Evolution of Vacancy Supersaturation in Relation to Electromigration in Thin Film Metallization*

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(Received 30 September 1974)

Theory of evolution of vacancy supersaturation in grain boundary in relation to electromigration based on the concept of the critical length for void growth is presented. The theory offers satisfactory explanation to some peculiar phenomena hitherto unexplained.

1. INTRODUCTION

IN electronic industry, people frequently quote the following relation")

$$t_f = Aj^{-n}\exp\{\Delta H/kT\} \qquad (1)$$

to characterize the quality of thin film metallization in terms of the mean-time-to-failure due to electromigration where A is a constant: j the current density, **AH** the (grain boundary) diffusion activation energy and n lies between 2 and 3. Among other things. this relation unequivocally su.ggests that the onset of electromigration begins upon the application of current. As a result, the metallization deteriorates gradually and continuously and apparently has no abrupt break away point. In contrast, what does one observe in a typical electromigration test is this: The thin film stripe resistance rises sharply in the first few minutes of test due to uniform joule heating, then it settles down at a new plateau for a considerable length of time accompanied only by a small scale of fluctuation until, all of a sudden, a catastrophic stage sets in, the stripe resistance breaks away and the circuit swung open. . A typical data depicts these features is shown in Fig 1.[2] Figure (1) and Eq (1) stand in sharp contrast against each other on several counts: Firstly, Fig (1) amply suggests that the effective mass transport due to electromigration does not take place during the early stage of test, in fact, not until the kink in the resistance curve appeared. Secondly, the resistance remains practically constant for a considerable length

* Work supported in part by National Science Council.

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(1) See, for example, a special issue on electromigration: Proc. IEEE. Vol. 57, No. 9, (1969).

(2) H. L. Huang: Unpublished results, 1971. For experimental procedures please consult: H. L. Huang and C.-Y. Chang: Chinese J. Phys. 11, 18-32 (1973).

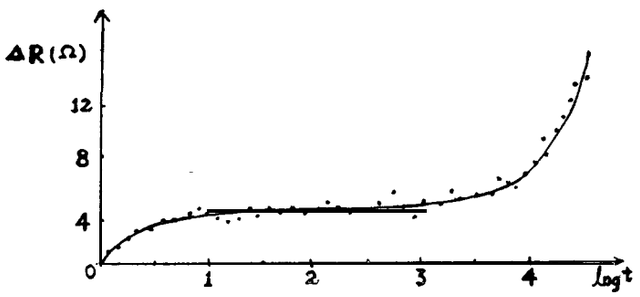

Fig. 1. Change in stripe resistance vs time on test as monitored by the automatic digital printer HP-5050A. Please note the fluctuation and the breakaway in resistance during and at the end of incubation period.

of time, instead of gradually deteriorating. The nearly-constant resistance period is normally termed as the incubation period.[3] Nonetheless: during this period, the stripe resistance does fluctuate a bit. The latter is hardly understandable in terms of Eq. (1).

The main purpose of this paper therefore is to offer a simple yet plausible explanation for the above dilemma in terms of the evolution of vacancy supersaturation at the grain boundary. We shall approach the problem from the phenomenological and statistical point of view.

2. VACANCY SUPERSATURATION AND NUCLEATION CENTERS

Mass flux along a certain direction is synonymous with vacancy flux in the opposite direction. As vacancies accumulate at and diffuse away from the grain boundary, the equation of continuity in the vacancy flux becomes:

$$\frac{\partial n}{\partial t} = -\nabla \cdot J - \frac{n-n_0}{\tau} \tag{2}$$

where $\boldsymbol{J} = -D\nabla n + \mu n \boldsymbol{F}$, in which $\boldsymbol{D}$, $n(n_0)$, μ, τ and F are, respectively, the diffusion constant, concentration (at equilibrium), mobility, relaxation time and effective force on the vacancy. At steady state, the left hand side of Eq. (2) vanishes, the vacancy supersaturation S has the following approximate form: [4]

$$S = \frac{n-n_0}{n_0} \simeq -\tau F \frac{\partial \mu}{\partial x} \tag{3}$$

where for no loss of generality the effective force is assumed to be applied along z-direction and that $\left|\frac{\nabla n}{n}\right| \ll \left|\frac{F}{kT}\right|$. Basically, μ depends on temperature, position and the direction of the effective force. At low temperature, μ is approximately

