out at a nominal current density of 4×10^6 A/cm^2.

- *Samples and sample preparation*

The sample configuration and preparation were identical to those described in Ref. 2. Typical aluminum-copper films, 5000 Å thick, were obtained by evaporation of aluminum from pyrolytic boron nitride crucibles and copper from molybdenum crucibles. Source heating was provided by coupling to a coil and an rf generator. The rate of deposition was 20 Å/s; the pressure prior to and during deposition was maintained at approximately 10^{-7} Torr. The substrates, which were oxidized silicon wafers, were normally kept at 200°C during deposition. A copper layer of the desired thickness was deposited, sandwich-like, between two layers of aluminum 2500 Å thick; homogenization of the samples occurred during subsequent annealing in a nitrogen atmosphere at temperatures of 450, 480, or 530°C.

Standard photoetching procedures were used to form stripes from the annealed films for electrical testing. The stripes on diced silicon chips were then mounted on TO-5 transistor headers.

- *Test conditions*

Testing at different temperatures was done in silicon oil baths controlled by mercury thermostats. The temperatures of the baths were controlled to ±0.03°C. However, the temperatures of the current-stressed stripes were known only as averages, since these temperatures were determined by using each stripe as its own thermometer. At 175°C the amount of self-heating varied from sample to sample from about 6 to 9°C for 5000-Å aluminum and aluminum-copper stripes, respectively. Rapid temperature changes were obtained by removing the samples from one bath and plunging them into another.

The current was provided by a modified commercial power supply used in the constant-current mode. The magnitude of the current (of the order of 500 MA) was determined from the voltage drop across a 10-ohm standard resistor mounted in series with the stripe, using a digital voltmeter. Through optimization of the characteristics of the power supply and careful temperature shielding of the monitoring resistors, the relative current variations were reduced to $\pm 2 \times 10^{-5}$. Since the voltages across the current-stressed samples were known with the same relative degree of accuracy, the resistances of the samples were known with an accuracy greater than 10^{-4}.

Experimental results

Electromigration-induced changes in the resistance ratio $\Delta R/R$ for various aluminum-copper alloys are shown in Fig. 2 as functions of time during tests at approximately 210°C. The current density was 4×10^6 A/cm². The stripes contained 0, 0.5, 2, 4, and 8 percent copper by weight. The maximum total change in resistance displayed in Fig. 2 amounts to three percent, as compared to a total resistance change of the order of 10 to 30 percent during the life of a stressed stripe up to the last moment before catastrophic failure.

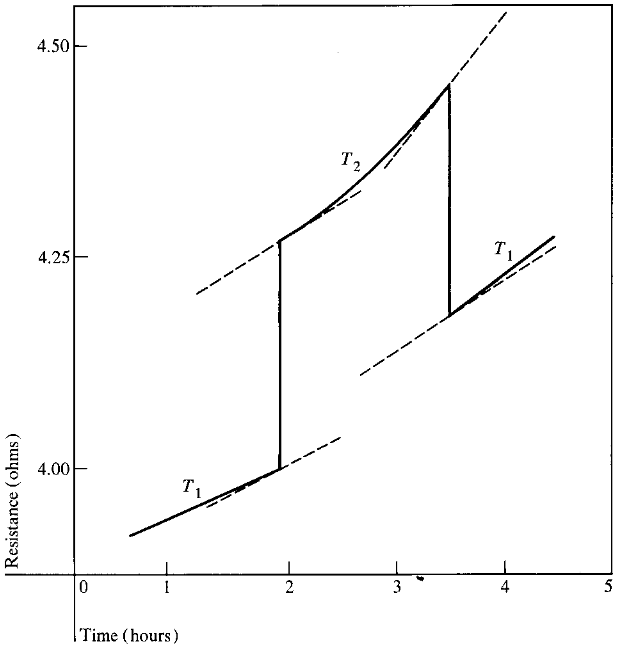
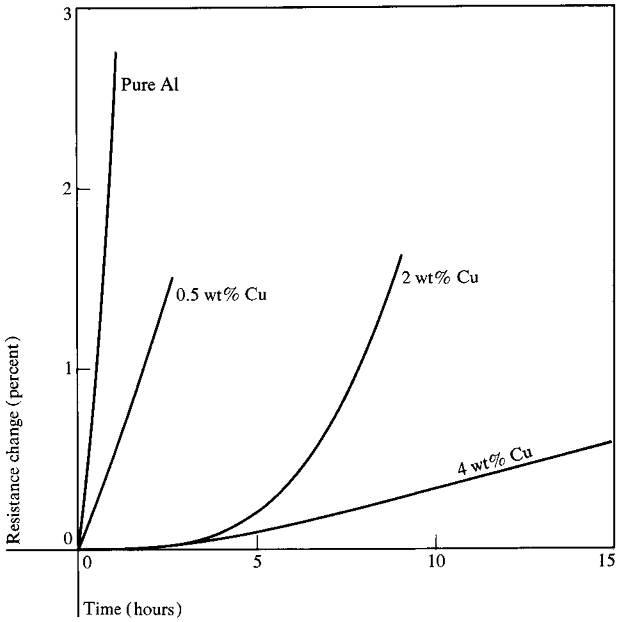


