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ELECTROMIGRATION IN THIN FILMS : THE EFFECT OF SOLUTE ATOMS ON GRAIN BOUNDARY DIFFUSION

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Résumé. — Des études portant sur des conducteurs en couche mince d'Al, d'Au et de Cu ont montré que l'addition de certains éléments d'alliage réduit considérablement la vitesse d'électromigration aux joints de grains des atomes du solvant. Les résultats quantitatifs obtenus jusqu'à maintenant sont résumés. Pour l'Au ces résultats sont comparés à des expériences sur l'autodiffusion aux joints de grains faites au moyen de traceurs radioactifs.

Deux conclusions sont établies. 1) En général la force (appelée charge effective) exercée par un courant continu sur des atomes placés dans les joints de grains n'est pas très différente de celle exercée sur un atome placé dans le réseau (à un facteur de 2 près). 2) Les résultats sur l'électromigration du Cu, du Mg et du Ni dans les joints de grains de l'Al suggèrent que l'adsorption de ces atomes sur les joints de grains est inversement proportionnelle aux différentes limites de solubilité.

Abstract. — It has been shown that certain alloying additions are effective in reducing the rate of electromigration of the host element in thin film conductors of Al, Au and Cu. The quantitative results obtained up to now are summarized. For Au these results are correlated with grain boundary autodiffusion data obtained by means of radioactive tracers.

Two conclusions are reached. 1) In most cases the force, usually called effective charge, excerted by a direct current on atoms within grain boundaries is not very different (within a factor of 2) from the force on atoms in the lattice. 2) The electromigration data for Cu, Mg and Ni atoms in Al grain boundaries suggest that the adsorption of these atoms on grain boundaries is inversely proportional to the respective solubility limits.

1. **Introduction.** — About ten years ago it became evident that electromigration, the transport of atoms by a direct current in a conductor, could be the cause of failures in thin film Al conductors used to make contacts to the active areas of planar Si transistors [1, 2]. Because of the structure of the conductors involved, namely their small grain size, about 10^{-6} m, and also because of the relatively low temperatures, from room temperature to about 250 °C, grain boundary diffusion is the prevailing transport mechanism in the phenomena leading to electromigration in thin films [1-3]. Thus, industrial applications were the impetus for wide spread studies dealing with the characteristics of grain boundary transport. The results of such work have added significantly to the growing literature on grain boundary diffusion [4-11]. The report that Cu additions to Al thin films reduce the rate of electromigration failure is interesting from a practical, as well as theoretical point of view [12]. In the present paper, recent results of electromigration and diffusion studies on Al, Cu and Au thin films and « bulk » solid samples will be reviewed, with special emphasis on the effects of various alloying additions. Experiments concerning the migration of grain boundaries [13-16] per se, as a result of a current flow across the boundaries, rather than the transport of matter along boundaries, will not be discussed here.

2. **General considerations.** — 2.1 Typically electromigration experiments are conducted with samples approximately 5 000 Å thick which have been vacuum deposited onto oxidized silicon wafers. The sample geometry, exemplified in figure 1, is obtained by photoengraving techniques. In figure 1 the conductor has a length of 250×10^{-6} m and a width of about 6 to 8×10^{-6} m. The dimensions of the two terminal pads which are used for bonding contact wires are approximately 1 and 0.5×10^{-3} m. In order to know precisely the temperature of the samples during electromigration testing, the resistance of the samples is calibrated as a function of temperature, and the samples are used as their own resistance thermometers. With current densities of the order of (1 to 5) 10^6 A/cm^2, the increase in temperature due to Joule heating in Al, Cu, or Au samples is about 10 °C. It is to be noted that with a grain size which is generally equal to the thickness of the films, the number of grain boundaries across any one section of the conductors is relatively small, between 6 and 16. Because grain boundary structures vary greatly with the relative orientations of neighboring grains [5, 7], no

