A new model for the nucleation and growth of thick polycrystal films. I. Calculation of volume transforms

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Volume transforms for the collision of 3D crystals are calculated for the case where the crystal centres are distributed randomly in a 2D plane. The transforms connect the volumes of collided crystals with the volumes the crystals would have had if they had not collided. The results obtained are consistent with the known mathematical bounds on the problem, and they also connect with nearest-neighbour theory in 2D. Because the transforms are calculated on the basis of 'almost catastrophic' collisions, it is not necessary to explicitly consider the detailed mechanisms responsible for the termination of the crystal growth processes.

1. Introduction

It is known that many polycrystal films are formed by a process loosely described as three-dimensional nucleation and growth [1]. Unfortunately, adequate theoretical models of this process have not so far been developed despite the fact that the mathematical and physical bounds on the problem are well known. The greatest stumbling block so far has been the choice of an appropriate 'volume transformation' which would account for intercrystal collisions in a proper way. The purpose of this paper is to suggest such a transformation.

One of the principal difficulties in understanding the volume transformation lies in relating the spatial distribution of the crystal centres to their subsequent growth (Fig. 1). Although the crystal centres may be assumed to be distributed randomly in two dimensions across the substrate surface, they are obviously *not* distributed randomly in three-dimensional space [2]. Nevertheless, crystal growth extends into one-half of the third dimension (the vertical axis in Fig. 1) while at the same time growth 'into' the substrate is forbidden. As a matter of fact the overall process is better described as '$2\frac{1}{2}$D' nucleation and growth rather than '3D' nucleation and growth as it is usually called[†].

In strictly n-dimensional crystal growth problems (integer n) the required coverage/volume transformations are calculated using arguments in geometrical probability. Under appropriate limits (discussed elsewhere [4]) these transformations can be described by the well-known Kolmogoroff–Avrami limiting law

$$(X_T)^n = 1 - \exp\{-(X_X)^n\} \qquad (1)$$

where X_T is a transformed normalized linear measure of the crystals, X_X is the untransformed normalized linear measure of the crystals, and n is the dimensionality of the growth process. E.g., in two dimensions $n = 2$ and $(X_X)^2 = S/S_{Total}$, where S is the basal area of the crystals and S_{Total} is the total available area of the substrate.

Because in '$2\frac{1}{2}$D' nucleation and growth the crystals are distributed in 2D but grow in '$2\frac{1}{2}$D' we cannot apply Equation 1 directly to obtain the appropriate volume transformation. Therefore, what we wish to find is an expression analagous to Equation 1 which will be applicable to the '$2\frac{1}{2}$D' case described above. Before doing this we briefly summarize some of the general features of the overall problem.

2. Some general features of the problem

Any model of '$2\frac{1}{2}$D' nucleation should be able to explain the following *experimental* facts:

[†] Proper 3D nucleation and growth occurs throughout spatial volumes and consists of both nucleation and growth, each of which occurs in full 3D. This type of behaviour is widely observed in transformations in metals, alloys, glasses etc., and should not be confused with the electrochemical formation of films and the like [3].

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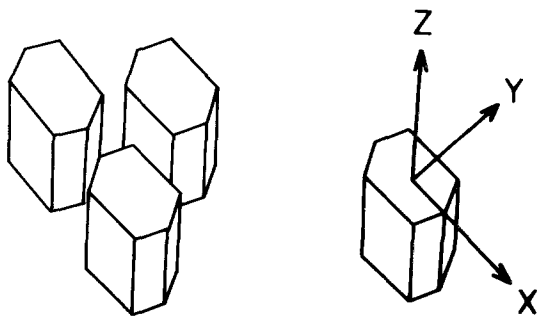
Fig. 1. The geometrical situation.

(a) The potentiostatic $i-t$ transient must be of the correct shape, e.g., of the form reported for Hg/HgO [5].

(b) The charge contained in the potentiostatic $i-t$ transients must be a decreasing function of η [5].

(c) The gradient of $\log (i_p)$ as a function of $\log(v)$ in LPS must be a constant between 0 and 1 [6].

There are also the following *mathematical* bounds:

(d) In common with other 'interfacial' models of crystal growth, the rate-determining step should be at the edge of the crystals [1].

(e) For sufficiently small volumes of crystal the solution obtained, taking collision into account, must asymptotically approach that obtained neglecting inter-crystal collisions as $t \to 0$.