Figure 1 Schematic representation of the resistance-change steps used for the activation energy measurements.

Figure 2 Time dependence of the change of resistance of pure and copper-containing aluminum stripes resulting from current flow with a density of 4×10^6 A/cm². The pure aluminum stripe was measured at 205°C and the alloyed stripes at 208°C. On the scale used, the curve for 8 wt% Cu would be near the abcsissa.



In Fig. 2, as well as in the corresponding measurements of rates, time zero is taken as the time when the first

Table 1 Activation energy measured in aluminum-copper stripes.

Annealing parameters[a]	*Wt % Cu*	*Temperature range (°C)*	*Number of cycles*	$\Delta H_{\text{Al-Cu}}$ *(eV)*
480°C-5 min and 225°C-6 h	0.5	228 ⟷ 187	2	0.60 ± 0.03
		139 ⟶ 93	1	0.45
450°C-30 min	2	177 ⟷ 212	5	0.62 ± 0.05
		177 ⟷ 212	4	0.60 ± 0.06
		152 ⟷ 212	3	0.63 ± 0.06
		123 ⟷ 153	3	0.56 ± 0.03
530°C-30 min (q) and 350°C-1 week (q)	4	180 ⟷ 211	6	0.60 ± 0.05
		212 ⟷ 162	1	0.65
		158 ⟶ 107	1	0.58
		106 ⟷ 145	2	0.56
		102 ⟶ 82	1	0.53
480°C-15 min	8	220 ⟷ 180	2	0.51 ± 0.1
		220 ⟶ 180	1	0.68

[a] The letter q indicates that after the heat treatment the sample was quenched in water.

positive change in resistance is observed. When a copper-containing stripe is first brought to a test temperature, its resistance usually displays a slight decrease, which is thought to be associated with the completion of copper precipitation, stress relief, and possibly some vacancy annihilation. As can be seen, the initial rate of resistance change for the pure aluminum film is at least a factor of 50 greater than for the material alloyed with four percent copper.

Table 1 shows values of $\Delta H_{\text{Al-Cu}}$ (the activation energy measured in aluminum-copper stripes) obtained by the slope-ratio technique as a function of alloy composition, heat treatment (annealing after deposition), and temperature. The temperature range investigated was 225 to 82°C and the temperature intervals were between 25 and 50°C. In the temperature-range column a doubly directed arrow indicates that the temperature was shifted between the two values, with one determination of ΔH being made with $T_2 < T_1$ and the other with $T_2 > T_1$. When more than one determination of ΔH was made, the error reported represents the extreme variation from the mean. As can be seen, the activation energy for electromigration, which is about 0.6 eV, is independent of composition. However, there is a positive correlation between ΔH and temperature: The activation energy decreases from a value of about 0.6 eV at temperatures around 200°C to a value of about 0.5 eV at temperatures near 80°C.