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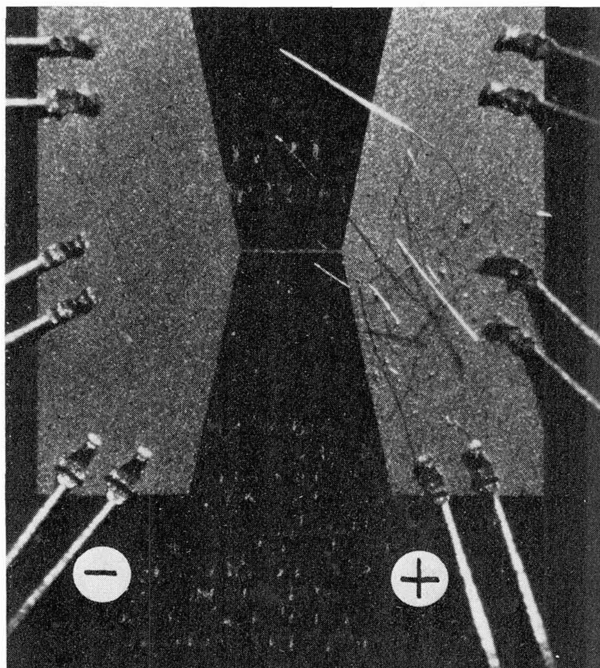

FIG. 1. — Photograph at an Al-Cr thin film conductor after testing at 175 °C and 2×10^6 A/cm² for 8 300 hours. The length of the conductor is 2.5×10^{-4} m (d'Heurle and Gangulee, ref. [29]).

two cross-sections of any one conductor are statistically identical ; in fact, no two conductors are exactly comparable. Thus, at a point of maximum divergence in grain boundary transport due to structural differences between two adjacent areas along the length of a conductor, failure occurs after a certain time of electromigration testing. Furthermore, in sets of seemingly identical samples tested under the same conditions of current density and temperature, failure occurs at different times for each of the individual samples. As shown in figure 2 it is commonly found that for a given set of samples, the logarithms of the failure times follow a Gaussian distribution (lognormal law) [12].

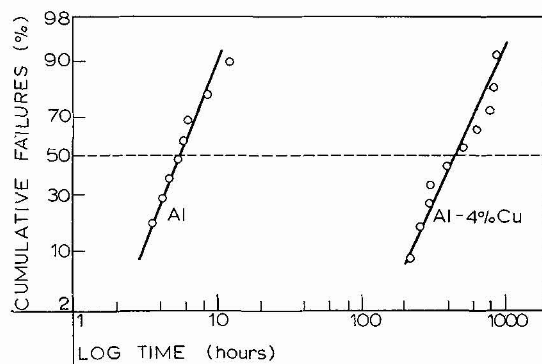

FIG. 2. — Cumulative percentage failure data for pure Al and Al-2 at % Cu. The conductors were annealed at 530 °C and tested at 175 °C and 4×10^6 A/cm² (Ames, d'Heurle, and Horstmann, ref. [12]).

2.2 Details in new considerations of electromigration theory [17-19] have not invalidated previously achieved results. The general transport relationship, known as the Einstein equation, whereby the average velocity of moving atoms is given by the product of the mobility, and the driving force has been applied to electromigration phenomena [20, 21]. From the basic equation, the volume of matter transported in a thin film conductor is given by

$$vol_a = (n.l.\delta) \times (D_a/kT) \times (Z^*.Ee) \times t, \quad (1)$$

where vol_a, in a pure material or in a dilute solid solution, is the volume of the matrix element transported in a time t ; n, l and δ are the number, the length (usually equal to the film thickness) and width of the grain boundaries ; Z^* is the effective charge of the matrix atoms ; E is the electric field, and e the charge of the electron. For saturated solid solutions the volume of transported solute, vol_b, is given by a slightly modified form of the above relation, namely

$$vol_b = (n.l.\delta) \times (c_s.\alpha) \times \times (D_b/kT) \times (z^*.Ee) \times t, \quad (2)$$

where c_s is the solid solubility limit at the temperature of the experiment, α is an adsorption coefficient measuring the ratio between the concentrations of solute atoms in the boundaries and in the lattice, and z^* is the effective charge of the solute atoms.

Generally, any single electromigration experiment will yield either the products $\delta.D_a.Z^*$, or $\alpha.\delta.D_b.z^*$, or both, but not the values of the different factors in these products. In a number of cases, the values of Z^* have been obtained independently from lattice electromigration experiments [22, 23]. It is possible then to assume thas Z^* has the same values in the grain boundaries and in the lattice. Since the effective charges Z^* and z^* are related to the specific resistivities of the mobile species, it has been shown [21] that

$$Z^* - z^* = \lambda/\rho.Z.z.(Z + z), \quad (3)$$

where ρ is the resistivity of the alloy, Z is the valence of the solvent metal, $Z + z$ is the valence of the solute, and λ is the proportionality constant between residual resistivities and z^2. This relation has been verified experimentally for lattice electromigration in a number of Ag alloys [24]. Presuming that for z^* as well as for Z^* the lattice values apply to grain boundaries, eq. (3) gives the magnitude of the effective charges for alloy elements when these have not been experimentally determined. In most metals, which are clearly electron conductors, electromigration is directed towards the cathode. Consequently, the effective charges are given a negative sign.