(f) At i_m in the potentiostatic transients (i.e., in the steady state) the following relation must hold

$$i_m \propto r_p \left(\frac{r_i}{r_t}\right)^{1/4} \qquad (2)$$

where r_i is a specific rate constant describing the immigration of 'growth sites' into the system, r_t is a specific rate constant describing the termination ('death') of sites in the system, and r_p is a specific rate constant describing the propagation of sites [7].

Unfortunately, bound (a)–(f) are not in themselves sufficient to uniquely define the non-steady-state problem. This is because it is not clear why a '$2\frac{1}{2}$D' crystal growth process should ever terminate. Thus, although the lateral spreading of the crystals is ultimately inhibited by intercrystal collisions, the tops of the crystals are not inhibited in the same way and hence should continue to grow indefinitely. Since this is not usually found experi-

mentally we are faced with the problem of explaining this behaviour. In the only successful model to date this was achieved by relaxing criterion (d) so that growth eventually became limited by diffusion of reactant through patches of uncovered surface [5]. However, in this model only the vertical spreading fell under diffusion control whereas the rates of lateral spreading remained under 'interfacial' control. This is a physically unreasonable proposition in as much as a diffusion-controlled growth might be expected to exhibit hemispherical-like diffusion zones surrounding the entire crystal, in which case the rates of lateral and vertical spreading should both be controlled by the mass transport process. Alternatively, if diffusion were truly concentrated at the top of the crystal, a dendritic growth form should result. Thus, although the diffusional model [5] exhibits the correct bounds as listed earlier its physical basis is nonetheless questionable.

In what follows we propose an alternative model in which it is possible to dispense with mass transport control to growth sites as a rate-determining step, although mass transport can be crudely incorporated. In this model we shall assume that crystals grow *in a shape-preserving way*, that is, the rates of lateral and vertical spreading will be assumed to be locked together via the crystallography of the growing crystal. In such a model the rate-determining step effectively becomes the spreading of the basal plane of the crystal. Growth into the third dimension can then be regarded as fast but constrained by the crystallography of the growth shape.

3. Formulation of the volume transform for 'instantaneous' nucleation

Let us denote all transformed quantities (i.e., those quantities including the effects of the collision of crystals) by subscript T. Let us denote all untransformed quantities (i.e., those describing the crystals but neglecting collisions) by subscript X. Considering only the basal area of crystals we have an essentially 2D problem and hence, using the Kolmogoroff–Avrami limiting law,

$$\theta_T = 1 - \exp(-\theta_X) \qquad (3)$$

where θ denotes the normalized surface coverage of the electrode by the basal planes of the crystals.

In terms of one centre this equation can be written

$$\rho_1 S_T = 1 - \exp(-\rho_1 S_X) \qquad (4)$$

where $_1S$ is the real mean basal area of one crystal, and ρ is the density of crystal growth centres in the plane. In order to transform this equation into one in V we need to relate $_1S_T$ to $_1V_T$ and we need to relate $_1S_X$ to $_1V_X$.

3.1. Relation between $_1S_X$ and $_1V_X$

This relation can be obtained rather trivially. We have

$$_1V_X \propto \int_0^t k_x(\tau)d\tau \times \int_0^t k_y(\tau)d\tau \times \int_0^t k_z(\tau)d\tau$$

$$(5)$$

and

$$_1S_X \propto \int_0^t k_x(\tau)d\tau \times \int_0^t k_y(\tau)d\tau \qquad (6)$$

where k is a velocity constant for the spreading of crystal in some linear direction. Setting $k_x = k_y = k_z$ (symmetric growth) shows

$$_1V_X = \alpha(_1S_X)^{3/2} \qquad (7)$$

where α is a geometrical constant.

3.2. Relation between $_1S_T$ and $_1V_T$: hemispherical growth

This is a complex relation which depends on the geometry of the individual crystals. First we shall consider hemispherical crystal growth. Since a complete analysis involving all the geometrical details of the randomly distributed crystals, plus their interactions, would be well-nigh impossible to obtain, we consider instead two hemispheres on an extensive plane and let the distance between their centres O_1O_2 be two units. Under our assumption that growth is 'shape-preserving', we can regard the collision of the two hemispheres as geometrically equivalent to an 'interpenetration', and hence the mean volume of one hemisphere as it grows can be obtained by simple mensuration. The basal areas can similarly be obtained. We have