(3) R. Rosenberg and M. Ohring: J. Appl. Phys., 42, 5671 (1971).
(4) H. Shul and P. A. Turner: J. Appl. Phys., 44, 4891 (1973).

zero everywhere except in a grain boundary. A grain generally looks like a polygon, hence a grain boundary like a straight line. Occassionally, it may look like a parabola, say $x=\frac{1}{2}ay^2$, stemming from a triple point, as shown in Fig 2. For the latter case, we have $\mu\simeq$constant and $S=0$ for $x<0$, and $\mu=\mu_0\cos\theta(x)$ hence $S=F\tau a/\sqrt{2ax(1+2ax)^3}$ since $\cos\theta(x)=\sqrt{\frac{2ax}{1+2ax}}$ for $x>0$. Obviously, S is non-zero in the region of positive x and has a maximum at $x=0^+$. That is to **say,** the grain boundary triple point has an opportune chance of becoming the sink of vacancies, resulting in discontinuity in flux divergence and formation of the nucleation center of void embryos. Meanwhile, the grain boundaries extending from the same triple point in the same positive region may get further and further delineated and depleted. These features are clearly discernible in

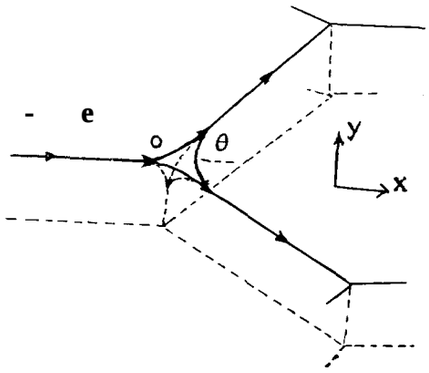

Fig. 2. An ideal parabolic grain boundary triple point.

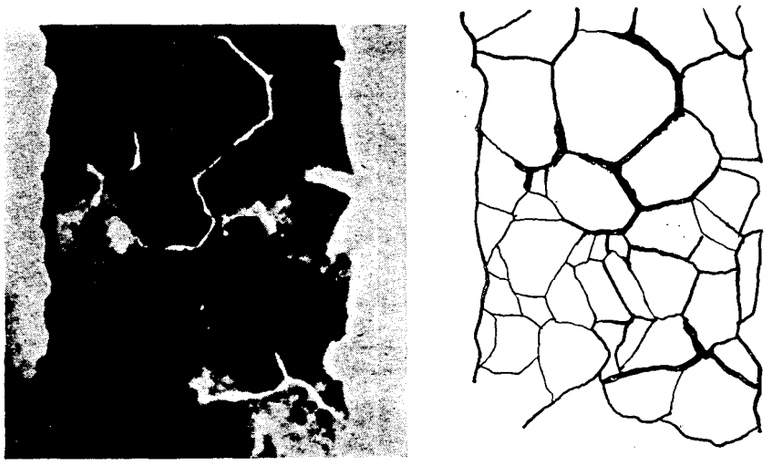

Fig. 3a, b. Evolution of vacancy supersaturation at the grain boundary triple point and the delineated and depleted grain boundaries as a result of electromigration. (photo reproduced from ref. 5)

Fig 3a, b.[5] Actually, S for the straight line portion of the grain boundary is not necessarily zero since the gradient of vacancy concentration there is by no means small. In a typical experimental condition for testing electromigration in thin film metallization at $j \simeq 10^6$ amp/cm^2 and $T \simeq 400$°K, the vacancy supersaturation S is found to be around 0.1.[3]