2.3 Electromigration results on thin film samples have been the object of recent reviews [25, 26]. Specific aspects related to quantitative measure-

ments of grain boundary diffusion will be considered presently. Aluminum samples with the geometry shown in figure 1 will often become electrically discontinuous through the formation of a grain boundary crack before any measurable transport can be observed. In other samples the transport will be so heterogeneous as to defy analysis. These observations are at least partly conditioned by the relationships between current density, transport and failure times. Since the transport of metal is proportional to the current density, achieving measurable transport at low current densities requires prohibitively long periods of time. However, since the time that elapses prior to failure decreases as some higher power [27] of the current density, at a high current density failure tends to occur before a significant amount of matter has been transported.

Figure 3 is illustrative of a well behaved sample in which areas of matter depletion as well as areas of matter accumulation are clearly identifiable. Through the use of the scanning electron microscope, and the electron microprobe, the volume of the holes and hillocks (accumulation) can be estimated accurately. In the case at hand [28] these volumes were found to be 38 and 33 $\times$ 10^{-18} m^3, respectively, for accumulation and depletion. Furthermore, generally in such a sample the electron microprobe gives accurate information about alloy concentrations, from which the transport of alloy atoms can be derived. On some samples, as in figure 1, accumulation did not only consist in the formation of whiskers which are visible in the optical microscope, but also in a general thickening of the positive terminal [29]. Conversely, electromigration was found to have transformed most of the negative terminal into a spongy material with extensive grain boundary depletion. In an Al sample, with Ni additions, the transport of Ni was found to be so rapid that after testing, the Ni concentration in the positive terminal was 17 % higher than in the negative terminal. In the same sample, the Al transport was too small to be measured, and is presumed to be less than 1 %.

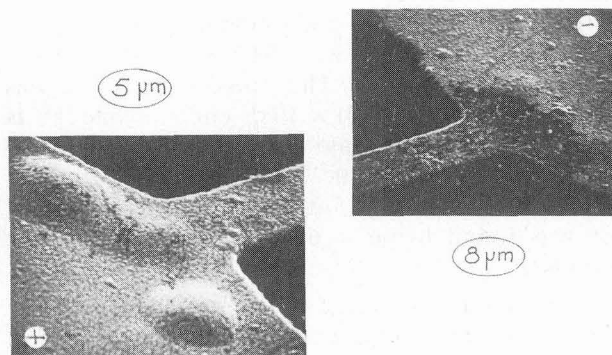

FIG. 3. — Positive and negative ends of a Cu-Al conductor after testing at 265 °C and 2 $\times$ 10^{-6} A/cm^2 for 1 440 hours (d'Heurle and Gangulee, ref. [28]).

2.4 A type of experiment which has yielded extensive information about solute electromigration in thin films deserves special attention. A dot of an alloying element, namely Cu, is deposited at a specific location along the length of an Al thin film conductor [30]. Prior to electromigration testing, the dot of alloying element is diffused through the thickness of the conductor by an appropriate annealing treatment. After testing it is observed that Al has accumulated on the negative side of the dot, while holes have formed on the positive side of the dot. This provides immediately qualitative evidence that Cu is effective in reducing the rate of Al electromigration in grain boundaries. Furthermore, it is observed that the position of the dot has drifted toward the positive terminal. Analysis of the profile of Cu concentration after electromigration testing [31], of the drift rate of the negative side of the alloyed dot (the drift is linear with time) [32], and of the motion of the void front on the positive side of the dot (the displacement varies as $t^{0.5}$) [33] has given independent values both for $\alpha.\delta.D_b$ and z^* for Cu in Al. Moreover, since in the case of Cu in Al, the void front moves into pure Al, while the negative side of the dot moves into Al-Cu, it is possible to obtain diffusion data for Cu in Al as well as in Al-Cu.

For obvious practical reasons attention has mostly been given to those alloying additions which reduce the rate of grain boundary electromigration in thin films. This reduction is a phenomenon which is specific of grain boundary diffusion. Generally, the addition of alloying elements is expected to increase the rate of lattice diffusion for the solvent atoms. The enhancement of the solvent diffusion coefficient in the lattice from a value $D_a(0)$ in the pure state to a value $D_a(c)$ in the presence of an alloying element of concentration c is usually expressed by the relation

$$D_a(c) = D_a(0)\ (1 + bc) \tag{4}$$

In the case of Ta additions to Au, at 300 °C the value of b is about 600 [34]. For Cu additions to Al, at 576 °C, b was found to be equal to 8 [35].