$$\frac{_1V_T^{2/3}}{_1S_T} = \left(\frac{2}{3}\right)^{2/3} \pi^{-1/3} \qquad r \leqslant 1 \qquad (8)$$
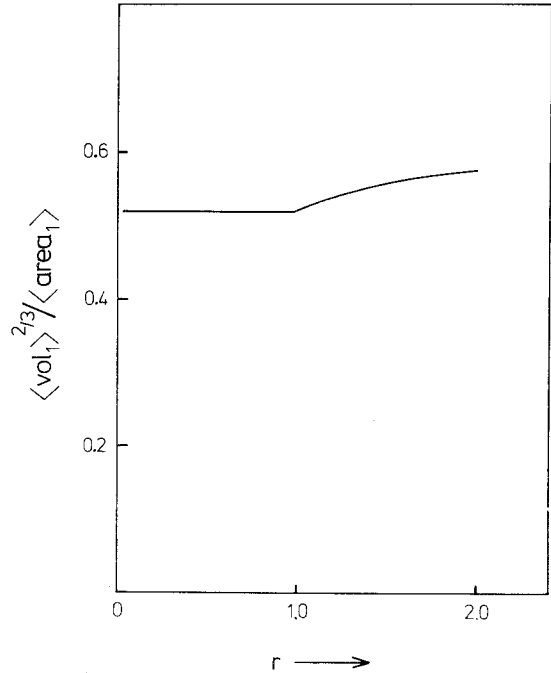

Fig. 2. Behaviour of two intersecting hemispheres as a function of their radius r. The distance between the centres of the hemispheres is assumed to be $2r$.

$$\frac{_1V_T^{2/3}}{_1S_T} = \frac{(\tfrac{1}{3}\pi r^3 + \tfrac{1}{2}\pi r^2 - \tfrac{1}{6}\pi)^{2/3}}{\tfrac{1}{2}\pi r^2 + [(r^2-1)^{1/2} + r^2\sin^{-1}(1/r)]}$$

$$r > 1 \qquad (9)$$

$$\frac{_1V_T^{2/3}}{_1S_T} \to \left(\frac{\sqrt{8}}{3}\right)^{2/3} \pi^{-1/3} \qquad r \to \infty. \qquad (10)$$

This function is illustrated in Fig. 2. It can be seen that for intersecting hemispheres the ratio $(_1V_T)^{2/3}/(_1S_T)$ is only a slowly-varying function of r and hence we can approximate Equations 8–10 by the expression

$$_1V_T = \beta(_1S_T)^{3/2} \qquad (11)$$

where β is a constant. Strictly speaking this approximation has only been shown to hold for the considered pair-wise interactions. Now, since it is known that for growth to be entirely inhibited by collisions requires on average six intercrystal collisions [7] then obviously Equations 11 will become increasingly in error as more collisions occur. This is because Equation 11 underestimates $_1V_T$ at $S \to 1$. However, we do not anticipate that this error will be large enough to invalidate Equation 11 up to $\sim 80\%$ coverage since later

collisions do not allow the crystals to 'inter-penetrate' too deeply. We also note in passing that an equation identical to Equation 11 can be obtained if a growth mode of right circular cones is assumed, in which case similar considerations apply.

Using Equation 11 with Equation 7 now allows us to evaluate the volume transformation.

3.3. Solution to the volume tranformation: hemispherical growth

Substituting Equations 11 and 7 back into Equation 4 gives the result

$$\rho \left(\frac{_1 V_T}{\beta} \right)^{2/3} = 1 - \exp \left[-\rho \left(\frac{_1 V_X}{\alpha} \right)^{2/3} \right] \quad (12)$$

in which $_1 V_T$, $_1 V_X$ are real, not normalized, volumes. By rearrangement

$$_1 V_T = \frac{\beta}{\rho^{3/2}} \left\{ 1 - \exp \left[-\rho \left(\frac{_1 V_X}{\alpha} \right)^{2/3} \right] \right\}^{3/2}. \quad (13)$$

Now $\rho_1 V_T = V_T'/A$ where V_T' is the total real volume. Calling $V_T'/A = V_T$, where V_T is the real volume per unit area of substrate, we finally obtain

$$V_T = \beta \rho^{-1/2} \left\{ 1 - \exp \left[-\rho \left(\frac{_1 V_X}{\alpha} \right)^{2/3} \right] \right\}^{3/2}. \quad (14)$$