3. EVOLUTION OF VOID EMBRYOS

As the processes of vacancy accumulation at the grain boundary continue, the void embryos so formed may, in due course of time, grow into voids of marcroscopic dimensions provided only a certain criterion is satisfied. In nature, a heterogeneous nucleation process is a far more favored process than a homogeneous nucleation process.[6] Thus, assuming that there is a void embryo formed on the wall of a grain boundary in the form of a spherical cap, as suggested in Fig 4, then, based upon the elementary nucleation theory for crystal growth, free energy required in forming a void of volume V surface area A at the degree of supersaturation S is

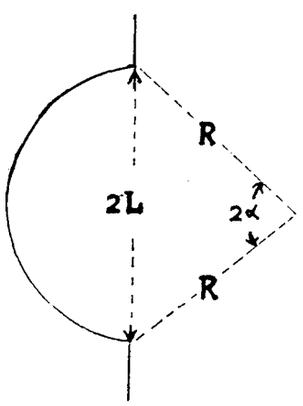

Fig. 4. A hypothetical spherical cap type void embryo at a grain boundary.

$$\phi = -N_0 VkT \ln(1+S) + A\left(\gamma_s - \frac{3}{8}\gamma_b\right) \qquad (4)$$

where N_0 is the atomic density of the thin film, $\gamma_s(\gamma_b)$ the surface (grain boundary) free energy density. The change in free energy per unit volume per adding one additional vacancy to the void is

$$\Delta G = \frac{1}{N_0}\left\{-N_0 kT \ln(1+S) + \left(\gamma_s - \frac{3}{8}\gamma_b\right)\frac{\Delta A}{\Delta V}\right\} \qquad (5)$$

(5) L. Berenbaum: J. Appl. Phys. 41, 883 (1971).
(6) Reed-Hill: *Physical Metallurgy Principles*, (Acad. Press, 2nd edition, 1973) Chap. 13.

Typically, $r_b \simeq \frac{1}{3} r_s$, S-0.1, hence $\ln(1+S) \simeq S$. Equation (5) is reduced to

$$\Delta G \simeq \frac{1}{N_0}\left\{-N_0 kTS + \frac{7}{8} r_s \frac{\Delta A}{\Delta V}\right\} \tag{6}$$

As part of the activated diffusion processes, the vacancies and the lattice atoms bordering on the void embryo are bound to diffuse into each other at different jumping rates due to the difference in the activation energy involved. Let $\nu_1(\nu_2)$ be the jumping frequency for a vacancy (lattice atom) to jump back into a lattice site (vacancy) bordering on the void embryo, we have $\nu_1 = \nu_0 \exp\{-\Delta H/kT\}$, $\nu_2 = \nu_0 \exp\{-(\mathrm{AH} + \Delta G)/kT\}$ where ν_0 is the equilibrium vibration frequency of the vacancy, AG as given in Es. (5) and AH as defined following Eq. (1). The rate of increase in the number of vacancies inside the void embryo is

$$\nu = \nu_2 - \nu_1 = \nu_0 \exp\left(-\frac{\Delta H}{kT}\right)\left\{\exp\left(-\frac{\Delta G}{kT}\right) - 1\right\} \simeq -\nu_0\left(\frac{\Delta G}{kT}\right)\exp\left(-\frac{\Delta H}{kT}\right) \tag{7}$$

where $\Delta G \ll kT$ for the case of present interest.

