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Formation of nodular defects as revealed by simulation of a modified ballistic model of depositional growth

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Nodular defects appear frequently in deposited films and coatings, especially in those deposited under higher deposition rate and lower substrate temperature. In order to understand the mechanism and to predict the effects of process parameters, a modified two-dimensional ballistic model of deposition growth has been developed and programmed for computer simulation. In this model, both scattering of depositing particles and surface diffusion of deposited particles are allowed. Simulated experiments have been carried out with respect to the effects of deposition rate, surface diffusivity of deposited particles, degree of scattering of depositing particles and presence of substrate asperities. Morphological features of the nodular defects are reproduced by the simulation. The results show that higher deposition rate, lower surface diffusivity of deposit and higher degree of scattering of depositing particles favour formation of nodular defects. Asperities on substrate are found usually responsible for formation of nodular defects; however, under favourable conditions, nodular defects can form without presence of any substrate asperity.

1. Introduction

Physical vapour deposition (PVD), chemical vapour deposition (CVD) and electrochemical deposition cover most of the modern film and coating processes. A common feature of them is that they are all atomic deposition, in which atoms travel through a distance and stick to a substrate or previously stuck atoms. As a result, some common structural feature of the deposited coatings have been observed, e.g. columnar or conical structure, cauliflower surface [1–3] and appearance of nodular defects [4–7]. Fig. 1 shows an example of nodular defects. They grow from within the coatings, mostly rooted from the substrate, and finally appear on surface as large nodules. The boundaries between nodular defects and the coating matrix are very porous, even gapped in some cases. Control of such kind of defects is crucial for a high performance coating or film.

On atomic scale, various deposition processes under different process parameters differ in (1) the deposition rate, (2) the way the depositing atoms travel, (3) their kinetic energy, (4) the way they stick to previously deposited atoms, and (5) the surface diffusion rate of the deposited atoms. In the present work, a general model of atomic deposition growth has been developed to account for the varieties (1), (2) and (5), which we previously suggested to be dominant in formation of nodular defects [7]. Computer simulations of the model have been carried out to see their effects on morphology and density of the deposits, especially on formation of nodular defects.

2. The model and the computer simulation

2.1. The original ballistic model of deposition growth

First proposed in the 1960s [8], also called the random rain model, the ballistic model received more attention in the 1980s [9, 10] when computer simulation and visualization became easier to realize. The model is very simple: the depositing particles are released one at a time at the top of a lattice and fall straight down until they touch a deposited particle or else come to rest on the substrate at bottom. The particles are stuck and become part of the deposit on such occasions. The horizontal co-ordinate of each successive particle is chosen randomly with equal opportunity over the range of substrate. Once a particle has been deposited (stuck), it never moves again. This model matches the condition of high rate, low substrate temperature deposition under high vaccum; high vacuum in the chamber ensures a parallel ballistic trajectory of the depositing molecules; high deposition rate and low substrate temperature minimize the chance for surface molecules to move.

However, most deposition processes significantly differ from this model. First, instead of falling straight down, the depositing particles undergo considerable scattering on the way toward the substrate, as in the case of sputter deposition and evaporation deposition. Secondly, under normal deposition rate and substrate temperature, surface diffusion of the deposited particles does exist, which smooths the surface and