3.4. Solution to the volume transformation: prismatic growth

The case of a growth mode of crystals as vertically-oriented prisms (Fig. 1) is an interesting one to consider because two limits on the volume trans-formation can be obtained rather easily by dimen-sional arguments. In the early stages of growth, in which intercrystal collision is statistically improb-able, the same relation between $_1 V_X$ and $_1 S_X$ is obtained as was found in the hemispherical case,

$$_1 V_X \propto (_1 S_X)^{3/2}. \quad (15)$$

Now, in the early stages of intercrystal collision this expression can be extended to include a result on $_1 V_T$ provided 'interpenetration' is not too developed. Thus we assume
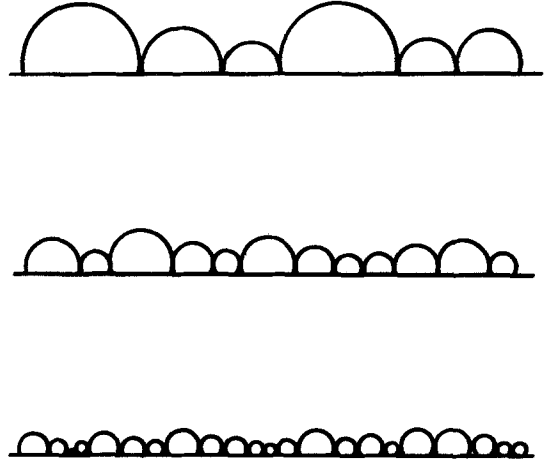
$$_1 V_T \propto (_1 S_T)^{3/2} \quad (16)$$

Fig. 3. A crude attempt to illustrate the fact that the thickness of a polycrystal layer is directly proportional to the mean centre-to-centre nearest-neighbour distance.

which is the same result as in the hemispherical case. In practice this limit would be observed provided growth occurred for a substantial period of time without overlap, whereupon growth would be rapidly inhibited by a fast sequence of collisions at the periphery of the crystal. Thus crystal death would be 'almost catastrophic'. The growth pro-cess in this limit is dominated by collision-free growth prior to the actual occurrence of collisions, and hence we can expect that the physical struc-ture of the crystal layer which results will be similar to that obtained by a random packing. We shall take this point up in a later section.

Another interesting limiting form of growth occurs if it is assumed that the prismatic crystals can 'interpenetrate' indefinitely, so that 'passi-vation' never occurs and hence the crystal layer thickens as a function of time. This is the 'opposite' limit to the one described above in as much as the early stages of growth are unimport-ant and 'interpenetration' is highly developed. In this case we have the simple relationship for $_1 V_T$

$$\frac{_1 V_T}{_1 V_X} = \frac{_1 S_T}{_1 S_X}. \quad (17)$$

Substitution of Equations 17 and 15 into Equation 4 together with the fact that $V_T = \rho_1 V_T$ yields the expression

$$V_T \propto \sqrt{_1 S_X} \left\{ 1 - \exp \left[-\rho \left(\frac{_1 V_X}{\alpha} \right)^{2/3} \right] \right\}. \quad (18)$$

Another way of viewing the limits described by Equations 16 and 17 is to write a general expression for $_1V_T$, of the type

$$_1V_T = {_1}S_T \times \bar{h} \qquad (19)$$

where $\bar{h}$ is defined to be the mean height of the transformed crystals. By the 'geometry-conserving' hypothesis we have immediately

$$\bar{h} \propto \sqrt{_1S_T} \qquad (20)$$

and substitution of Equation 20 in 19 leads immediately to Equation 16.

On the other hand if $\bar{h}$ is not bounded by $_1S_T$ but instead can increase indefinitely then

$$\bar{h} \propto \sqrt{_1S_X} \qquad (21)$$

and substitution of this result in Equation 19 gives

$$_1V_T \propto {_1}S_T\sqrt{_1S_X} \qquad (22)$$

which indicates that

$$\frac{_1V_T}{_1V_X} = \frac{_1S_T\sqrt{_1S_X}}{(_1S_X)^{3/2}} = \frac{_1S_T}{_1S_X} \qquad (23)$$

which is identical to Equation 17.

It is important to note that Equations 20 and 21 really represent rather extreme limiting types of behaviour, and they are obtained here only because they are mathematically tractable. In reality '$2\frac{1}{2}$D' crystal growth is likely to fall somewhere between these limits and indeed it seems probable that the volume transformation for any specified system may well be unique to that system. This could easily be the case because the number of variables controlling the geometry, orientation, growth rates and spatial distributions of crystals in such a system is so vast. To properly consider these 'intermediate' cases we would have to quantify how the volume of crystals varied between the 1st collision and the nth (terminal) collision, and then sum these results over the entire 2D plane.

