

SOLID-LIKE GROWTH

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In this paper we consider particulate growth and coalescence beyond the liquid-like model when surface energy anisotropy effects are important. First the idea of multiple minima for composite particles via a modified Wulff construction is described. Experimental results for room temperature gold thin films are then presented, showing clear evidence for two-dimensional polyparticle network growth. These results are then combined with models of liquid-like and amorphous growth by a structure map for thin film structure. It is proposed that the structural aspects of particulate thin film growth can be described via such structure maps.

1. INTRODUCTION

In areas ranging from the deactivation of catalysts to the sintering of ceramics, the mechanisms of particulate growth and coalescence play a crucial role. Since the early work of Pashley and coworkers^{1–3}, an extensive amount of work has been performed using the liquid-like model, *i.e.* a continuum approach which neglects any crystallographical or surface energy anisotropy. Without intending to denigrate this work, it should be recognized that this is a severe approximation. For instance, surface diffusion rates on f.c.c. surfaces can be as much as 11 orders of magnitude faster on a {111} surface than on a {100} surface⁴.

One area where it is necessary *a priori* to include such anisotropic effects is for multiply twinned particles (MTPs), *e.g.* see refs. 5–16. To first order these can be thought of as collections of twin-related single-crystal tetrahedra, inhomogeneously strained (see refs. 13 and 16 and references cited therein) to form a space-filling structure. These particles can have a lower energy^{7–10,13} than single crystals when small since the particles have more low energy surface facets (primarily {111} facets¹²). Thus these particles can only be understood by using a model which takes account of anisotropic effects.

Whilst MTPs are one of the dominant species in small particles, particularly for silver and gold, there are also many more complicated structures. From high resolution electron microscopy^{17,18} it has been shown that many of these arise from particulate coalescence. However, rather than recrystallization taking place to

produce single-crystal particles, the composite structures frequently produce polyparticles. These are analogues of polycrystals, but with discrete particle building blocks such as MTPs rather than single crystals. These complicated particles can theoretically¹⁸ be explained, as can the MTPs¹², using a model that specifically includes the surface energy anisotropy.

In this paper we consider some of the wider implications of particulate growth and coalescence beyond the liquid-like model when surface energy anisotropy effects are built into the models. First, we shall briefly detail the modified Wulff construction^{12,18} that can be used to explain the structure of both MTPs and polyparticles. We then describe experimental results for room-temperature-evaporated gold films. These show that it is possible to obtain continuous partially coalesced networks of polyparticles. When the film grows thick enough, the energy stored within the twin boundaries and in inhomogeneous strains becomes sufficient to initiate substantial recrystallization. Combining the modified Wulff construction with the above results, the results of Pashley and coworkers¹⁻³ and some models of amorphous materials^{19,20}, we are able to start to construct a generalized structure map for particulate thin film growth. From this structure map we can start to see how parameters such as temperature and thickness affect film growth.

2. MODIFIED WULFF CONSTRUCTIONS AND MULTIPLE MINIMA

In this section we briefly sketch the basics of a modified Wulff construction and the important physical results to which it leads. In a liquid-like continuum model, there is only one minimum for the energy of a composite particle, namely a spherical single crystal. With an anisotropic surface and taking account of boundaries via a modified Wulff construction, we instead find that there are many different local minima such as single crystals, MTPs and polyparticles. The additional dimensions that this opens up have important implications for thin film growth as we shall see below.

The modified Wulff construction is used to determine the equilibrium shape of a particle containing boundaries whilst the total volume remains constant. Its simplest use is when the boundaries are twin boundaries, although it can also be used, for instance, for grain boundaries. The derivation of the construction has been dealt with elsewhere¹⁸ and will not be repeated here.

The following recipe is used.

(1) Dissect the particle along the boundaries, partitioning the boundary energy into (what are for the moment) two arbitrary parts ascribed to the segments on either side of the boundary.

(2) Minimize by the standard Wulff construction the shape of each segment separately, treating the boundary facets as surface facets of energy determined by the partition in (1).

(3) Find any solutions for the partition of the boundary energy and total volume for the segments such that the segments fit to produce a complete particle without any unmatched boundary facets.

If there are only discrete, point solutions for (3), these are almost certainly local minima. If there is a continuous line or surface of solutions, further analysis is

required to look for any local minima. At present there is no formal mathematical proof of the construction; it is straightforward to show that the solutions correspond to stationary points, but it is not straightforward to derive the sign of the second derivative. It is possible to justify the construction on the physical grounds that it is far more important to minimize the surface energy than that of any boundaries as the surface energy (per unit area) is substantially larger. The most compelling proof at present is that the predictions of the construction agree with the experimental results¹⁸.

