Surface Free Energy and Surface Reconstruction on Thin Film Metallizations

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(Received October 3, 1980)

Surface reconstruction on thin film metallizations with disk-like or spherical-mound-like growths are analyzeda bsed on surface free energy consideration. It is shown that the general shapes of the surface accumulation contours will remain unchanged once the surface free energies are determined, disregarding the amount of diffusing atoms accumulated at the surface. Comparison with the experimental observations are very satisfactory.

I. INTRODUCTION

SURFACE reconstruction on thin film metallization surfaces due to electromigration and surface grain boundary diffusions take place in a variety of ways and forms. There are at least four distinct types of mass growths known to be in existence. They are: (1) a faceted hillock growth type[1~4], (2) a whisker-like growth[3~5], (3) a spectacular protruding growth as observed by Rosenberg and coworkers[6] in situ in a scanning electron microscope, and (4) a disk-like growth or a growth in the form of a spherical mound or a section of it as shown in Figs. 1-3[7,8] etc. The explanations to these growth mechanisms and processes have been rather skimpy and incomplete, and mostly qualitative, too. The only possible exception is related to the type (3) growth. This has qeen explained through the divergence of surface mass fluxes across a grain boundary and in superposition with the thermal grain boundary grooving processes[7]. The combination of these two mechanisms are capable of successfuly reproducing the growth contour to some details. In the present communication we offer to give a reasonable explanation to the fourth type growth shown in Figs. 1-3 based solely upon free energy considerations.

II. FREE ENERGY CONSIDERATION

Consider a schematic surface configuration in which the diffusing atoms emerge from a grain boundary and form a local accumulation immediately above as shown in Fig. 4. To simplify calculations we shall consider the case from a 2-dimensional point of view. We define the following quantities:

2d: The grain boundary width.

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(2) L. J. Gauckler, S. Hoffman and F. Haessner, Act. Metall. 23, 154 (1975).
(3) J. R. Black, Proc. IEEE, 57, 1587 (1969).
(4) R. E. Hummel and H. M. Breitling, Z. Naturf. **26A**, 36 (1971).
(5) I. A. Blech and E.S. Meieran, J. Appl. Phys. 40, 485 (1969).
(6) M. Ohring and R. Rosenberg, J. Appl. Phys. 42, 5671 (1971); L. Berenbaum and R. Rosenberg, Seventh Annual Reliability Physics Symposium, Washington, D. C. 1968.
(7) The experimental conditions under which these metallographs are taken are described in: H. L. Huang and C.Y. Chang. Chin. J. Phys. 11, 18 (1973).
(8) R. E. Hummel and R.T. DeHoff, Appl. Phys. Lett. 27, 64 (1975).

A_2: Surface free energy of the diffusant per unit length.
A,: The change in the surface free energy at the interface as the diffusant making contact with the matrix surface atoms.
M: The range of spread of the diffusant at the interface along the s-direction.

The free energy of the system enclosed within the area S can be written as

$$U=2\int_d^M A_1\,dl_1+\int_{-M}^M A_2\,dl_2$$
$$=2A_1(M-d)+A_2\int_{-M}^M dl_2 \qquad (1)$$

where dl is the line element of the curve.

In order to keep U at minimum it is essential that A_1 be negative and $A_2>|A_1|$. The awements are as follows,

Fig. 1. Al-5 wt% Cu thin film metallization surface with disk-like growths.