Table 2 contains values of ΔH_{Al} for pure aluminum deposited at a substrate temperature of 200°C with a grain size of the order of 1 to 2 μm. These electromigration results are in agreement with previously published values[5] obtained from determinations of time to failure.

The values of ΔH for pure aluminum are equivalent to those obtained with the copper-alloyed samples. These values are also similar to the value that had been obtained previously[4] by the same measurement technique in the case of pure aluminum. However, examination of the present results indicates a trend toward a decrease in activation energy with temperature. This trend is visible in Fig. 3, where the values of activation energy for both pure and copper-alloyed samples are plotted against the mean temperatures of the ranges in which the values were obtained; the activation energy decreases from about 0.6 eV at 200°C to 0.5 eV at 100°C.

Discussion

Analysis of the results depends on the interpretation of the terms in the transport equation that has been found[7,8] to describe electromigration phenomena,

$$J_i = c_i\, z_i^*\, eE\, D_{0i} \exp(-\Delta H_i/kT)/kT, \tag{3}$$

i.e., the flux J_i of atoms of species i is proportional to the concentration c_i, the diffusion coefficient $D_{0i} \times \exp(-\Delta H_i/kT)$, the effective atomic charge z_i^*, and the electric field strength E.

The measured values of activation energy for electromigration in small-grain aluminum and aluminum-copper stripes are commensurate with the values, e.g., 0.55 eV[10], previously reported for grain boundary dif-

Table 2 Activation energy measured in pure aluminum stripes.

Annealing parameters	*Temperature range (°C)*	*Number of cycles*	ΔH_{Al} *(eV)*
480°C-15 min	$67 \longrightarrow 113$	1	0.50
	$92 \longleftrightarrow 69$	1	0.52
	$93 \longrightarrow 131$	2	0.57 ± 0.05
	$150 \longleftrightarrow 175$	2	0.73 ± 0.07
	$150 \longleftrightarrow 175$	2	0.50 ± 0.05
	$150 \longleftrightarrow 175$	2	0.59 ± 0.05
560°C-20 min	$177 \longleftrightarrow 211$	4	0.60 ± 0.10

fusion in aluminum. However, the difference (a factor of 50) observed between the rates of electromigration in pure and copper-alloyed aluminum stripes would require a difference of 0.16 eV between the respective activation energies if it were assumed that the pre-exponential factors in the transport equation (3) were equal in both cases. Examination of the data in Fig. 3 indicates that such a difference was not found. Hence it must be concluded that the species-dependent pre-exponential factors in the transport equation are decreased in value by a factor of 10 to 100 by the addition of copper to aluminum.

A precise analysis would require a systematic knowledge of the nature of grain boundaries and of the effects of alloying additions on diffusion. In spite of much work (see, for example, Refs. 11 through 14), no consistent model for impurity effects on lattice diffusion is available. Studies of the effect of impurities on grain boundary diffusion are quite scarce[15,16], although it has been reported that the rate of diffusion of gold in copper grain boundaries decreases with increasing gold content[16].

For lattice diffusion, although contrary evidence can be mustered, it seems that, for a broad class of solutes, solute diffusion is characterized by a lower activation energy and a lower value of $D_0 = A\exp(\Delta S/k)$ than those for self-diffusion. This solute effect has been verified experimentally in a number of aluminum alloys[11-13]. Moreover, the presence of alloying additions tends to enhance the self-diffusion of the host atoms[12,14], as well as the diffusion of a variety of solutes[12].

