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Coalescence and percolation in thin metal films

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Metals thermally evaporated onto warm insulating substrates evolve to the thin-film state via the morphological sequence: compact islands, elongated islands, percolation, hole filling, and finally the thin-film state. The coverage at which the metal percolates (p_c) is often considerably higher than that predicted by percolation models, such as inverse swiss cheese or lattice percolation. Using a simple continuum model, we show that high-p_c's arise naturally in thin films that exhibit a crossover from full coalescence of islands at early stages of growth to partial coalescence at later stages. In this interrupted-coalescence model, full coalescence of islands occurs up to a critical island radius R_c, after which islands overlap, but do not fully coalesce. We present the morphology of films and the critical area coverages generated by this model.

Most metals do not wet insulating surfaces such as glass or silicon, and in such a case, a thin film grown by thermal evaporation passes through a sequence of morphological changes as the film thickens.[1,2] When sufficiently thin, the film consists of isolated, compact islands which, as more material is deposited, grow and coalesce into larger, but still compact, islands. At some critical island size, islands that touch no longer fully coalesce into near-equilibrium compact shapes, but instead form elongated structures. As growth proceeds, these elongated structures grow longer and connect to form a percolating structure, and, finally, the channels between the structures fill in to form a continuous, hole-free film. This morphological sequence is illustrated in Fig. 1, which shows an indium film evaporated onto a room-temperature SiO_2 substrate.[3] For this film, the critical area coverage for percolation is quite high ($p_c = 0.82 \pm 0.02$),[4] a result of the fact that the channels between the elongated structures are very long and narrow compared to the width of the structures. High p_c is a puzzling feature of the morpholo-

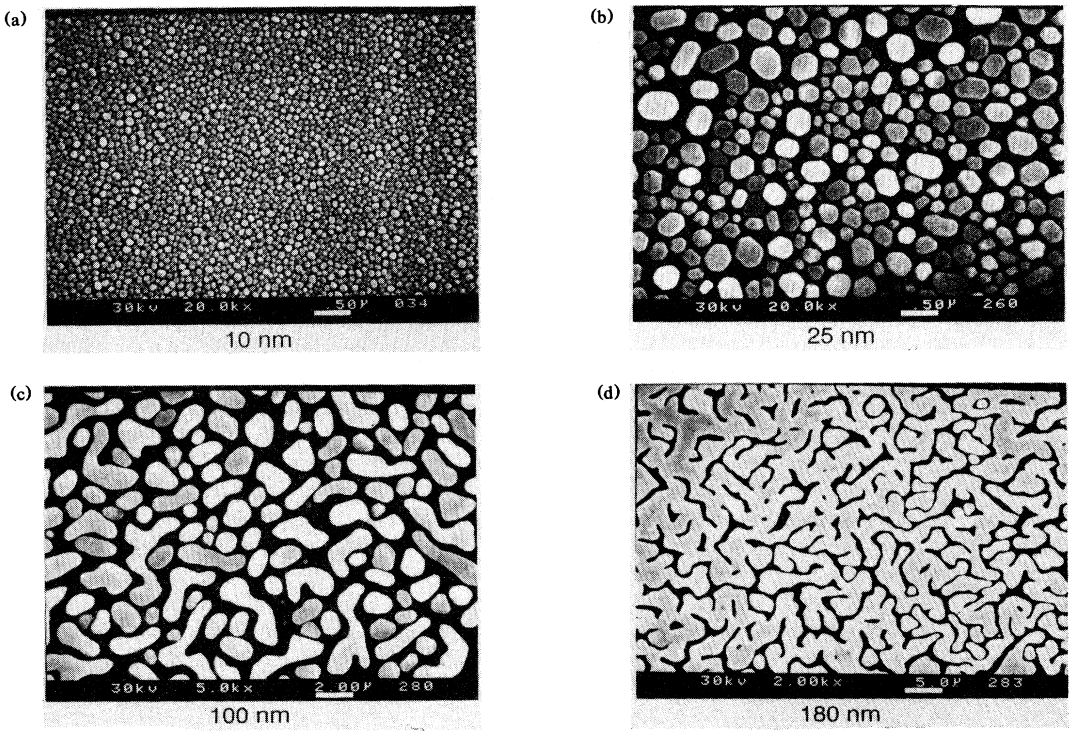

FIG. 1. SEM photographs of indium evaporated onto SiO_2 at room temperature. The average film thickness is given below each photograph. (a), (b) Growth and coalescence of islands; (c) elongated structures; (d) percolation. Note the reduced magnification in (c) and (d).

gy of many metal films[5,6] grown on warm substrates, and in this Rapid Communication we introduce a simple continuum model that resolves this puzzle.