The problem of solute effects on the lattice electromigration of solvent atoms involves considerations of correlation terms as well as terms due to *vacancy flow* [35, 36]. For Al it was first reported that impurities increase the rate of electromigration in the lattice [22]. More recently this effect was expressed quantitatively [35]. In the presence of an alloying element, the product $D_a.Z^*$ should be multiplied by the factor $(1 + B''\ c)$. At 576 °C the addition of Cu to Al the quantity B'' was found to be equal to about 8 [37]. It is not necessarily true that for all alloying systems the terms b and B'' should have the same sign.

3. **Grain boundary effects in thin films.** — 3.1 AU FILMS AND RELATED RESULTS. — 3.1.1 While it is

well established [20] that in Cu, Ag and Au the lattice electromigration proceeds from the negative to the positive terminal, in the direction of electron flow, in thin films and for grain boundaries it has been claimed that for these three metals, electromigration proceeds in the opposite direction against the flow of electrons [38]. A number of experiments [39-41] conducted on Au films have led to the opposite conclusion, namely, in grain boundaries the direction of electromigration is the same as in the lattice from the negative to the positive terminal. The same conclusion may hold for Ag [10] and for Cu [25, 29].

Failure experiments were conducted with groups of ten conductors tested simultaneously at a current density of 6×10^6 A/cm^2, and at temperatures from 200 to 300 °C [42]. The median failure times, t_f, were obtained from plots as in figure 2. In figure 4 the log of t_f/T (where T is the absolute temperature) is plotted as a function of $1/T$. The activation energy is 0.92 ± 0.06 eV. The term t_f/T comes from eq. 1 (when log t_f is plotted against $1/T$, as is erroneously done quite often, the derived activation energy is somewhat too small). In figure 5 the log of the grain boundary diffusion coefficient obtained by tracer techniques [34], both on bulk and thin film samples, is plotted against $1/T$. The pre-exponential factor, $\delta . D_{0a}$ is 8×10^{-10} cm^3/s, and the activation energy value of 0.95 eV is very close to the value derived from electromigration failure experiments.

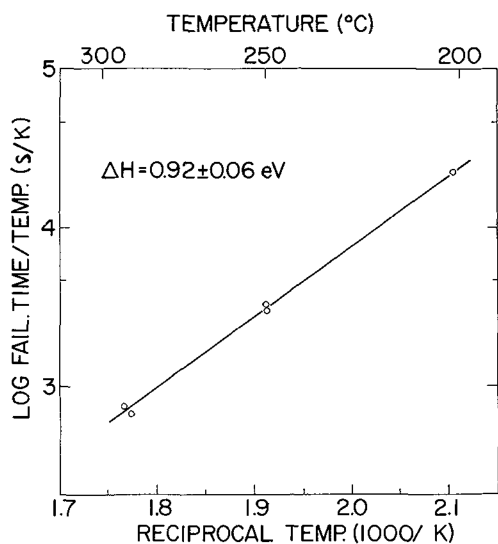

FIG. 4. — Arrhenius plot of failure times — t_f/T — for Au thin film conductors (Gangulee and d'Heurle, ref. [42]).

3.1.2 In experiments on Au films with either a Mo or Ta adhesion layer [43], at a temperature of about 300 °C, and a current density of 4×10^6 A/cm^2, it was found that failure times were more than 100 times longer for the Au-Ta films than for the Au-Mo films. The results of Au tracer experiments on polycristalline Au-Ta samples, which are plotted on figure 5, indicate that the increase in failure times for the Au-Ta films is due to the retarding effect of Ta additions on the grain boundary diffusion of Au. This is perhaps not a full explanation, since according to the data on figure 5 the effect of Ta is minimal at about 300 °C. Observe that in the case being considered, the presence of Ta solute atoms increased both the pre-exponential factor, $\delta . D_{0a}$, to a value of 5×10^{-7} cm^3/s, and the activation energy to a value of 1.26 eV, for the grain boundary diffusion of the solvent Au atoms. This is possibly the first thorough study of this type. In order to be exhaustive, the data should also include the grain boundary diffusion of Ta tracers, both in pure Au and in Au-Ta. Unfortunately, because of the high reactivity of Ta, the necessary experiments would be extremely difficult to complete.