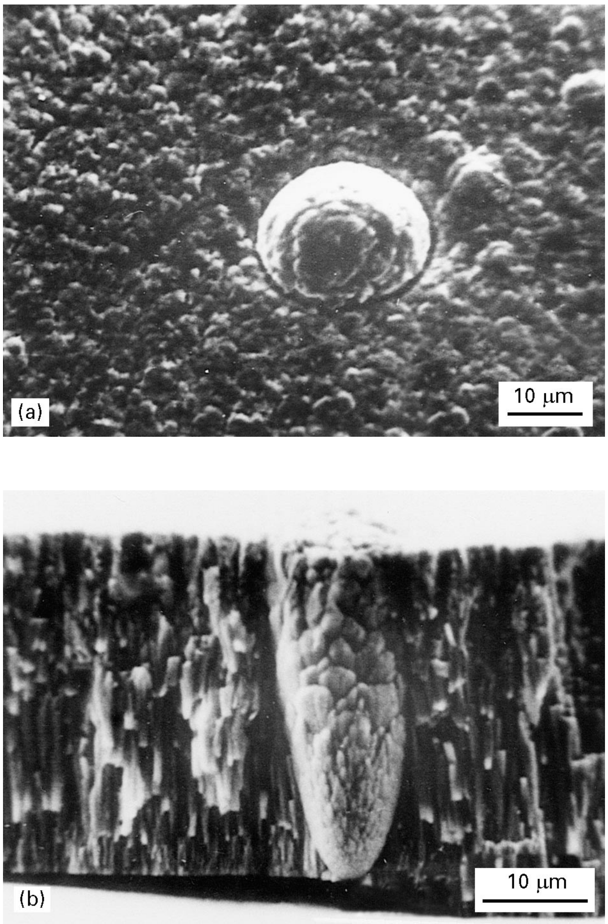

Figure 1 Nodular defect in a sputter deposited Co–Cr alloy coating (scanning electron microscopy). (a) Top view; (b) cross-sectional view.

increases the density. A modified ballistic model that allows scattering of depositing particles and surface diffusion of deposited particles, as described next, has been developed for a more realistic approach.

2.2. The modified ballistic model of deposition growth and the simulation

Scattering of the depositing particles is modelled as follows. On each step in falling towards the substrate, the depositing particle is given an opportunity to move left or right each at a probability of $P/2$, with the probability left for downwards movement to be $(1 - P)$. The particle keeps moving this way until it hits the deposited cluster or the substrate and then becomes part of the deposit. The probability P serves as a measure of the degree of scattering of depositing particles.

Surface diffusion of the deposited particles is allowed as long as they are still on the surface, i.e. before they are covered by subsequently deposited particles. It is modelled as random walk of the particles along the surface.

The diffusion rate is measured by the number of random walk steps during deposition of one layer of particles, N_{dpl}. Assuming the time for deposition of one particle layer to be τ, and using the Einstein equation in two dimensions, the surface diffusion coefficient D_s can be given by

$$D_s = \frac{1}{4}\frac{N_{dpl}}{\tau} \quad (1)$$

(in a^2 per unit time), where a is the distance of each random jump, i.e. the size of the unit square of the lattice. If R is the deposition rate in terms of the number of particle layers deposited per unit time, it follows that

$$\tau = \frac{1}{R} \quad (2)$$

So we have

$$N_{dpl} = 4\frac{D_x}{R} \quad (3)$$

N_{dpl} is actually a measure of effective surface diffusivity of the deposited particles, as τ is actually the average life-time of a surface particle before it is buried by the subsequent layer of particles. A particle can move as a surface particle only during its life-time τ. Equation 3 shows that the effective surface diffusivity is decided by D_s/R ratio.

The parameters P and N_{dpl} are made adjustable in the simulation to account for a range of degree of particle scattering and D_s/R ratio.

One more modification has been made to the original ballistic model: only just-hit is considered as an occasion of deposition, while in the original ballistic model just-miss is considered so as well. This is closer to reality when the kinetic energy of depositing particles is considerably high, as in sputtering, ion plating and evaporation processes.

The lattice size chosen for simulated experiments of deposition was 240×260, with the range of deposit being 240 lattice sites wide. Periodic boundary conditions were imposed on the two sides of the lattice to mimic an infinitely wide range of deposit.

3. Results and discussion

3.1. Structure and density of the deposit

Fig. 2 shows the structures obtained by the simulated deposition under different degrees of particle scattering and surface diffusivity. It can be seen that scattering of particles makes the deposit structure ramified and porous, and surface diffusion of deposited particles densifies and smooths the surface of the deposit. Fig. 3 gives the measured relative density versus the effective surface diffusivity in terms of N_{dpl} for depositions under different degrees of particle scattering.

