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Orientation effects in thin-film crystallization

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A simple two-dimensional model has been used to examine the influence of growth-rate anisotropy, nucleation (seeding) density, and orientation of nuclei on the crystallization kinetics and extent of crystal orientation in thin films. It has been shown that variations in growth-rate anisotropy produce large changes in the kinetics, but relatively small changes in crystal orientation. On the other hand, the orientation of the nuclei has a small influence on the kinetics of crystallization, but strongly influences the extent of crystal orientation at early times.

1. Introduction

The synthesis of oriented crystal structures is of considerable interest because such materials may exhibit highly superior mechanical [1, 2], electrical [3, 4], or superconducting [5] properties. The production of oriented crystals in amorphous thin films is an important subset of the latter process. Although a variety of techniques has been employed to evoke crystal orientation in thin films [6], it is often observed that crystal orientation occurs "spontaneously". If one edge of a film is seeded and the crystal growth is anisotropic, then one observes that at some distance from the edge there is crystal orientation perpendicular to the edge direction. This is a well-known phenomenon [7], and is due to the fact that the fast growth direction eventually predominates. Recently, this feature was demonstrated directly by comparing the measured rate of advancement of a $Li_2O \cdot 2B_2O_3$ crystal front in a glass with the measured fast axis growth rate of a lithium diborate crystallite which formed in the bulk of the glass [8].

Thus, although this type of crystal orientation is understood qualitatively, there is a number of related questions which warrant quantitative investigation. For example, how important is growth rate anisotropy in the development of crystal orientation? How will non-random (preferred) orientation at the substrate influence the extent of orientation? What is the effect of the seeding density at the interface? Some of these questions have been addressed with the aid of a simple model system. In addition, the crystallization kinetics of such systems have been studied. Recently, expressions have been given and calculations performed for surface-nucleated crystallization processes [9,10]. In the present paper, these results have been generalized to include orientation effects.

2. Model

A simple two-dimensional model is chosen with the following characteristics. The height (thickness) of the film is designated by L and it is of infinite extent in the orthogonal direction (see Fig. 1). It is assumed that the film edge ($y = 0$) is random nucleated at $t = 0$ and that no subsequent nucleation occurs. The seeding density is designated by ρ, and is measured in number of nuclei/length. The nuclei are formed with the fast growth direction either parallel or perpendicular to the film height (y direction) with probabilities P_y and P_x, respectively. Constant rectangular growth is assumed and the growth-rate anisotropy (the ratio of fast to slow axis growth rates) is given by the fast axis growth rate, because the slow axis rate is taken as unity. The standard assumption is made regarding the impingement of growing crystals; namely that growth terminates at the point of contact and continues unabated at other points. Finally, attention is restricted to times sufficiently short so that crystals cannot grow "beyond the edge of the film". This condition will imply that not all films are fully crystallized. This limitation will be of significance only for very thin films.

Although this model is extremely idealized, it is sufficient to illustrate the salient points regarding the influence of growth-rate anisotropy, seeding density, and preferential orientation upon the crystallization kinetics.

3. Governing equations

The governing equations can be derived easily with the aid of Fig. 1. The area fraction transformed as

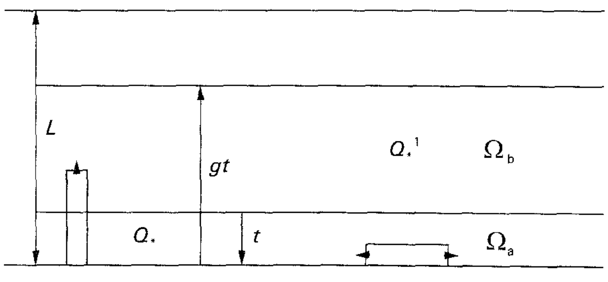

Figure 1 Schematic drawing of the model system.

a function of time, $x(t)$, may be written as

$$x(t) = f_a x_a + f_b x_b \quad (1)$$

where x_a, x_b are the area fractions transformed in regions Ω_a, Ω_b and as one can see from Fig. 1, the area fractions, f_a, f_b, are given as

$$f_a = t/L = y/z \quad (2a)$$

$$f_b = t(g_r - 1)/L = y(g_r - 1)/z \quad (2b)$$

where g_r is the fast growth rate, $y = \rho t$ is a dimensionless time, and $z = \rho L$. The fractions x_a, x_b are equivalent to the probabilities that random points in Ω_a (i.e. Q), Ω_b (i.e. Q') are transformed.