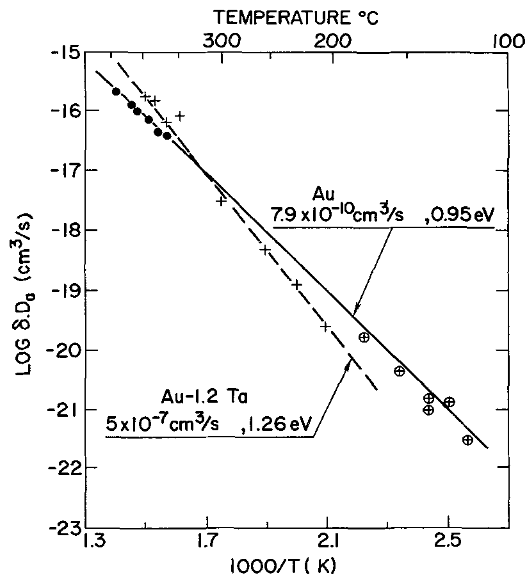

FIG. 5. — Temperature dependence of $\delta . D_a$ D_a in Au and Au-1.2 at % Ta (Gupta and Rosenberg, ref. [34]).

3.1.3 One experiment carried out according to the *dot* technique mentioned previously (2.4) with Ag alloying additions to Au has been reported [23]. Silver atoms were found to be without effect on the grain boundary diffusion of Au. The temperature was 250 °C and the current density 2×10^5 A/cm^2. The value of $\alpha . \delta . D_b$ was found to be $(1.7$ to $4) \times 10^{-17}$ cm^3/s, while z^* is about — 10. At the same temperature according to figure 5, $\delta . D_a$ is 1×10^{-18} cm^3/s. In lattice electromigration experiments, at 930 °C in Ag-Au alloys, Z^* was found to be — 6.5 for Ag and — 8.2 for Au [44].

3.2 Cu FILMS. — 3.2.1 Electromigration experiments on Cu films containing a small amount of Al (about 1 at %) gave somewhat uncertain results because of the oxidation of the Al solute [28]. Because the failure times were not significantly

different for the Cu-1 at % Al and for pure Cu, the transport data obtained on the Cu-Al samples are presumed to be representative of pure Cu films. For a test at 265 °C, with a current density of 2×10^6 A/cm², and a duration of 1 400 hours, analysis of the transport seen in figure 3 gives for $\delta . D_a$ a value of 2.5×10^{-18} cm²/s. (The value of Z^* was estimated from lattice electromigration experiments [23] which give Z^* equal to — 10 at about 900 °C). Observations relating to the formation of a surface layer of Al oxide on the same Cu-Al films have been interpreted as providing experimental evidence for a vacancy mechanism for grain boundary diffusion. More recent results, still to be analyzed fully, with Cu films containing about 5 at % Al indicate that Al additions do not affect the failure times of Cu conductors undergoing electromigration testing. Thus, it may be tentatively concluded that Al solute atoms do not affect the grain boundary diffusion of the Cu solvent.

3.2.2 With Cu films containing Be additions and tested at 291 °C, the electromigration failure times were found to be about 100 times longer than for pure Al films [28]. Analysis of void formations at the negative end of one sample gave for $\delta . D_a$ at 291 °C a maximum value of 3.8×10^{-19} cm³/s. Comparison of this value with the value obtained above with Cu-Al (or pure Cu), taking into account the difference in test temperature indicates that the addition of Be to Cu reduces the rate of grain boundary diffusion of the solvent by a factor of at least 15, while failure times would indicate that the same factor might be as high as 100. Such an effect of Be on Cu had been previously reported [45], but it does not appear that any quantitative data were given.

3.3 Ag. — The author does not know of quantitative transport measurements on Ag films. However, for the sake of completeness, one should mention here the study of Sb electromigration in a Ag bicrystal [10]. It is reported that the value of z^* measured in the vicinity of 500 °C is about twice as big for grain boundary diffusion as for lattice transport.

3.4 Al AND Al ALLOY FILMS. — Al thin film conductors have been studied quite extensively. However, because of the lack of a suitable isotope, and of difficulties inherent to the formation of a surface oxide layer, information similar to that obtained on Au from tracer studies in polycrystalline material remains missing in the case of Al. For the purpose of comparison, the solubility limits of three alloying additions which have been found to reduce the grain boundary diffusion of Al, namely Cu, Ni and Mg, are plotted on figure 6.