As can be seen in Figs. 1(a) and 1(b), in the early stage of growth, the film has distinctive morphology, consisting of compact islands, all of about the same size, separated by gaps which are comparable to or smaller than the island radius. Actually, the gaps are filled with a population of smaller islands which do not show well in these scanning-electron-microscopy (SEM) photographs. During film growth, islands are always growing because of deposition of material and accretion of smaller droplets at the island perimeter. In this early growth stage, when two islands touch, they quickly coalesce into a larger similar island, and in so doing wipe clean part of the substrate which was covered. This wiping action constantly creates gaps comparable to the island radius and results in ever-larger islands separated by gaps filled with smaller islands nucleated since the last wipe.

At a later stage of growth [Fig. 1(c)] full coalescence no longer occurs. Instead, a partial coalescence of touching islands occurs, resulting in elongated structures and little wiping.

To accurately mimic the film growth we have described, a model must have the following key features: an early stage of full coalescence of compact islands, a crossover to elongated structures, and, under certain conditions, a very high p_c.

The morphology of discontinuous films has been analyzed in terms of percolation models.[7] Various geometrical exponents (fractal dimensionality, correlation length, etc.) have been measured in real films and are found to coincide with values found in two-dimensional pure percolation patterns.[6,8,9] It may, therefore, be natural to assume that simple lattice models will accurately reproduce the morphology of real discontinuous films. However, we have found that a large class of lattice models with short-range attractive interactions fail to reproduce the essential phenomena of full coalescence of islands, late stage elongated structure growth, and high p_c that occur in the growth of many thin metal films on room-temperature substrates.[10] The primary difficulty with Monte Carlo lattice models is that even small coalescing islands tend to freeze into metastable configurations and thus fail to exhibit full coalescence and wiping.

The long and intertwined elongated structures seen in Fig. 1(d) appear to be repelling each other. We will show that a simple continuum model which incorporates the essential feature of interrupted coalescence of large islands and which contains only short-ranged attractive interactions accurately reproduces this apparent repulsion and the high p_c which results from it.

Direct observation of growing metal films[11] on warm substrates has verified that full coalescence occurs when the metal islands are small and partial coalescence occurs when the islands reach a radius greater than a critical value R_c. In the regime that we are considering, the substrate temperature is well below the droplet melting temperature and the mechanism of coalescence is surface diffusion (not bulk diffusion).[12] The reason for the interruption of full coalescence beyond a critical island size is not understood, to our knowledge. We speculate that the surface diffusion rate slows markedly at some critical value of the local curvature, resulting in greatly reduced coalescence rates. Here we consider R_c to be empirically determined.

The full coalescence stage has been previously studied by Family and Meakin,[13,14] and here we extend their model to include the island–to–elongated-structure crossover and eventual percolation.

The Family and Meakin model (FMM) is defined as follows. All islands are assumed to be circles (D=2 model) or spherical caps (D=3 model). Droplets of radius R_0 rain down ballistically on a two-dimensional substrate. If they land on a pre-existing droplet, a new droplet of size

$$R^D = R_1^D + R_2^D \tag{1}$$

is generated. Here R_1 is the radius of the pre-existing droplet on the surface, while $R_2 = R_0$ is the radius of the droplet that is ballistically deposited onto the substrate. The center of the droplet is located at the center of mass of the old droplet and the added droplet. If the new droplet now overlaps an adjacent droplet on the surface, these two droplets also coalesce according to rule (1). Complete relaxation of the pre-existing droplets on the surface occurs before the next new droplet is ballistically added to the surface.