The important aspect of the construction for our purposes here is that the *only* local minimum for a liquid-like model is a single crystal. All the local minima particle morphologies that are observed experimentally are *only* stable when the surface energy is anisotropic.

3. EXPERIMENTAL METHODS

The experimental samples were prepared by evaporating gold onto room temperature KCl which had previously been cleaved *in situ* in ultrahigh vacuum. A razor edge was used to mask the KCl substrate so as to obtain various different thicknesses. The specimens were then coated with a thin carbon film and transferred by water floatation onto copper grids for electron microscopy. High resolution imaging in the Cambridge High Resolution High Voltage Electron Microscope²¹ and bright field–dark field imaging techniques in a Siemens 102 were used to examine the particles.

4. RESULTS

The main results are shown in Fig. 1 which consists of a series of images from regions of increasing thickness. At low coverages (Figs 1(a) and 1(b)), discrete particles and polyparticles were observed similar to those described previously¹⁷. Some of the icosahedral (I) and decahedral (D) units are arrowed on Fig. 1. As the thickness increased (Figs. 1(c)–1(e)), the structure of the film developed into a semicontinuous two-dimensional polyparticle network. For the relatively thick specimens, recrystallization regions were present, the initial stage of one such region being shown in Fig. 1(d). These grew in size as the thickness increased (Fig. 1(e)). Figure 1(f) is a low magnification image showing extensive recrystallization. Figures 2 and 3 are high resolution images showing respectively an icosahedral element from the thickness used for Fig. 1(c) and a decahedral element from the thickness used for Fig. 1(d).

5. STRUCTURE MAP

We now analyze the results described above, combining these with the results from the liquid-like model^{1–3} and some models of amorphous film growth^{17,18} to produce an overview. We shall show how these can all be considered in terms of a structure map for thin film growth.