3.4.1 Failure data for pure Al films with a random orientation plotted according to figure 4 indicate that the activation energy for $\delta . D_a$ is very close to 0.55 eV [46]. This value is confirmed by a number of related experiments. Reports of higher activation energy values in *large grain films* (see ref. 46) are undoubtedly due not to the size of the grains, but to the structure of the grain boundaries. Films with large grain size are usually deposited on substrates at high temperatures and under high vacuum. These conditions reduce O_2 absorption, while favoring the formation of films with a (111) orientation and the growth of grains with low energy boundaries. The transport for the Al-Cr sample in figure 1, tested at 172 °C and 2×10^6 A/cm² for 8 300 hours, was analyzed [29]. The results are given in table I. Z^* was assumed to be — 30 from lattice experiments [22]. From the value of $\delta . D_a$, and using an activation energy of 0.55 eV, one obtains $\delta . D_{0a}$ to be 3.6×10^{-10} cm³/s, which is very close to the value for Au (3.1.1). For this reason, as well as others, the grain boundary transport results obtained here for Al-Cr are thought to be representative of pure Al.

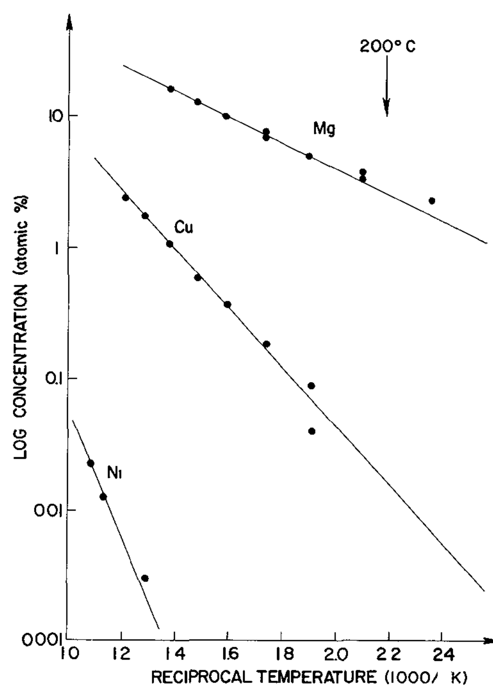

FIG 6. — Arrhenius plot of the solid solubility limits for Mg, Cu and Ni in Al.

3.4.2 As shown on figure 2, additions of Cu to Al increases the failure times of Al thin film conductors by a factor of about 70. The results of transport [29] analysis for an Al-Cu sample are also found in table I. The sample contained 1 at % Cu, and was tested at 175 °C and 1×10^6 A/cm² for 25 000 hours. Detectable transport was localized, as in figure 3. The value of z^* was estimated to be — 30 from eq. (3). The value of $\delta . D_a$ is about 80 times smaller than in Al (— Cr), see above (3.4.1). This factor which is almost equal to the

TABLE I

Grain Boundary Diffusion Parameters in Al Alloys (cm^3/s)

	Al δD_a	c_s	Solute $c_s\,\alpha.\delta.D_b$	$\alpha.\delta.D_b$	Ref.
At 175 °C					
Al-(Cr)	2.2×10^{-16}				[29]
Al-Ni	5.6×10^{-18}	10^{-9}	1.5×10^{-18}	1.5×10^{-9}	[50]
Al-Cu	2.8×10^{-18}	2×10^{-4}	2.4×10^{-19}	1.2×10^{-15}	[29]
At 231 °C					
Al	1.1×10^{-15} (*)				
Al-Mg	6×10^{-18}	4×10^{-2}	2.4×10^{-19}	6×10^{-18}	[48]
At 250 °C					
Al	2×10^{-15} (*)				
Al-Cu		9.4×10^{-4}	1.7×10^{-17}	1.8×10^{-14}	[33]
At 300 °C					
Al	5.8×10^{-15} (*)				
Al-Cu		2.1×10^{-3}	2.7×10^{-16}	1.3×10^{-13}	[32]

(*) Extrapolated from Al-(Cr) at 175 °C with an activation energy of 0.55 eV.

increase in failure times indicates that the reduction of the failure rate in Al-Cu is due to the decrease in the grain boundary diffusion of Al. Comparison of the diffusivity values for Cu in Al-Cu, for Al in Al-Cu, and for Al in Al (3.4.1) led to the hypothesis that the migration of Cu atoms in Al is not greatly affected by the presence of Cu in grain boundaries.