Scattering of the depositing particles leads to lateral growth, which shields the region underneath. This is the general reason for its causing porous structure, as we observed during the simulated deposition processes. In physical vapour deposition, lower working pressure leads to lower degree of particle scattering; higher substrate temperature leads to higher surface diffusivity, and on basis of this correlation, the above results are found to agree well with general experimental observation in PVD processes [1, 2]

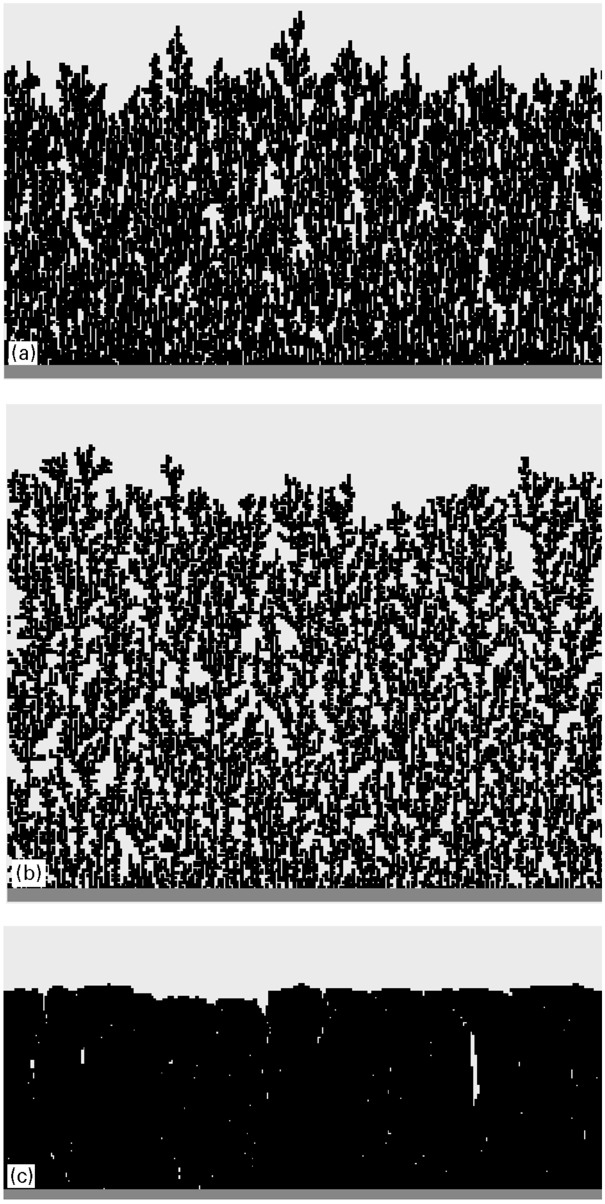

Figure 2 Structures of deposits generated by the simulated deposition under different conditions: (a) $P = 0.1$, $N_{dpl} = 0$; (b) $P = 0.4$, $N_{dpl} = 0$; (c) $P = 0.4$, $N_{dpl} = 960$. (P is scattering probability of depositing particles; N_{dpl} is number of surface diffusion steps per single layer deposition time, a measure of the effective surface diffusivity of deposited particles.)

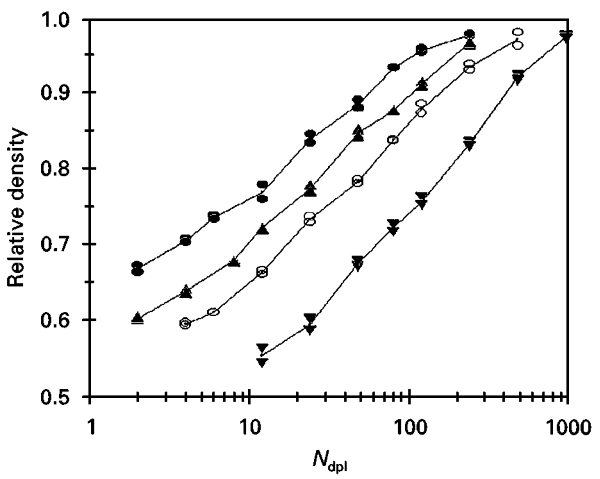

Figure 3 Measured relative deposit density versus effective surface diffusivity (N_{dpl}) for deposition under different level of scattering of depositing particles. (●) $P = 0.2$; (▲) $P = 0.3$; (○) $P = 0.4$; (▼) $P = 0.6$.