The probability that point Q' is *not* transformed (i.e. $1 - x_b$) can be found from the probability that no seed whose fast growth direction is along the y-axis was nucleated in a strip of length $2t$. Only seeds oriented in the latter direction can transform region Ω_b because those oriented along the x-axis have not had sufficient time to grow into the region. From elementary probability theory one finds

$$x_b = 1 - \exp(-\rho P_y 2t) = 1 - \exp(-2P_y y) \quad (3)$$

The computation of the probability that Q is not transformed is only slightly more complicated. Here, one must compute the probability that neither an x-axis nor y-axis oriented particle formed on a segment of the edge such that it could grow to Q in time t. Again the use of elementary probability theory leads to the following expression for x_a

$$x_a = 1 - \exp[-\rho(2tP_y + 2tg_r P_x)] = 1 - \exp[-2y(P_y + g_r P_x)] \quad (4)$$

Equations 1–4 allow one to compute the transformation kinetics.

As an aside, one may compare the above equations with that given by a simple Johnson–Mehl–Avrami (JMA) [11–15] expression. In the latter case,

$$x(t) = f_1 x_1 \equiv (f_a + f_b)[1 - \exp(-x_e)] \quad (5a)$$

and x_e, the extended area fraction transformed is given by

$$x_e = 2t\rho = 2y \quad (5b)$$

One notes that the JMA expression for the area transformed is independent of P_x, P_y and $x(t)$ is simply proportional to g_r.

Finally, it is of interest to compute the area fraction transformed with the fast growth direction oriented along the y-axis, x_{fast}. The latter quantity is given by

$$x_{fast} = f_b x_b + f_a x_a \cdot [1 + R\exp(-2P_y y)]^{-1} \quad (6)$$

where R is the ratio of the probabilities that any arbitrary point is transformed by a seed oriented parallel to the x-axis to that oriented parallel to the y-axis, and may be expressed as

$$R = \frac{1 - \exp(-2g_r P_x y)}{1 - \exp(-2P_y y)} \quad (7)$$

The fraction of the total transformed area which is y oriented, F_y, is x_{fast}/x.

4. Transformation kinetics

First, we consider the crystallization kinetics when there is an equal probability for growth parallel to x and y-axes (i.e. $P_x = P_y = 0.5$). The solid dots in Fig. 2 show the area fraction of the film crystallized as a function of time for $z = 20$ and a growth rate ratio (fast to slow axis) of 5. The crosses show $x(y)$ computed with the aid of the simple JMA equation (i.e. Equations 5a, b). Although there is fairly close agreement between the results of these two sets of calculations, the distribution of transformed areas in regions Ω_a and Ω_b is poorly represented by the JMA equation, as can be seen from an inspection of the lines in Fig. 2. The JMA equation does not distinguish between the transformation rates in these two regions, although one observes that the transformation in region Ω_a occurs much more rapidly than in region Ω_b. Fig. 3 illustrates the influence of the orientation probability of the seeds on the transformation kinetics. The crystallization rates for $P_y = 0.8$ and $P_y = 0.5$ are much more similar than those for $P_y = 0.2$ and $P_y = 0.5$. This feature is primarily due to the smaller difference in the rates at which the Ω_b region is transformed in the former case, as illustrated in Fig. 4. Also, doubling the seeding density does not have a dramatic effect upon the transformation rate, as one can see from an inspection of Fig. 5. On the other hand, increasing the fast axis growth rate accelerates the transformation significantly because the penetration of the crystalline material into the film is enhanced (see Fig. 6).

5. Oriented crystallization

If one desires to produce crystals oriented perpendicular to the nucleation edge, then it is of interest to