3.4.3 Extensive work has been done with the dot technique (2.4) on the effect of Cu alloying in Al thin film conductors [31-33]. Experiments were conducted both at 250 °C and 300 °C. Separate values of z^* and $\alpha.\delta.D_b$ where obtained for Cu diffusion in Al, and for Cu diffusion in Al-Cu. At 250 °C, at least there appears to be no systematic difference for these two sets of diffusivity values. Different modes of analysis give z^* equal to (— 14 to — 20), and $\alpha.\delta.D_b$ equal to (1.4 to 2.1) $\times 10^{-14}$ cm^3/s at 250 °C and 1.3×10^{-13} cm^3/s at 300 °C. Considering the difference in temperature and in experimental conditions the Cu diffusivity values obtained at 175 °C (3.42) and those obtained at 250 °C or 300 °C are in good agreement. That the experimentally derived value of z^* (av. — 17) should be close to a value (— 30) estimated from considerations valid for lattice electromigration (eq. 3) is evidence that the magnitude of the electron-atom scattering process in the grain boundaries is not too different from that in the lattice.

3.4.4 As with Cu, the addition of Mg to Al thin films was found to increase failure times by a factor of about 100 [47, 48]. Measurement of the volume of voids and hillocks (akin to those shown in Fig. 3) for a conductor containing 6 at % Mg, tested at 231 °C and 4×10^6 A/cm^2 for 230 hours, yielded the value for the diffusion coefficient of Al, while the determination of composition changes allowed the determination of Mg transport. The results are displayed in table I, together with a value of $\delta.D_a$ for pure Al, which has been extrapolated from the section 3.4.1 with an activation energy of 0.55 eV. By comparing the two values of $\delta.D_a$ (with and without Mg), one reaches the same conclusion for Mg additions as for Cu additions, the increase in failure times is the result of a proportional decrease in the rate of Al grain boundary diffusion.

3.4.5 Ni additions have also been reported to increase the failure times for Al thin film conductors [49]. In a sample containing about 0.5 at % Ni tested at 175 °C and 2×10^6 A/cm^2 for 3 000 hours it was found that Ni depletion to the extent of 8 % of the original concentration was not locally limited as in figure 3, but was spread over the whole negative terminal (see Fig. 1). The Al transport could not be determined and is presumed to be less than 1 %. The diffusion of Ni is all the more surprising, since the solubility limit of Ni in Al is so low — extrapolation of the data in figure 6 to the test temperature gives c_s equal to 10^{-9}. The magnitude of z^* was estimated from eq. 3, taking z as — 3 (see ref. 29). Diffusivity values were derived from the volume of Ni transported [50]. The product $c_s.\alpha.\delta.D_b$ is 1.5×10^{-18} cm^3/s and $\alpha.\delta.D_b$ is equal to 1.5×10^{-9} cm^3/s. The diffusion of Al can be derived from failure times — this would give $\delta.D_a$ equal to 5.6×10^{-18} cm^3/s.

3.4.6 To some extent it appears that the effect of Cu, Mg and Ni on Al grain boundary diffusion are additive. The longest failure times for polycrystalline thin film Al conductors were obtained with samples prepared with an alloy containing all three additive element [51]. This may be partly explained

if the relatively slow moving Mg atoms are effective in preventing the rapid diffusions of Cu and Ni.

Finally, after considering three additions which decrease the rate of Al grain boundary migration one may gather further information from the knowledge that additions of either Ag or Au to Al were found to be without effect [49].

4. **Discussion.** — 4.1 From results obtained with the electromigration of Sb in Ag, Ag in Au, and of Cu in Al it seems that the values of z^* for solute atoms in the lattice and in the grain boundaries are approximately equal (within a factor of 2). It may be assumed that the same applies for the values of z^* for solvent atoms. For Al, the use of this hypothesis led to the derivation of a value for $\delta . D_{0a}$ similar to that found by tracer techniques in Au.

4.2 The results obtained with Al and Al alloy films are gathered in table I. The values of $\alpha . \delta . D_b$ for Ni, Cu and Mg at 175 °C and 231 °C can be seen to vary as the reciprocal of the solubility limits c_s. Since it is unlikely that the variations of D_b should be sufficient to account for this observation, one must conclude that it is largely due to the adsorption parameter, α. Although an inverse relationship between α and c_s has already been suggested [52] it does not seem that evidence for this had been previously derived from grain boundary diffusion results. The product $c_s . \alpha . \delta . D_b$ also varies as the reciprocal of c_s, although the effect in this case is not very pronounced. If $c_s . \alpha$ is presumed to be constant, the changes in the product $c_s . \alpha . \delta . D_b$ from solute to solute may be partly attributed to D_b — the smaller the solubility limit, the higher the diffusion coefficient — for grain boundary diffusion as is known to occur for lattice diffusion. Theoretical considerations, based on valence and size factors [53], would indicate that in the Al lattice the diffusion of Mg should be slower than that of Cu ; the prediction has not been extended to a transition element such as Ni.