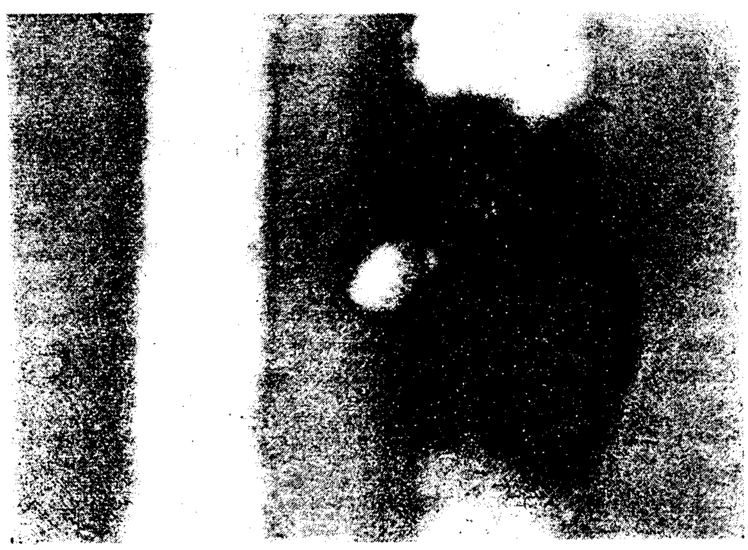

Fig. 2. Al-5 wt% Cu thin film metalization surface with a spherical mound growth.

Fig. 3. Al-5 wt% Cu thin film metallization surface with a multiple disk-like growth in superposition.

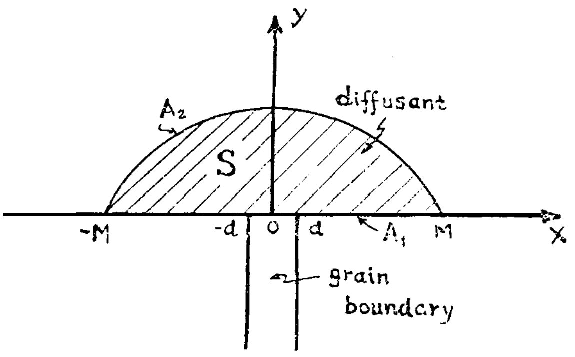

Fig. 4. A schematic surface configuration of mass growth in 2-dimension.

(1) If A_1 is negative and $A_2<|A_1|$, then the diffusant is such that it will increase its interface area to its fullest extent, spreading thin and wide over the film surface to keep the free energy of the system at minimum. Under the situation the shape of the surface accumulation should look like as an elongated ellipse, effectively a flat surface.

(2) If A_1 is positive and $A_2<A_1$ then any increase in the interface area will surely increase U. To keep U at minimum therefore the diffusant will avoid making contact with the matrix atoms. Thus, the accumulation surface should look like a circle (sphere in the 3-dim. case), ignoring the gravity effect.

(3) If $A_2>|A_1|$ the situation becomes more complex and need be explored more carefully as follows.

Consider a case in which the accumulation surface area S has a constant value. Let

$$S=\int_{-M}^{M} y\,dx=\text{const},$$

then by the method of Lagrange multiplier and the calculus of variation of the quantity

$$W = U + \lambda S$$
$$= 2A_1(M-d) + A_2 \int_{-M}^{M} dl_s + \lambda \int_{-M}^{M} y\,dx\,, \tag{2}$$

we obtain immediately

$$\frac{A_2 \dot{y}}{\sqrt{1+\dot{y}^2}} = \lambda x + c\,, \tag{3}$$

with c being an integration constant and λ the Lagrange multiplier. Now if the accumulation distribution is such that it is symmetrical with respect to the y-axis and the curve joins smoothly at $x=0$, we have $\dot{y}(0)=0$, hence $c=0$. Solving for Eq. (3) we obtain

$$x^2 + (y-c')^2 = \left(\frac{A_2}{\lambda}\right)^2 = a^2 \tag{4}$$

which is an equation of a circle and c' is related to the coordinate of the center of the circle and a its radius.