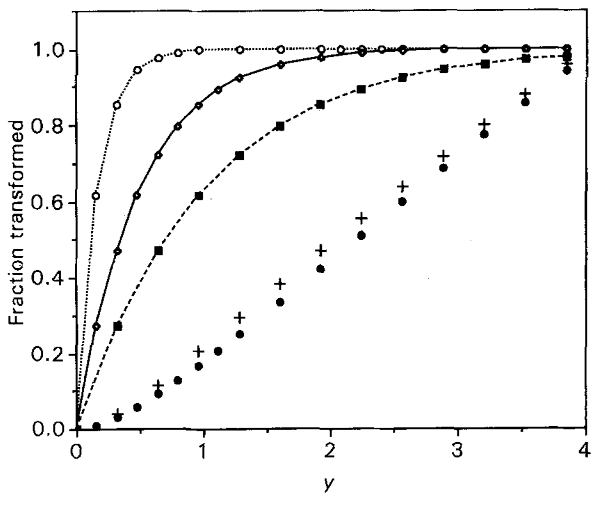

Figure 2 Area fraction crystallized as a function of time. $P_x = P_y = 0.5$, $g_r = 5$, and $z = 20$. (○) x_a (Equation 4), (■) x_b (Equation 3), (◇) $x_a (= x_b)$ (JMA), (●) x (Equation 1), (+) x (JMA).

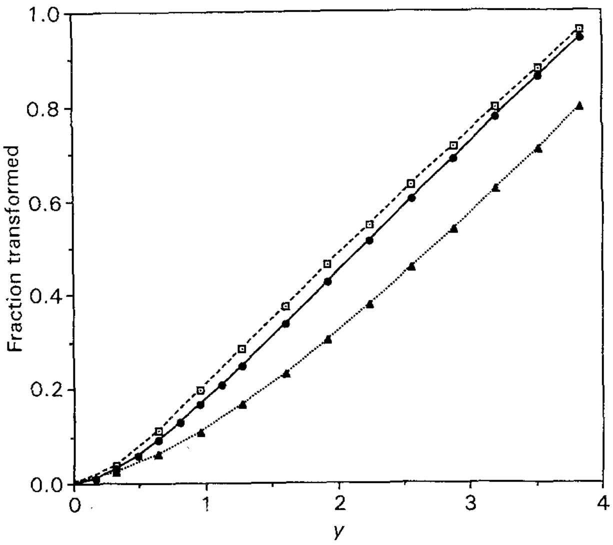

Figure 3 Area fraction crystallized as a function of time for different seeding orientation probabilities. $z = 20$ and $g_r = 5$. (⊡) $x\,(P_y = 0.8)$, (●) $x\,(P_y = 0.5)$, (▲) $x\,(P_y = 0.2)$.

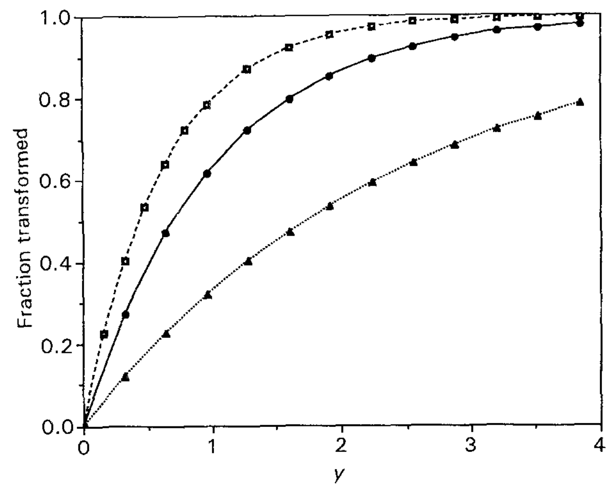

Figure 4 Area fraction crystallized in Ω_b region as a function of time. $z = 20$ and $g_r = 5$. (●) $x_b(P_y = 0.5)$, (▲) $x_b(P_y = 0.2)$, (■) $x_b(P_y = 0.8)$.

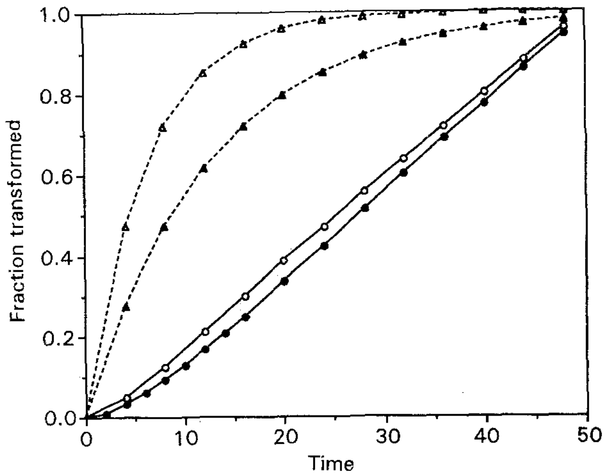

Figure 5 Area function crystallized as a function of time for $z = 20$ and $z = 40$. Also, $P_x = P_y = 0.5$ and $g_r = 5$, $L = 250$. (▲) $x_b(z = 20)$, (●) $x(z = 20)$, (○) $x(z = 40)$, (△) $x_b(z = 40)$.