Suppose that the lattice parameter of the thin film metallization is b and that the volume occupied by a lattice atom is approximately equal to that of a vacancy, the number of vacancies (or atoms) surrounding the surface of the void embryo is approximately A/b^2. At thermal equilibrium, the number of vacancy is $N_v = N_0 \exp\{-Q/kT\}$ where N_0 is the density of atoms and Q the formation energy for a vacancy. Thus, the number of vacancies surrounding the surface of the void embryo is simply $N_v = \frac{A}{b^2}\exp(-Q/kT)$. To the void embryo, the rate of the volume increase per unit time is therfore

$$\frac{dV}{dt} = \frac{A}{b^2}\exp\left(-\frac{Q}{kT}\right) b^3 \nu = -Ab\nu_0\left(\frac{\Delta G}{kT}\right)\exp\{-(Q+\Delta H)/kT\} \tag{8}$$

For brevity, put $f = \frac{\nu_0}{N_0 kT}\exp\{-(Q+\Delta H)/kT\}$, we rewrite Eq. (8) as

$$\frac{dV}{dt} = Abf\left\{N_0 kTS - \frac{7}{8} r_s \frac{dA}{dV}\right\} \tag{9}$$

Let us discuss closely the significance of Eq. (9) in relation to the evolution of the void embryo: Referring to Fig. (4), the linear dimension of the spherical cap is $L = R\sin\alpha$. If length L remains fixed during the course of time[7], the condition for the void growth is to have the subtending angle α increasing, i. e., $\frac{d\alpha}{dt} > 0$. Since the surface area of the cap is $A = 2\pi R^2(1-\cos\alpha)$, that of the

(7) The idea was first proposed by J. E. Bailey and P. B. Hirsch: Proc, Roy. Soc., **267A**, 11-30 (1962).

base plane of the cap is $A_b=\pi$ (Rsina) ^{2} and its volume $V_c=\frac{\pi}{3}R^3$ (2−3cosα + cos^{3}α), equation (9) is transformed easily into the form:

$$\frac{da}{dt}=\frac{2bf}{L}\left\{N_0kTS-\frac{14\gamma_s}{8L}\sin\alpha\right\}(1+\cos\alpha) \tag{10}$$

Thus, the condition for the void embryo to continue growing is to require that $N_0kTS-\frac{14\gamma_s}{8L}\sin\alpha>0$. Or, approximately, $L>\frac{2\gamma_s}{N_0kTS}=L_0$ If this condition is satisfied the void embryo will be able to grow and evolves into a void of marcfoscopic dimension ! On the other hand, if $L<L_0$, the void embryo so formed is unstable, and is liable to dissipate and collapse as a result of further diffusion. Thus, L_0 is the ever important critical length for void growth and the corresponding supersaturation the critical supersaturation S_0. For $S_0\simeq0.1$, $\gamma_s\simeq10^3$erg/cm^2, $T=400$°K, $N_0\sim6\times10^{22}$ *we* have $L_0\sim10^2A$.

4. RESULTS AND DISCUSSIONS

The descriptions given above seems to attest the plausibility and accountability to the present theory that the phenomenon of the formation, evolution and the ill-fated collapse of the void embryos with dimension falling below the critical length L_0 are certain to give rise to fluctutation in resistance (before its break-away) as suggested in Fig. (1). The fluctuation is therefore non-accidental. This picture becomes clearer as we proceed further as follows.

Integrating Eq (10) one obtains

$$t=\frac{\gamma_s}{b(N_0kTS)^2}f\left\{\frac{x}{\beta}+\ln(x^2-2\beta+1)+\frac{2\beta}{\sqrt{1-\beta^2}}\left(\tan^{-1}\frac{x-\beta}{\sqrt{1-\beta^2}}+\tan^{-1}\frac{\beta}{\sqrt{1-\beta^2}}\right)\right\} \tag{11}$$

in which $\beta=L_0/L$ and $x=\tan\left(\frac{\alpha}{2}\right)$. Substituting x for a in the expression for *Vi, we* have

$$V_c^{1/3}=\left(\frac{\pi}{6}\right)^{1/3}\left(\frac{x^3+3x}{\beta^3}\right)^{1/3}L_0 \tag{12}$$

expressing the linear dimension of the spherical cap (i. e. the void embryo) in term of the critical length L_0. Combination of Eqs (11) and (12) yields the most important correlations between the linear dimension of a growing void in relation to time on test. Fig 5 depicts these relations in terms of $\left(\frac{x^3+3x}{\beta^3}\right)^{1/3}$ versus $t\left(\frac{b(N_0kT)^2f}{\gamma_s}\right)$ for several values of βs. Let us examine these relations