In the FMM, the distribution of droplet sizes is asymptotically bimodal for D=3 and polydispersed for D=2. In either case, there is no percolation transition in the usual sense. At fixed sample size, a connected metal path only occurs when a single droplet spans the sample.

We now introduce a interrupted coalescence model (ICM) which generalizes the FMM to include a cutoff radius R_c above which overlapping islands no longer coalesce. The ICM rules are thus the following: (i) if $R_1 < R_c$ or $R_2 < R_c$, droplets coalesce according to (1), and the new droplet is at center of mass of the old droplets; (ii) if $R_1 > R_c$ and $R_2 > R_c$, the droplets do not coalesce. R_c sets the length scale at which the crossover from the droplet to the elongated structure stage occurs. With R_0 the radius of the small droplets being ballistically deposited onto the surface, and L the edge length of the system, the important independent variables in our simulations are the ratios R_c/R_0 and L/R_0. Note that when $R_c/R_0 < 1.0$, no coalescence occurs, and both the D=2 and D=3 models reduce to the D=2 inverse-swiss-cheese model ($p_c = 0.676 \pm 0.002$).[15]

Figure 2 presents the growth morphology generated by the ICM for the case $R_c/R_0 = 8$, $L/R_0 = 200$, and D=3. (The D=3 case mimics real films.) It is seen that in the early stages of growth, the model is very similar to the FMM. As deposition continues, the large droplets begin to overlap, until finally a percolation path of the large droplets occurs. The configuration at percolation [Fig. 2(b)] shows the high percolation coverage generated by the ICM (in this configuration about 0.82).

The reason for this high p_c is that the initial droplet state is correlated, and that percolation from this correlated state requires a higher coverage than would random percolation of discs (inverse swiss cheese). The small droplets ($R < R_c$) do not lie on the final percolation path,

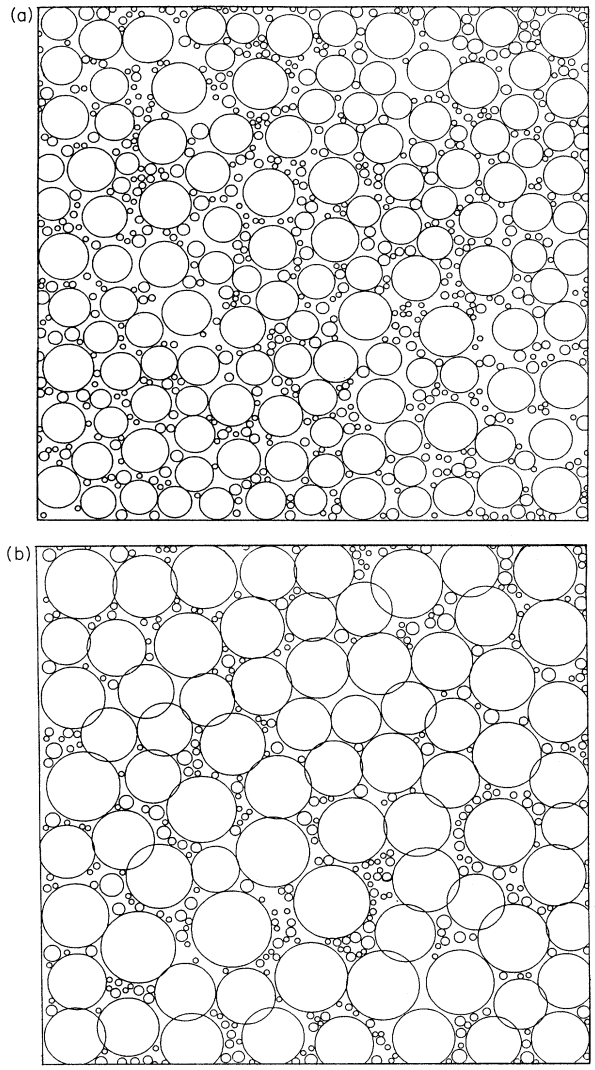

FIG. 2. The morphology generated by the D=3 ICM with $R_c/R_0=8$ and $L/R_0=200$. (a) $p<p_c$ and (b) $p=p_c$.