3.2. Formation of nodular defects

As it had been suggested that asperities on substrate are responsible for formation of nodular defects [5], simulations of deposition with presence of substrate asperities were carried out. Fig. 4a,b show that the inverted cone-shaped nodular defect does form as a result of the presence of an asperity on substrate, and that a higher degree of scattering of depositing particles results in larger cone-angle and hence larger nodules. Fig. 4c shows further that when the degree of scattering is lowered to a certain level the nodule may not form at all, even with the presence of substrate asperity. Surface diffusion of deposited particles tends to diminish the nodular defects, as can be seen by comparing Fig. 4a and e. Fig. 4d shows that at lower effective surface diffusivity, nodular defects can form without presence of any asperity on substrate. When the diffusivity is even lower, as in the case of Fig. 4f, nodular defects grow everywhere, resulting in porous deposits consisting of the closely neighboured nodular defects. On such deposits, we actually cannot see any of the normally referred distinguishable nodular defects.

The cone-angle of the nodular defects formed were measured and plotted against the scattering probability P, as given in Fig. 5. The data are found to be widely scattered, resembling the real behaviour in deposited coatings.

The results agree well with our previous experimental observations [7]. On the basis of the observations, we suggested that inverted cone-shaped nodular defects enlarge linearly with thickening of deposit during deposition by a geometrical mechanism [7] which requires only that the depositing particles are scattered. The higher the degree of the scattering, the larger the cone-angle will be. It was further proposed that if the effective surface diffusivity is very low, small micro-protrusions formed by statistical clustering of deposited particles may grow into visible nodules, and asperities on the substrate will not be needed for formation of nodular defects. Indeed this possibility is now revealed by Fig. 4d.

4. Concluding remarks

A relaxed ballistic model of deposition growth, which adds scattering of depositing particles and surface diffusion of deposited particles to the original ballistic model, along with a modification on condition of deposition, has been developed and programmed for computer simulation in two dimensions. The surface diffusivity to deposition rate ratio (D_s/R) has been identified as a parameter determining the effective surface diffusivity of deposited particles. Results of the simulated depositions show that:

1. Scattering of depositing particles enhances formation of nodular defects. Higher degree of the scattering leads to larger size of nodular defects, lower density and more ramified structure of deposits.
2. Surface diffusion of deposited particles inhibits formation of nodular defects. Higher effective surface diffusivity (higher D_s/R) tends to eliminate nodular