For the purpose at hand, which is to evaluate the effect of impurities on grain boundary diffusion, the effect of solutes on lattice diffusion may be explained on the basis of Zener's thermodynamic considerations[17,18]. The addition of impurities to a metal causes strain, which results in a decrease in the modulus of elasticity[17]. It follows therefrom that the activation energy for diffusion should be reduced[19], and that the entropy and D_0 should also decrease[18]. The same reasoning, when applied to the effect of impurities on grain boundary diffusion should lead to the opposite conclusion: Because alloying additions reduce the strain inherently present in grain boundaries[20], their presence should increase the values of ΔS and ΔH for grain boundary diffusion. The large atomic size difference[21] between aluminum (2.862 Å) and copper (2.556 Å) should cause the activation energy $\Delta H^{\mathrm{Al}}_{\mathrm{Al\text{-}Cu}}$ for grain boundary motion of aluminum atoms in aluminum films containing copper to be appreciably greater than the activation energy $\Delta H^{\mathrm{Al}}_{\mathrm{Al}}$ for motion of aluminum atoms in pure aluminum films. The magnitude of this difference is probably not much greater than 0.1 eV (estimated from the size of impurity effects on lattice diffusion) and $\Delta H^{\mathrm{Al}}_{\mathrm{Al\text{-}Cu}}$ is probably equal to about 0.7 eV.

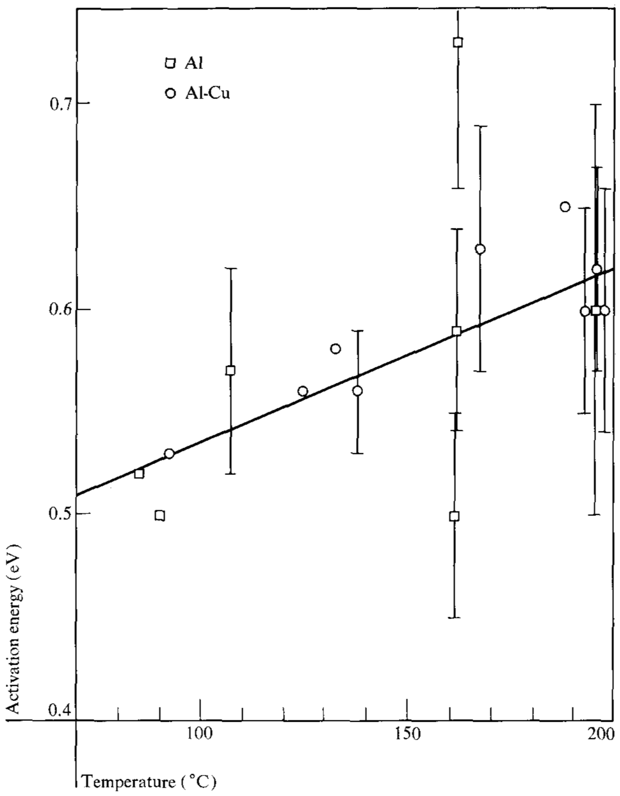


Figure 3 Activation energy as a function of the average measurement temperature for pure and copper-containing aluminum stripes.

The effect of copper additions on the value of D_0 cannot be anticipated on the basis of thermodynamic considerations alone, since D_0 for grain boundaries is a function not only of entropy but also of the effective width of the boundaries and the density of diffusion paths, dependences that have been the object of several investigations[22-24]. Thus the decrease in D_0 for grain boundary diffusion in silver, which has been observed[23] when the purity is decreased from a 99.999 to a 99.97 percent-pure grade, is probably due to a modification of the grain boundary structure. Since copper additions to aluminum films do not change the activation energy for electromigration (as measured by resistance changes), and are not expected to decrease the entropy term for grain boundary diffusion, the observed decrease in the rate of migration (which results from copper additions) must be explained by a reduction in the number of available diffusion paths in alloyed grain boundaries. This reduction may be due simply to the relaxation of strained atomic bonds or to more complex effects of copper on dislocation pipes and on grain boundary configurations. Such a change in the structure of grain boundaries has been reported for pure and impure iron[15], and more specifically for the case of sulfur additions to iron[25].