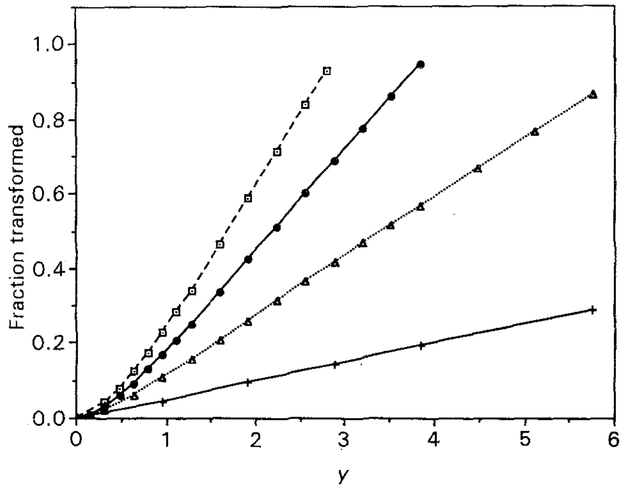

Figure 6 Area fraction crystallized for different growth rate anisotropies. $P_x = P_y = 0.5$ and $z = 20$. (⊡) $x(g_r = 7)$, (●) $x(g_r = 5)$, (△) $x(g_r = 3)$, (+) $x(g_r = 1)$.

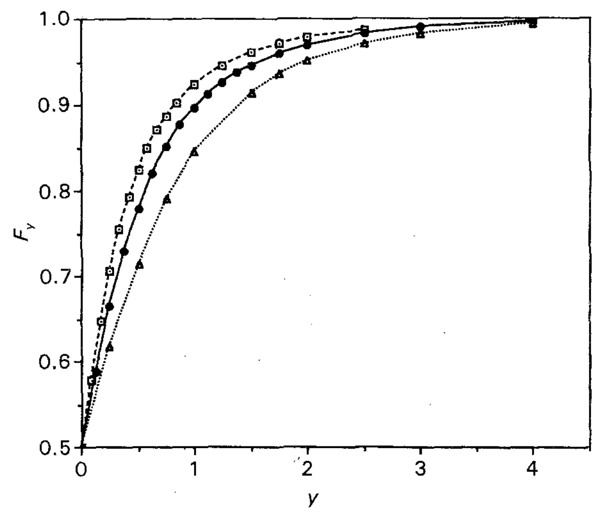

Figure 7 Fraction of crystallized area oriented in the y direction for different growth rate anisotropies with $z = 20$ and $P_x = P_y = 0.5$. (⊡) $g_r = 7$, (●) $g_r = 5$, (△) $g_r = 3$.

inspect the influence of growth-rate anisotropy, seeding-orientation probability, and seeding density on extent of orientation. Fig. 7 shows the fraction of transformed area which is oriented in the y direction as a function of time for $z = 20$, $P_x = P_y = 0.5$ and several different fast axis growth rates. For anisotropic growth the fraction of oriented area changes with time and depends upon the growth anisotropy. Using the governing equations it is easy to show that at sufficiently short times, the fractional area oriented approaches P_y, independent of the value of g_r, and thus for $P_y = 0.5$ all the plots intersect this point at $y = 0$. On the other hand, at long times the fractions of oriented area approach the value of unity, as shown in Fig. 7. The influence of seed orientation on the development of orientation of crystalline area, for fixed growth-rate anisotropy, is shown in Fig. 8. Here, at short times the fraction of oriented area is determined primarily by the number of oriented seeds which formed initially, and there are large differences in the fraction of oriented crystals. As time progresses, however, these large differences diminish owing to the rapid growth of the crystals with their fast growth axes in the y direction into the Ω_b region. At the longest