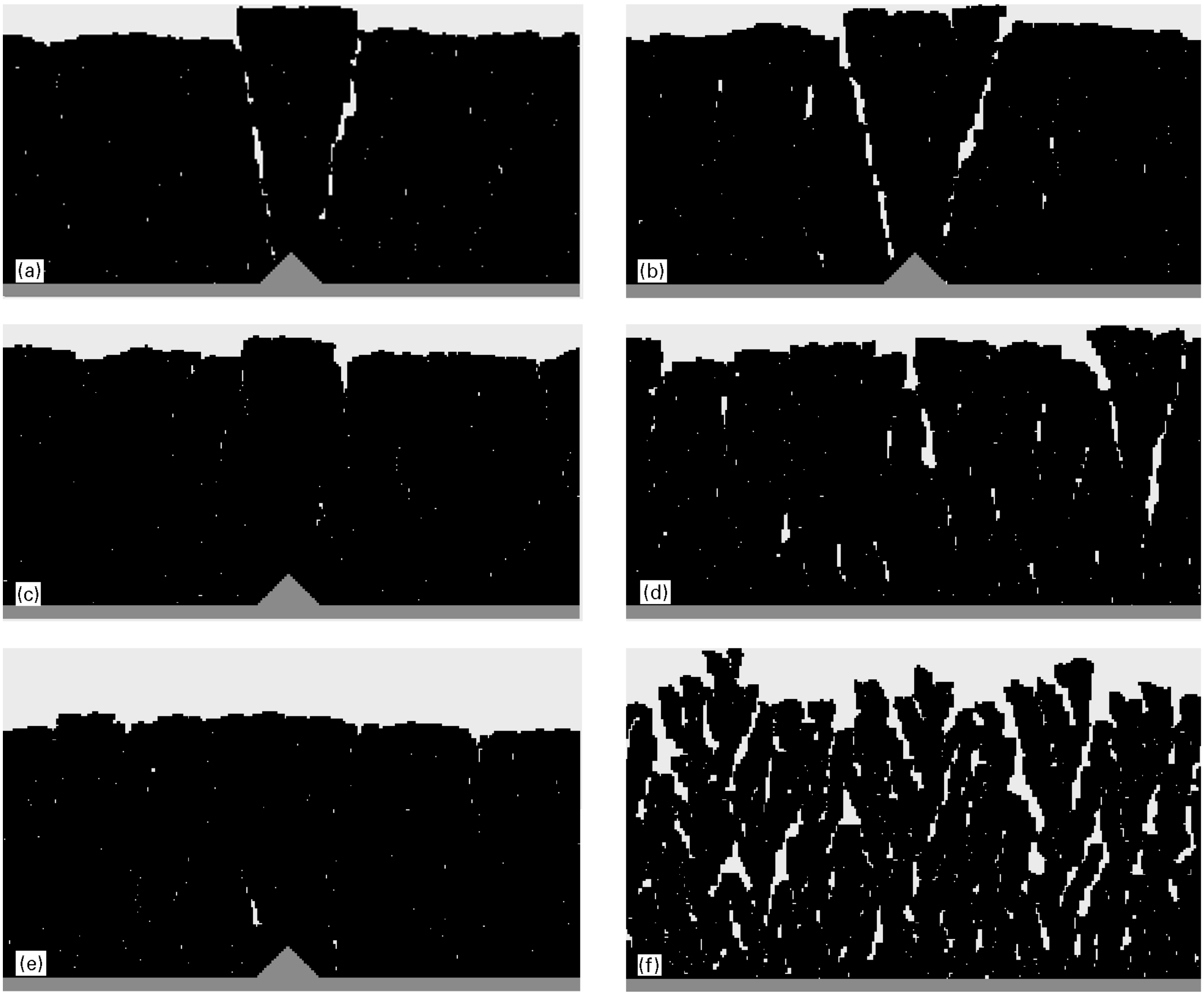

Figure 4 Structures of a group of deposits showing the behaviour of formation of nodular defects under different conditions of simulated deposition: (a) $P = 0.2$, $N_{dpl} = 960$, on asperity; (b) $P = 0.4$, $N_{dpl} = 960$, on asperity; (c) $P = 0.14$, $N_{dpl} = 960$, on asperity; (d) $P = 0.4$, $N_{dpl} = 480$; (e) $P = 0.2$, $N_{dpl} = 1200$, on asperity; (f) $P = 0.4$, $N_{dpl} = 120$. (P is scattering probability of depositing particles; N_{dpl} is number of surface diffusion steps per single layer deposition time, a measure of the effective surface diffusivity of deposited particles.)

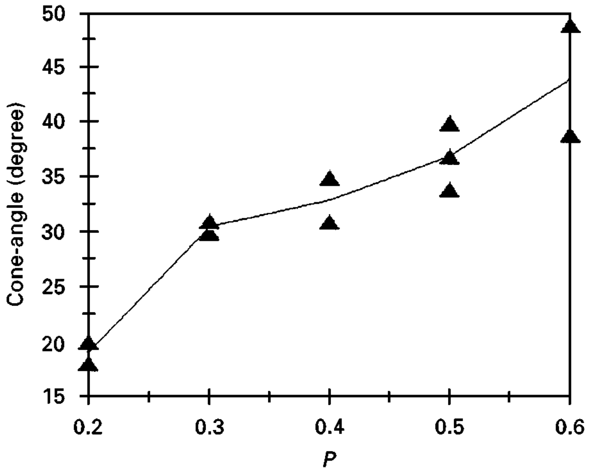

Figure 5 The cone-angle of nodular defects formed under different degrees of particle scattering as measured by the scattering probability, P ($N_{dpl} = 960$).

defects, and leads to higher density, smoother surface and less ramified structure of deposits.

3. When effective surface diffusivity is low enough, nodular defects can be formed without presence of any asperity on substrates.

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