The experimental results give quite straightforward evidence for an extension of

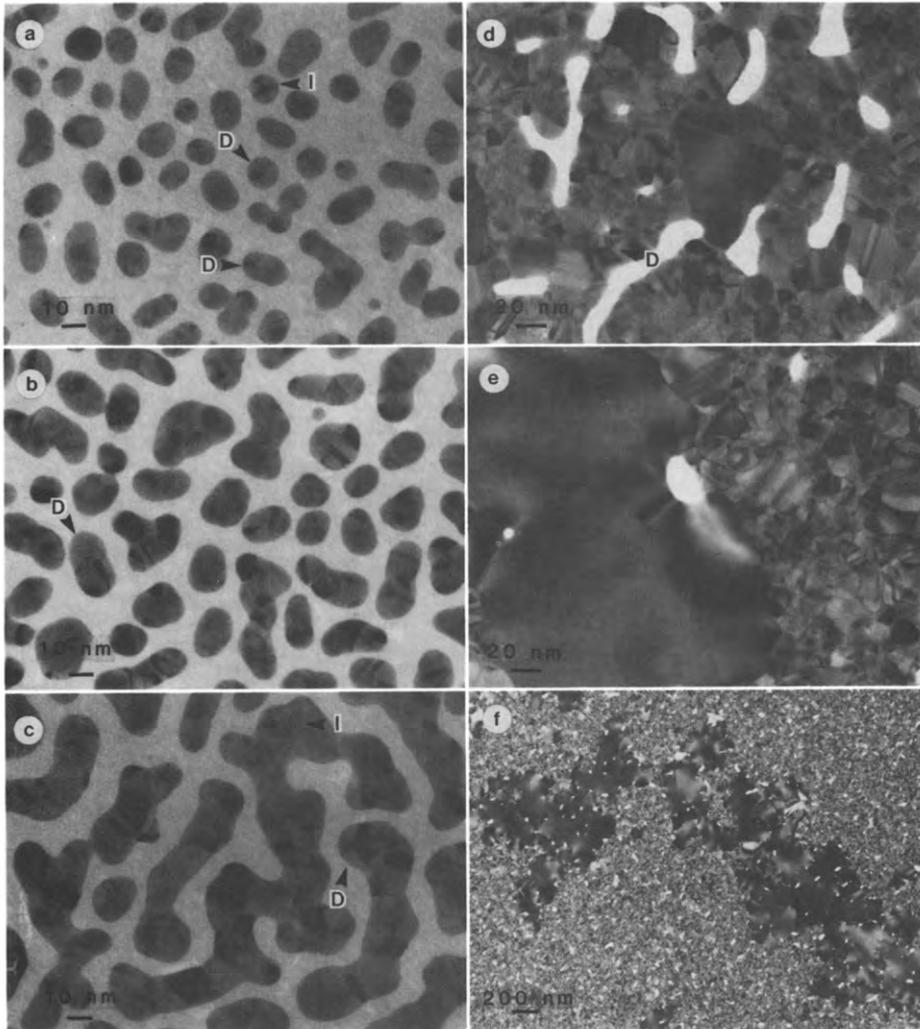


Fig. 1. Electron micrographs from a room temperature gold film, increasing in thickness from (a) to (e) with (f) being a lower magnification image from (e).

the modified Wulff construction. We know that we can have multiple local minima for discrete particles and polyparticles. With coalescence producing a network, rather than the minima leading to single crystals as in a liquid-like model, we can obtain a locked polyparticle network. This network is stabilized by both modified Wulff local minima and deactivation of surface diffusion at low temperatures. When the film grows thick enough the energy stored in the boundaries and strains can become sufficient to initiate recrystallization. If there is no recrystallization we can produce a three-dimensional polyparticle network. With a small grain size this network film would be an amorphous film as in the polytetrahedral model of Hoare and Pal¹⁹ and Gaskell²⁰. On the other extreme, if the surface energy anisotropy is

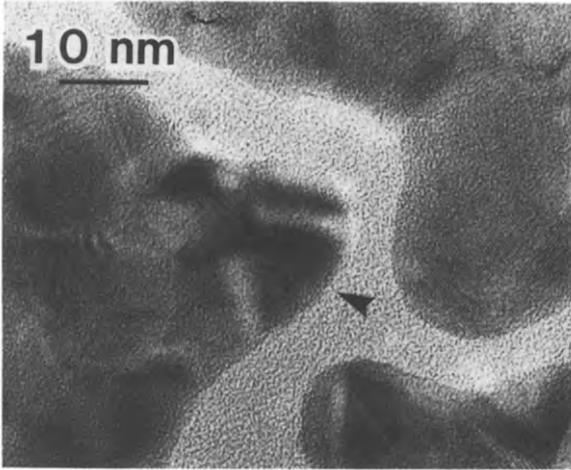


Fig. 2. High resolution image from approximately the thickness used in Fig. 1(c), with an icosahedral element arrowed.

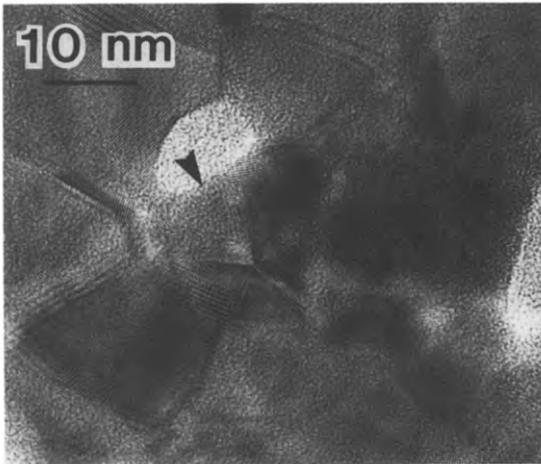


Fig. 3. High resolution image from approximately the thickness used in Fig. 1(d), with a decahedral element arrowed.

reduced, we can destabilize the polyparticles. Then we shall tend to produce primarily single-crystal particles with polycrystalline growth as in the liquid-like models.

Therefore by varying the parameters we can see how film growth can be amorphous, polyparticle or liquid-like in nature. This implies that it is possible to represent the growth in terms of a structure map as shown in Fig. 4. The boundaries of this map are not intended to be hard, and at present we have very little experimental evidence with which to delineate them. There may well be further complications in the physically accurate structure map, but this is a subject for future research.

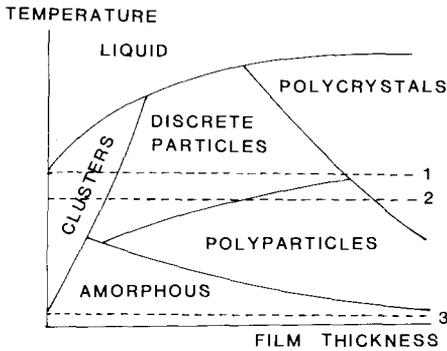


Fig. 4. Schematic structure map for particulate thin film growth. Paths 1, 2 and 3 correspond to liquid-like, polyparticle and polytetrahedral amorphous growth respectively. The different regions are as follows: (i) clusters, typically less than 100 atoms, 1 nm in diameter with dynamic structure variations; (ii) discrete particles, either single crystals or MTPs, separate and roughly spherical; (iii) polycrystals, large grain material with twin or grain boundaries; (iv) polyparticles, metastable structures arising from incomplete coalescence; (v) amorphous, polytetrahedral or random network structure.