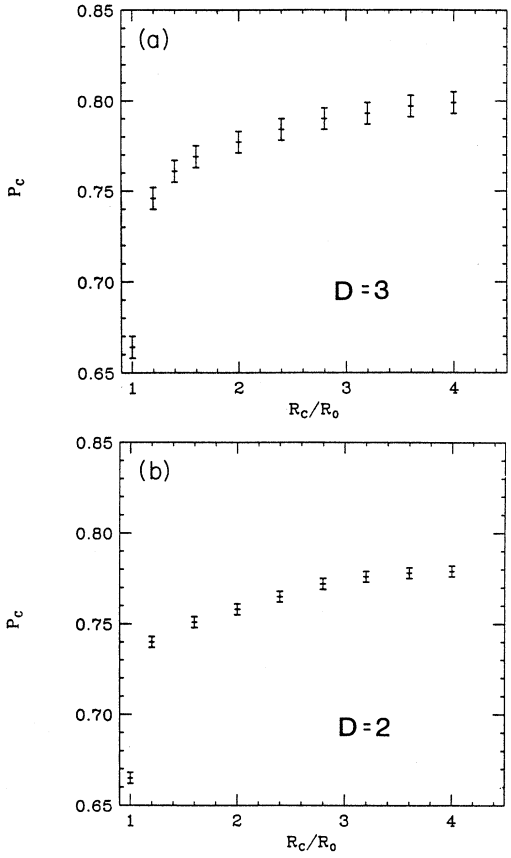

FIG. 3. p_c as a function of R_c/R_0 in the ICM. (a) D=3, $L/R_0=66$. Each point is an average over 100 configurations. (b) D=2, $L/R_0=100$. Each point is an average over 100 configurations.

so the large droplets play the dominant role. Given this, we can think of the final percolation path as evolving from a set of repelling disks (the large droplets) with packing fraction about 0.57 [as measured on configurations such as Fig. 2(a)]. If we now increase the radius of these random disks (at a rate proportional to their original radius—to model the cross section available to the ballistically depositing droplets), we naturally find a high p_c. If the original droplets lie on a triangular lattice $p_c=0.907$, while if the initial state is like random packing, we expect[16] $0.82<p_c<0.89$. The point is that starting from a distribution of repelling droplets always leads to high p_c, and given an initial droplet configuration such as Fig. 2(a), it is not surprising that the ICM model does, too.

It takes the FMM many iterations to settle into a self-similar evolution. Prior to this equilibration time, the droplets are not as strongly correlated. We would thus expect that small R_c/R_0 implies lower p_c. This expectation is supported by the data of Fig. 3, which shows results for p_c as a function of R_c/R_0 for D=3 and D=2.

Although the D=2 and D=3 cases of the FMM lead to a very different distributions of droplet sizes, in the ICM the final percolation coverage in D=2 and in D=3 are similar.

An important feature of the dependence of p_c on R_c/R_0, in both D=2 and D=3 (see Fig. 3) is that there is a first-order jump in p_c as $R_c/R_0\rightarrow 1$. At $R_c/R_0=1.0^-$, $p_c=0.676\pm0.003$ in both D=2 and D=3, while we find that $p_c(1.0^+)=0.745\pm0.005$ (D=3) and $p_c(1.0^+)=0.740\pm0.005$ (D=2). These nonanalytic changes in p_c at $R_c/R_0=1.0$ are physically reasonable, because, as soon as $R_c/R_0>1$, all the droplets that are being ballistically deposited onto the surface will coalesce with any pre-existing droplet with which they overlap, i.e., an infinite sequence of coalescence events occur in an infinite system. When $R_c/R_0=1.0^-$, however, no coalescence at all occurs.

Since there is a jump singularity in p_c at $R_c/R_0=1.0$, we must consider whether the universality class of the percolation geometry is altered for all $R_c/R_0>1$. We have tested the universality class of the percolation problem at p_c in the ICM, and find that, to within 15% in the critical exponents, the ICM percolation process appears to remain in the same universality class as the uncorrelated case.