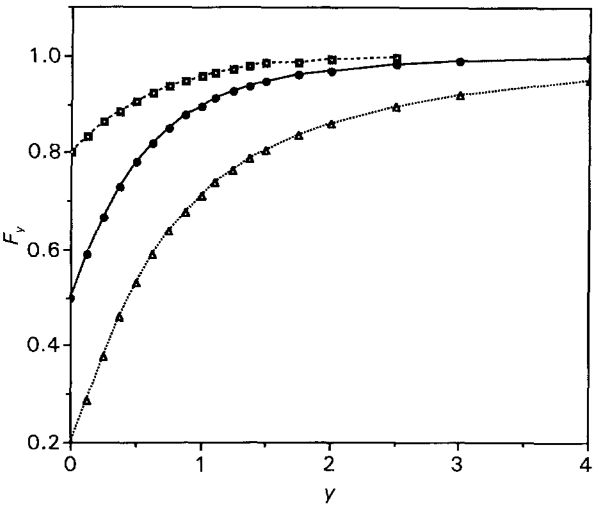

Figure 8 Fraction of crystallized area oriented in the y direction for different seeding orientation probabilities with $z = 20$ and $g_r = 5$. (△) $P_y = 0.2$, (●) $P_y = 0.5$, (■) $P_y = 0.8$.

time shown in this figure, the fraction of oriented crystallized areas is nearly unity for $P_y = 0.8$ and $P_y = 0.5$, but is somewhat smaller for $P_y = 0.2$. Finally, one may consider the effects of changes in z, the product of the seeding density and film thickness, on the orientation probability. If one inspects the ratio of Equation 6 to Equation 1, then one finds that F_y does not depend explicitly upon z. However, there is an implicit dependence upon z in that the upper limit of y, y_{up}, for which the present model is valid, is given by $y_{up} = z/g_r$. Because, at smaller y, the fraction of y-oriented crystals is less than at larger y, one finds that as z increases the film will contain a larger percentage of y-oriented crystals. The precise dependence of F_y upon z for fully crystallized films will be given in a future publication [16].

6. Discussion

It was observed that an increase in the growth-rate anisotropy produced a rapid increase in the crystallization kinetics. This feature follows from the fact that the growth rate in the slow direction was held fixed, so that increasing the growth-rate anisotropy was tantamount to increasing the fast axis growth rate. On the other hand, the seed orientation probabilities have a somewhat smaller influence upon the crystallization kinetics, especially for $P_y \geqslant 0.5$. From an inspection of Equations 3 and 4 one notes that x_b will be more sensitive to the value of P_y than x_a. A larger value of P_y will produce more y-oriented seeds which will cause a more rapid transformation of the Ω_b region (as shown in Fig. 4). However, because the Ω_a region transforms so rapidly, at intermediate times this region is nearly completely transformed regardless of the value of P_y. Hence, the sensitivity of x to P_y is not very dramatic. The crystallization rate is not influenced strongly by seeding density, as can be seen from Fig. 5. For both values of the seeding density chosen ($\rho = 2/25$ and $4/25$), the Ω_a region transforms nearly completely at short times ($t \approx 8$), and the term $f_a x_a$ is practically the same in both cases. Furthermore, because g_r is the same for both calculations, the crystallization front propagates at the same rate in both cases. Hence, $x(t)$ does not differ dramatically for the two different seeding densities.

The fraction of y-oriented crystalline area produced as a function of time depends only weakly upon the growth-rate anisotropy. This feature follows, in part, from the fact that at short and long times F_y will be nearly identical. It is easy to show that at $t = 0$, F_y is independent of g_r and is given by P_y. At long times, for relatively large z, F_y is nearly unity. Hence, regardless of the growth-rate anisotropy F_y will be similar at short and long times. When g_r is small, however, it takes longer for the y-oriented area to develop. Finally, it was noted that F_y is strongly dependent upon seeding orientation probability. As noted, at short times F_y is very sensitive to P_y. At long times, the x-oriented seeds tend to become encapsulated by the faster growing y-oriented seeds so that the differences between the F_y values are reduced. In the case of very thin films (not treated here) the large differences in y-oriented areas persist.

7. Conclusion

Using a simple model, the influence of seeding density, growth rate anisotropy, and seeding orientation probability on the crystallization kinetics and extent of crystal orientation in thin films has been examined. It has been shown that an increase in the crystal growth rate anisotropy greatly accelerates the crystallization kinetics but has a very small influence on the final degree of crystal orientation. Also, it has been observed that for anisotropic growth there is an asymmetry in the effects on the transformation kinetics of decreasing or increasing P_y by the same amounts in that decreases in P_y have a larger impact on the crystallization rate. Also, it has been observed that seeding orientation probability strongly influences orientation at all times. Finally, we have seen that increasing the seeding density causes the development of more y-oriented crystal area and increases the crystallization kinetics to some slight degree.

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