4. Comparison of the volume transformation with nearest-neighbour theory

So far we have obtained two volume transformations depending on whether the '$2\frac{1}{2}$D' crystalline film passivates the electrode (Equation 14) or continues to thicken indefinitely (Equation 18). The passivating case was obtained under the assumption that

$$_1V_T \propto (_1S_T)^{3/2} \qquad (24)$$

and we have already referred to this as a 'geometry-conserving' solution. It was also suggested that this type of intercrystal collision should have features in common with random packing. Here we take up this point in more detail by comparing the result-in volume transformation with nearest-neighbour theory in 2D.

Let $w(r)dr$ be the probability that the nearest-neighbour to a growth centre chosen at random occurs between r and $(r + dr)$. This probability must equal the probability that no growth centres exist interior to r, times the probability that a growth centre does exist in the circular region between r and $(r + dr)$. Let the density of points in the 2D plane of the substrate be ρ. Then

$$w(r)dr = \underset{0 \to r}{P_0} \times \underset{r \to (r+dr)}{P_1} \qquad (25)$$

$$= [1 - \int_0^r w(r)dr]\, 2\pi r\rho\, dr. \qquad (26)$$

After a little rearrangement, and using the fact that $w(r) \to 2\pi r\rho$ as $r \to 0$, the distribution of nearest-neighbours is found to be

$$w(r) = 2\pi r\rho \exp(-\pi r^2\rho). \qquad (27)$$

The 'average distance' between nearest-neighbour growth centres D is thus

$$D = \sum_0^\infty r[w(r)]\, dr \qquad (28)$$

and replacing the sum by an integral, and solving, gives

$$\langle 2D \rangle = \rho^{-1/2} \qquad (29)$$

with variance

$$\langle (2D)^2 \rangle - \langle (2D) \rangle^2 = (\pi\rho)^{-1}(4 - \pi). \qquad (30)$$

Comparing Equation 29 with Equation 14 shows that after completion of the crystal growth in the 'passivating' case the mean thickness of the layer is directly proportional to the mean centre-to-centre nearest-neighbour distance. This is clearly a physically reasonable conclusion; Fig. 3 is intended to illustrate the fact.

It follows that the simple relation between Equations 29 and 14, i.e., between nearest-neighbour distance and layer thickness, might be used as an experimental test of the suggested model.

5. Calculation of the volume transformation for progressive nucleation

Using the Kolmogoroff–Avrami limiting law we have for the basal area of crystals

$$\theta_T = 1 - \exp\left[-\int_0^t A_X(t)_1\theta_X(\tau - t)dt\right] \tag{31}$$

where $A_X(t)$ is the appearance rate of crystals neglecting collisions. An important point to note here is that even after passivation (100% coverage of electrodes by basal areas) the number of nuclei N_X continues to increase without bound according to

$$N_X = \int_0^t A_X(t)dt. \tag{32}$$

These nuclei do not manifest themselves in reality, however, because they nucleate 'inside' pre-existing crystal (i.e., they are so-called 'virtual' nuclei). This complicates the model, because our next step is to suppose that the thickness of the passivating layer varies as the mean of the crystal centre nearest-neighbour distances, and if we use Equation 32 then the layer thickness $\rightarrow 0$. To resolve this difficulty we need to consider only those nuclei which *actually appear* on free surface, so Equation 32 needs to be replaced by the more complex expression

$$N_T = \int_0^t A_X(t)[1 - \theta_T(t)]\,dt. \tag{33}$$

Proceeding as in the 'instantaneous' case, we set

$$_1V_X \propto (_1S_X)^{3/2} \tag{34}$$

and

$$_1V_T \propto (_1S_T)^{3/2}. \tag{35}$$

Now inserting Equations 33–35 into Equation 31 we obtain

$$V_T \propto \left\{\int_0^t A_X(t)[1 - \theta_T(t)]\,dt\right\}^{-1/2}$$
$$\times \left\{1 - \exp\left[-\int_0^t A_X(t)_1\theta_X(\tau - t)dt\right]\right\}^{3/2} \tag{36}$$

which is the appropriate volume transformation for progressive nucleation.

Acknowledgement

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