4.3 It would be nice to be able to classify solvents and solutes in some way which would allow predictive selection of elements likely to reduce grain boundary diffusion in a given material. One obvious approach is to consider atomic sizes, listed in table II. Most of the *effective* solutes, Be in Cu, Ni, Cu, Mg in Al, have relatively big atomic size differences with respect to their solvent. Conversely, there is no appreciable atomic size difference for *ineffective* solutes — Ag and Au in Al, Ag in Au. The case of Ta in Au may be considered separately. There is little atomic size difference, but the *effectiveness* of Ta may not be very high — according to the diffusion data Ta is not effective above 300 °C, or at a reduced temperature (T/T_m, where T_m is the melting temperature of the solvent) of 0.44. Magnesium remains very effective in Al at 231 °C, at a reduced temperature of 0.54. Of course, size alone is not enough, otherwise one would expect that Al in Cu would be as effective as Cu in Al. This suggests another criterion of effectiveness — a limited solid solubility. Certainly the value of C_s for Al in Cu, is several orders of magnitude greater than c_s for Cu in Al. All of the other effective solutes in table II have limited solubilities in their respective solvents (Ta would seem to be an exception also). However, the solubility of Au in Al is as small as that of all the other solutes except perhaps Ni. It has been suggested [52] that there exist two types of adsorption on grain boundaries — one due to atomic size differences and the other to other factors. It would seem that in order for a solute to be effective, the two types of adsorption should be present simultaneously, hence the two requirements, large atomic size differences and limited solubilities. Even this may not be enough — Cr in Al does not seem to fit.

TABLE II

Atomic Diameters (10^{-10} m)

Solvent	Solutes	
	Effective	Ineffective
Al 2.86	Cu 2.56	Au 2.88
	Mg 3.2	Ag 2.89
	Ni 2.49	Cr 2.5
Cu 2.56	Be 2.22	Al 2.86
Au 2.88	Ta 2.86	Ag 2.89

A full understanding of the problems of grain boundary diffusion and alloy atoms will require deeper knowledge of correlation and vacancy wind effects in boundaries, which were neglected in the present paper.

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DISCUSSION

P. GUYOT : Le déplacement des joints par vent d'électrons peut être important dans vos essais, étant donné la très forte densité de courant utilisée. L'avez-vous observé, car il pourrait éventuellement jouer un rôle sur la rupture ?

F. d'HEURLE : Le déplacement des joints de grains n'a pas été reporté, ou même simplement invoqué, par les auteurs qui ont travaillé aux températures relativement basses qui nous intéressent. Remarquez que jusqu'à maintenant le déplacement des joints de grains sous l'influence d'un courant électrique n'a été observé que lorsqu'il est accompagné d'autres phénomènes (recristallisation, croissance normale des grains) ou à des températures élevées.

E. D. HONDROS : In view to the fact that the surface to volume ratio of your specimens is high, and furthermore, since surface diffusion is much faster than grain boundary diffusion, have you considered whether in principle mass transport by surface diffusion may play a role : although it is not likely to be important in these aluminium alloys which have a thin oxide film on the surface.

F. d'HEURLE : With respect of Al you are quite correct : surface transport during electromigration in Al films has not been observed. Experiments conducted with Al single crystal films are quite conclusive on this point. More limited results with Au lead to the same conclusion : namely, no significant surface transport during electromigration in Au films. Surface effects have been observed during electromigration in Ag films, however, these results remain to be positively separated from chemical effects such as the formation of oxide and sulfide layers. Surface transport has been clearly identified by Frohberg and Adam (Berlin) with respect to faceting during high temperature electromigration in W filaments.

C. L. BAUER : On a observé la croissance des whiskers. Est-ce que vous pouvez préciser le mécanisme de cette croissance ? De plus, quel est l'effet de la taille des joints de grains sur le transport des atomes le long de couche mince pendant la croissance ?

F. d'HEURLE : Des trichites telles que l'on voit sur la figure 1 ne sont obtenues qu'assez rarement, et nous n'avons pas cherché à définir les conditions (diamètre des grains, température, composition, densité de courant, etc...) nécessaires à leur formation. Dans la région (borne positive) où les trichites apparaissent la densité de courant est mal définie, cela complique l'analyse d'un phénomène évidemment très hétérogène.