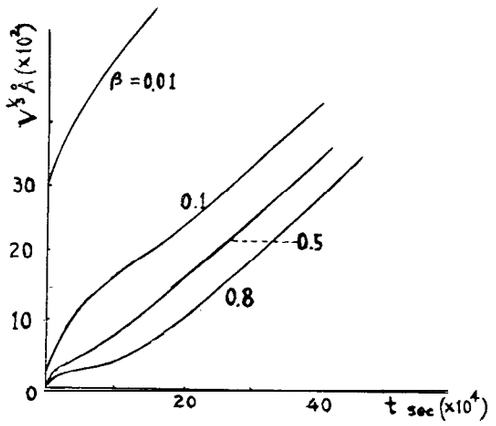

Fig. 5. Growth of void embryo in terms of $\left(\frac{x^3+3x}{\beta^3}\right)^{1/3}$ vs $\frac{bf(N_0kT)^2}{Ys}t$ for several valus of βs. Note that at low t, the degree of supersaturation is small and β large. As a result, the growth rate of the void embryo is relatively slow. As time goes on, β turns small, the void's growth rate becomes much higher and the embryo quickly evolves into a void of marcroscopic dimensions as suggested by the steep slope for $\beta=0.01$.

closely. At relative low t, that is, when the sample is first put on test, the degree of supersaturation S is small, hence the critical length L_0 is correspondingly large. Thus, it is highly inprobable, if not impossible, for a nucleation center to grow into a void of marcroscopic dimension. The frequent occurrence during this period of time is to witness the nucleation of the void embryos and their uneventful collapse. This is exactly the reason why the fluctuation in resistance occurrs as suggested in Fig (1) during the early stage of test, though remaining practically constant on the average. As time goes on, the degree of supersaturation at the grain boundary grows bigger and bigger and L_0 becomes correspondingly smaller and smaller. The chance is much improved now for a void embryo to grow beyond the critical length L_0 in grain boundary. Once this is achieved, $\beta=\frac{L_0}{L}$ gets smaller, the void's growth rate becomes higher. Therefore the void embryo grows into a void of macrroscopic dimensions before long and breaks away the stripe's resistance and we have a kink in the resistance-vs-time curve. Apparently, the critical length L_0 or the corresponding critical supersaturation S_0 plays a key role in characterizing the mean-time-to-failure due to electromigration in thin film metallization. We denote the period of time before reaching this critical stage as the incubation period for the void growth. The incubation period thus is of the same order of magnitude as the mean-time-failure as far as electromigration is concerned in thin film metllization. Taking S-0.1, $b\simeq 3A^0$, $\nu_0\simeq 10^{13}$ cps, $T\simeq 400^0K$, $Q\simeq 0.35$ev, $\Delta H\simeq 0.65$ev, $r_s\simeq 10^3$erg/cm^2 w e

have $L \simeq 10^2 A^0$ and the incubation period approximately $\sim 10^4$ sec, roughly in agreement with our experimental observation for t_f. In actual laboratory test, β is ever changing with time since the degree of supersaturation in the grain boundary is changing. For that matter, the growth rate for a void embryo is not at a constant rate at any time. Consequently, it is not an easy task to estimate the incubation period to a good accuracy.

As a concluding remark, it is fair to say that the simpleminded approach to the problem, that is, the evolution of nucleation centers due to vacancy supersaturation in grain boundaries is fully capable of explaining the change in the stripe resistance at all stages due to electromigration in this film metallization, at least, to qualitative satisfaction.