We note that the elongated structures of Fig. 1 do not at first sight resemble the percolation structure of Fig. 2(b). The main reason for this is that sharp grooves occur at the intersection of the circles in Fig. 2(b), but do not occur in Fig. 1. In a real film these grooves would round out to a radius of curvature R_c, producing the elongated appearance so characteristic of these films. Unfortunately, we have found no efficient method for simulating this rounding process in random continua such as that shown in Fig. 2(b).

Finally, we note that because of the slight overlap of percolating caps (disks) in the $D=3$ ($D=2$) case, the ICM model does not quite conserve volume (area). We have calculated that this missed volume (area) changes the area coverage at percolation by at most 0.5%. This small error would be even less in a model in which sharp grooves were rounded out.

In summary, we have introduced a simple continuum model of film growth. Our model is an extension of one by Family and Meakin and includes a crossover from an early island stage to a later elongated structure stage. This model provides a natural explanation for the high p_c observed in many thin metal films grown on insulating substrates.

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[4]Our measured values of p_c are obtained from SEM photographs, which do not show the very small islands in the channels between elongated structures. Hence, our measured p_c is a lower bound.

[5]We also have studied films of Sn and Pb on room-temperature SiO_2 substrates and find that for Sn, $p_c=0.86\pm0.02$, and for Pb, $p_c=0.67\pm0.02$. Again, these are lower bounds.

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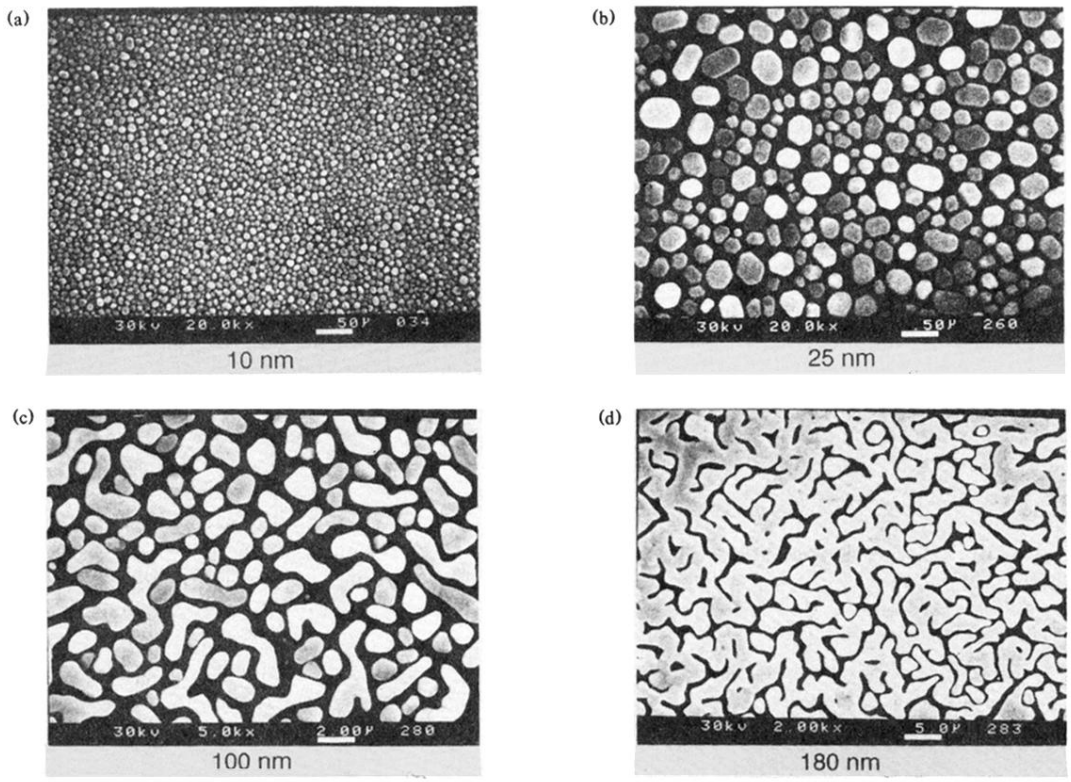

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