Case (i): $c'<0$. If we let $y(x) \geq 0$ and $y(\pm M)=0$, we have

$$y = (a^2-x^2)^{1/2} - (a^2-M^2)^{1/2}$$
$$S = a^2 \sin^{-1}\left(\frac{M}{a}\right) - M(a^2-M^2)^{1/2} \tag{5}$$

and

$$U = 2A_1(M-d) + 2A_2 a \sin^{-1}\left(\frac{M}{a}\right) \tag{6}$$

Furthermore, from the variational condition $dU/dM=0$, we have the following results

$$M^2 = \frac{S}{\left[\frac{\alpha^2}{\alpha^2-1}\right] \sin^{-1}\left[\frac{\alpha^2-1}{\alpha^2}\right]^{1/2} - \frac{1}{(\alpha^2-1)^{1/2}}} \tag{7a}$$

$$a^2 = \frac{S}{\sin^{-1}\left(\frac{\alpha^2-1}{\alpha^2}\right)^{1/2} - \frac{(\alpha^2-1)^{1/2}}{\alpha}} \tag{7b}$$

and

$$\alpha = -\frac{A_2}{A_1} = \frac{a}{(a^2-M^2)^{1/2}} \tag{7c}$$

which is the ratio of the surface free energy.

Case (ii): $c'>0$. By the same method as in the case (i) we obtain easily

$$S = \pi a^2 - a^2 \sin^{-1}\left(\frac{M}{a}\right) + M(a^2-M^2)^{1/2} \tag{8}$$

and, similarly,

$$M^2 = \frac{S}{\left(\frac{\alpha^2}{\alpha^2-1}\right)\left[\pi - \sin^{-1}\left(\frac{\alpha^2-1}{\alpha^2}\right)^{1/2}\right] + \left(\frac{1}{\alpha^2-1}\right)^{1/2}} \tag{9a}$$

$$a^2 = \frac{S}{\pi - \sin^{-1}\left(\frac{\alpha^2-1}{\alpha^2}\right)^{1/2} + \left(\frac{\alpha^2-1}{\alpha^2}\right)^{1/2}} \tag{9b}$$

$$\alpha = \frac{A_2}{A_1} = \frac{a}{(a^2-M^2)^{1/2}} \tag{9c}$$

Note the apparent difference in the signs between Eq. (9c) and Eq. (7c). In actuality, however, the two equations are consistent since the free energy A_1 is negative in Eq. (7c) while it is positive in (9c). Thus α is more appropriately defined as $\alpha = A_2/|A_1|$ than in either form of Eq. (7c) or (9c). Clearly, with Eqs. (7) and (9), we are able to obtain the shape of the surface accumulation once the related surface properties are given.

III. RESULTS AND DISCUSSIONS

In Table I and II we arbitrarily set $S=1$ and list some relevant numerical values for several values of α for $c'<0$ and $c'>0$, respectively. The quantities b, H and H' are defined in the accompanying figures shown in Figs. 5 and 6.

Figure 5 shows the shapes of surface accumulations for three different values of α each satisfying the condition: $A_1<0$ and $A_2>|A_1|$. It is seen that as $|A_1| \to A_2$ (i. e., $\alpha \to 1$) the accumulation contour flatens, while as $A_1 \to 0^-$ ($\alpha \to \infty$), the contour curve approaches a semi-circle. In Fig. 6 we show the shapes of accumulations with A_1 positive and again $A_2>|A_1|$. This time, as $\alpha \to 1$ the shape of the accumulation curve approaches a complete circle, while it tends toward a semi-circle as $\alpha \to 0^+$.

From these figures it clearly suggests that the ***general shapes of the accumulations will remain unchanged once the ratios of the surface free energies are determined*** disregarding the amount of diffusing atoms accumulated at the surface.

Figures 1-3 show surface mass growth in Al-5 wt% Cu co-deposited thin film metallizations of 1.2 μm thickness upon power stressing for some duration of time in air in a Blue-*M* oven. Note that the growth contours are generally disk-like (Figs. 1 and 3) or in the form of a spherical mound (Fig. 2) and bear good resemblance to the drawings depicted in Figs. 5 and 6. In addition, in the middle section of Fig. 3, there is a peculiar shape of growth composing of a number of disk-like

Table I. Surface Accumulation Configuration of the Diffusing Atoms. $S=1, c<0$.