The equality of the activation energies for electromigration measured in pure and in copper-alloyed aluminum films appears to be somewhat fortuitous. The effect of copper in reducing electromigration in thin aluminum films may be explained according to two different models that share a common feature, namely, that the reduction in the rate of migration is due to copper atoms adsorbed on aluminum grain boundaries.

According to the first model the observed changes in resistivity are due to the motion of aluminum atoms restrained by the presence of copper in the grain boundaries. In this case the measured activation energy should be given by

$$\Delta H_{\mathrm{Al\text{-}Cu}} = \Delta H^{\mathrm{Al}}_{\mathrm{Al\text{-}Cu}} + Q - H, \tag{4}$$

where Q is the heat of adsorption of copper atoms on grain boundaries and H is the heat of solution of copper atoms in aluminum.

According to the second model the changes in resistivity are controlled by the motion of copper atoms in the grain boundaries. Because of its low solubility, copper does not contribute significantly to the resistivity of aluminum-copper alloys. However, if the motion of copper atoms necessarily precedes that of aluminum atoms, resistance changes could be directly dependent on copper diffusion. The measured activation energy should then be given by

$$\Delta H_{\mathrm{Al\text{-}Cu}} = \Delta H^{\mathrm{Cu}}_{\mathrm{Al\text{-}Cu}} + H - Q. \tag{5}$$

In the two expressions (4) and (5) the signs of Q and H are quite naturally reversed, because in the one case the motion of aluminum atoms is more hindered as the concentration of copper atoms in the grain boundaries increases, whereas in the second case the flux of copper atoms increases with increasing copper concentration. The value of H is probably quite accurately derived from the Al-Cu equilibrium diagram as being equal to 0.42 eV [26]. The value of Q is not known but is unlikely to be greater than 0.22eV[27]. A value for $\Delta H^{\mathrm{Cu}}_{\mathrm{Al\text{-}Cu}}$ of 0.55 eV can be obtained from measurements[28] on the rate of growth of $\mathrm{Al_2Cu}$ precipitates, and $\Delta H^{\mathrm{Al}}_{\mathrm{Al\text{-}Cu}}$ has been estimated as being about 0.7 eV. However, better measurements and more accurate knowledge of these quantities are necessary to allow one to distinguish between the two models with any degree of certainty.

Conclusions

1) The addition of copper to aluminum films reduces the rate of change of resistance due to the flow of direct current. About 4 wt% Cu reduces the rate of change by a factor of about 50, which is commensurate with the increase in lifetime of aluminum stripes that have been alloyed with the same amount of copper.

2) The activation energy measured for resistance change in aluminum-copper stripes is equal to that measured in pure aluminum stripes, namely, 0.5 to 0.6 eV in the temperature range 100 to 200°C. This value is approximately equal to that which is characteristic of grain boundary diffusion in aluminum.

3) The observed decrease in activation energy by 0.1 eV when the temperature decreases from 200 to 100°C appears to be real regardless of experimental uncertainties of the same order of magnitude. It is perhaps inherent to grain boundary diffusion in films.

4) The decrease in the rate of migration caused by copper additions is due to a modification of the pre-exponential terms of the transport equation. Copper atoms absorbed on the grain boundaries reduce the density of effective diffusion paths in grain boundaries either by simply plugging dislocation pipes or by a more complex modification of the grain boundary structure.

5) The equal values of activation energy measured in aluminum and aluminum-copper films hide the complexity of the migration phenomena in aluminum-copper films. Migration in aluminum-copper films has been discussed in terms of two hypotheses in which either copper reduces the rate of aluminum migration or copper migration precedes aluminum migration. Lack of knowledge about the values of the energy of adsorption of copper atoms on grain boundaries and the energies of activation for motion of aluminum in aluminum-copper grain boundaries and for motion of copper does not allow an unequivocal choice between the two mechanisms.

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The authors are located at the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598.