6. DISCUSSION

We have indicated above how we can at least start to construct a generalized model for the structures found in thin film growth by generating a structure map. One of the key components in the procedure is the use of anisotropic surface energy models. This is then tied in with the concept of local minima indicating that, depending upon the kinetics of growth, the system finds a local minimum and not a global thermodynamic minimum.

Of course we have only considered growth when there are weak particle-substrate interactions and MTPs are common, and we have employed a Wulff construction model which neglects many of the atomistic effects. Strictly speaking, the phase map is multidimensional and not two-dimensional as in Fig. 4. For instance, the strength of the particle-substrate interaction should be included as a separate dimension. Non-continuum aspects of the Wulff construction are important for typical particle diameters of less than about 10 nm²². However, these and other "particle size" phenomena such as surface stress contributions (*e.g.* see refs 13 and 23), changes in the phonon entropy and quantum size effects (*e.g.* see refs. 14 and 24) will cancel to first order when one compares the energies of different morphologies. Therefore we expect that these phenomena only become important down in the cluster range of a few thousand atoms.

In any case, overriding such technical questions we have found that the modified Wulff model seems to agree with the experimental results. Hopefully in the future we shall see both experimental data which will enable the phase boundaries to be refined and more detailed theoretical models.

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REFERENCES

- 1 D. W. Pashley, M. J. Stowell, M. H. Jacobs and T. L. Law, *Philos. Mag.*, *10* (1964) 103, 127.
- 2 M. H. Jacobs, D. W. Pashley and M. J. Stowell, *Philos. Mag.*, *13* (1966) 121, 129.
- 3 D. W. Pashley and M. J. Stowell, *J. Vac. Sci. Technol.*, *3* (1966) 156.
- 4 G. Ayrault and G. Ehrlich, *J. Chem. Phys.*, *60* (1974) 281.
- 5 S. Ino, *J. Phys. Soc. Jpn.*, *21* (1966) 346.
- 6 S. Ino and T. Ogawa, *J. Phys. Soc. Jpn.*, *22* (1967) 1369.
- 7 S. Ino, *J. Phys. Soc. Jpn.*, *27* (1969) 941.
- 8 J. G. Allpress and J. V. Sanders, *Aust. J. Phys.*, *23* (1970) 23.
- 9 M. B. Gordon, F. Cyrot-Lackmann and M. C. Desjonqueres, *Surf. Sci.*, *80* (1979) 159.
- 10 J. L. Martins, R. Carr and J. Buttet, *Surf. Sci.*, *106* (1981) 265.
- 11 L. D. Marks and D. J. Smith, *J. Microsc. (Oxford)*, *130* (1983) 249.
- 12 L. D. Marks, *Philos. Mag. A*, *49* (1984) 81.
- 13 A. Howie and L. D. Marks, *Philos. Mag. A*, *49* (1984) 95.
- 14 J. Buffett and J. P. Borel, *Helv. Phys. Acta*, *56* (1983) 56.
- 15 B. Mutaftschiev, *J. Cryst. Growth*, *65* (1983) 50.
- 16 L. D. Marks, *Surf. Sci.*, *150* (1985) 302.
- 17 D. J. Smith and L. D. Marks, *J. Cryst. Growth*, *54* (1981) 556.
- 18 L. D. Marks, *J. Cryst. Growth*, *61* (1983) 556.
- 19 M. R. Hoare and P. Pal, *J. Cryst. Growth*, *17* (1972) 77.
- 20 P. H. Gaskell, *Philos. Mag.*, *32* (1975) 211.
- 21 D. J. Smith, R. A. Camps, L. A. Freeman, R. Hill, W. C. Nixon and K. C. A. Smith, *J. Microsc. (Oxford)*, *130* (1983) 127.
- 22 L. D. Marks, *Surf. Sci.*, *150* (1985) 358.
- 23 R. G. Linford, in M. Green (ed.), *Solid State Surface Science*, Dekker, New York, 1973, p. 1.
- 24 J. Freidel, *Helv. Phys. Acta*, *56* (1983) 507.