α	M	a	b	H
1.01	3.2596	23.2186	22.9916	0.2270
1.1	1.8451	4.4291	4.0265	0.4026
1.5	1.2705	1.7045	1.1363	0.5681
2	1.1050	1.2760	0.6380	0.6380
5	0.9044	0.9231	0.1846	0.7385
10	0.8497	0.8510	0.0854	0.7656
100	0.8029	0.8030	0.0080	0.7949
∞	0.7978	0.7978	0	0.7978

Table II. Surface Accumulation Configuration of the Diffusing Atoms. $S=1, c'>0$.

α	M	a	b	H'	H
1.01	0.0792	0.5643	0.5587	0.0055	1.1231
1.1	0.2369	0.5688	0.5171	0.0517	1.0859
1.5	0.4456	0.5978	0.3985	0.1992	0.9964
2	0.5447	0.6290	0.3145	0.3145	0.9435
5	0.6984	0.7128	0.1425	0.5702	0.8553
10	0.7477	0.7515	0.0751	0.6763	0.8267
100	0.7928	0.7928	0.0079	0.7984	0.8007
∞	0.7978	0.7978	0	0.7978	0.7978

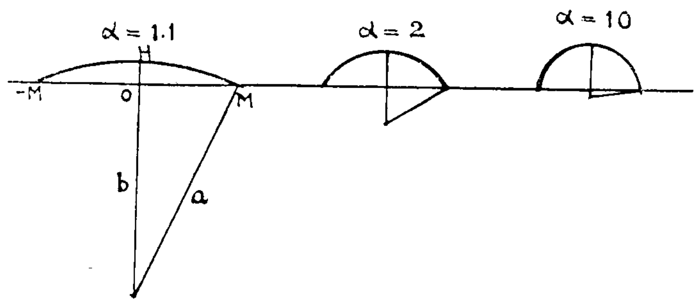

Fig. 5. The surface growth contours in 2-dim with the surface free energy A_1 negative and $\alpha = \frac{A_2}{|A_1|} = 1.1$, 2 and 10, respectively. Note that the contour flatens as $\alpha \to 1$, while it approaches a semi-circle when $A_1 \to 0^-$.

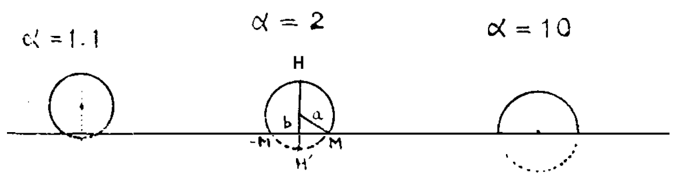

Fig. 6. The surface growth contours in 2-dim with the surface free energy A_1 positive and $\alpha = 1.1$, 2 and10, respectively. Note that the contour approaches a complete circle as $\alpha \to 1$, while it becomes a semi-circle as $\alpha \to 0^+$.

growths, of different pitches and radii, superposing one another. Apparently this phenomena can be explained based on the same line of arguements if the surface accumulation extends over several grains and contains as many numbers of active diffusing pipes.

It has been recently reported that the surface diffusivity depends sensitively upon surface cleanliness, ambient gases[9], atomic arrangements and packing densities[10], etc. We have reason to believe that these same factors will similarly affect the surface free energies. Consequently, the disk-like growths of different surface characteristics (pitches, radii, etc.) over nominally the same this film metallization surfaces are not unexpected. In light of this, the experimeutal determination of surface free energies would be most useful and is strongly suggested.

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(10) See for example: H. P. Bonzel, "Surface Physics of Materials", edited by J. M. Blakely (A. P. New York, 1975) Vol. II, p. 280.