Porosity control in zig-zag vapor-deposited films

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Abstract

Many of the physical, chemical and mechanical properties of vapor-deposited films are strong functions of the volume fraction and morphology of pores that are entrained during film growth. It has recently been shown that by growing films under low surface mobility conditions (at homologous growth temperatures \( T/T_m \) of 0.5 or less) and alternating the inclination of a substrate to the vapor plume, it is possible to grow columnar zig-zag structures. Films with such a microstructure are of significant interest for thermal protection applications because they reduce the through-thickness thermal conductivity and the in-plane elastic modulus. They therefore provide a means for increasing the coating’s thermal resistance while retaining its ability to accommodate thermal expansion mismatch with the underlying substrate during thermal cycling. A kinetic Monte Carlo (KMC) method has been utilized to simulate void evolution during physical vapor deposition of zig-zag microstructures and is used to explore methods for controlling pore morphology. The pore morphology of zig-zag coatings is found to depend strongly on the angular distribution of the incident flux. As the flux incidence angle changes from highly collimated to a cosine distribution, the coating changes from a uniform columnar to a hierarchical structure incorporating many length scales of porosity. The hierarchical nature of this structure is accentuated by increasing the substrate oscillation angle. A more narrowly distributed flux is found to result in denser films. Simulations have also revealed that the widely observed competitive growth phenomenon responsible for intercolumn porosity depends strongly on the incident flux distribution and is amplified by oblique deposition.

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1. Introduction

Vapor-deposited films grown at homologous temperatures \( T/T_m \) (where \( T_m \) is the absolute melting temperature) less than 0.5 without ion assistance often exhibit a columnar microstructure \([1,2]\). These films consist of relatively dense columns surrounded by wide pores that form the column boundaries. Smaller pores are often distributed within the columns. These pores form when low-energy incident vapor atoms (such as those created by thermal evaporation or by high-pressure sputtering) impinge on a substrate and self-assemble into small islands either immediately (Volmer–Weber growth \([3]\)) or after a couple of layers of planar growth (Stranski–Krastanov mode \([4]\)). Exceptions occur when the rate of growth is very low and/or the energy barrier for atom migration over terrace ledges is comparable to that for migration on the ledge surfaces themselves. Under these conditions, step flow growth (Frank–Van der Merwe mode \([5]\)) occurs \([6]\). For collimated, normal incidence fluxes, island coalescence can take place at the interfaces between adjacent growth features, resulting in polycrystalline films and little or no porosity. If, however, the flux has an oblique component, the islands can create flux-shadowed valleys between them. At low to moderate temperatures, this flux-depleted region cannot be compensated by surface diffusion to the valley bottom. This results in a structure consisting of rod-shaped columns with surfaces defined laterally by intercolumn pores. The process can be repeated at finer length scales within the column and additional fine-scale porosity then results. These pore structures are therefore a manifestation of flux shadowing by islands and kinetically inhibited surface diffusion to the shadowed region.

The pores found in these columnar structures affect the physical properties of coatings that contain them \([7]\). For example, porosity significantly reduces the electrical conductivity, thermal conductivity and elastic moduli of coatings \([7]\). For applications where this must be avoided,
high-temperature [2] or ion-assisted [7] deposition conditions are used to promote mass transport to flux-shadowed regions. However, for some applications such as thermal protection coatings [8,9], catalyst supports [10], solid oxide fuel cell anodes and cathodes [10] and some sensor concepts [10], the creation of a voided, columnar structure is highly desirable [10]. For each such application, the pore morphology has significant effects upon the coatings performance. As a result, there is a great interest in learning how to control the pore topology in a coating synthesized by vapor deposition.

Experiments and simulations have revealed that the use of an oblique flux enhances the pore volume fraction, but also results in growth columns that are inclined to the substrate normal [11]. This growth process is sometimes called glancing angle deposition (GLAD) [10,12–15]. These studies reveal that the growing film’s column directions can be manipulated during the growth process through various substrate motions combined with different flux incident angle distributions. For example, by alternating the substrate normal between two orientations or by manipulating the sample so that the normal prescribes a conical, zigzag or spiral path, a wide variety of pore topologies can be obtained [15]. Such manipulated thin film structures have been envisioned for thermal protection, optical sensors and circuits, low-k dielectrics, biomedical devices and specialized reactors [10].

Recently, efforts have been made to enhance the thermal resistance of thermal barrier coatings (TBCs) by creating zig-zag structures using a directed physical vapor deposition approach [8,16]. An example microstructure is shown in Fig. 1 [16]. It shows an yttria-stabilized zirconia coating grown using a directed vapor deposition process at a deposition temperature of 1050 °C ($T/T_m$=0.44 where $T_m$ is the absolute melting temperature taken as 2988 K for ZrO$_2$) [8]. In this approach, a nickel alumide-coated superalloy substrate was oscillated between stationary positions of ±$\theta$ (where $\theta$=45° was the angle between the substrate normal and the incident direction of the flux). Because of the oscillation, the usually straight void channels in the columnar structure now zig-zag through the film. The porosity was also hierarchical. The coating was made up of zig-zag growth columns several micrometers in width separated by intercolumnar pores. Within the growth columns themselves, a similar zig-zag pattern of intra-columnar porosity existed. It resulted in coatings with significantly reduced through-thickness thermal conductivity [2] while retaining the high in-plane compliance needed to accommodate thermal expansion mismatch strains between the oxide and metallic substrates to which it is applied. Both the thermal conductivity and elastic compliance are strongly dependent on the topology and volume fraction of the pores (see Ref. [16] for a detailed analysis).

![Diagram of a zigzag yttria-stabilized zirconia thermal barrier coating cross-section micrograph made with the substrate positioned alternatively at −45° and +45°. The substrate temperature was 0.44$T_m$, dwell time was 150 s. The flux had an incident angular distribution of $\cos^2\theta$. Note that there exist two types of pores: the primary pores separate the overall structure into columns, and secondary pores are embedded inside the columns. Both were sensitively influenced by the angle of inclination, the period of deposition at each angle and the temperature at which the coating was applied.]

The pore topology in a vapor-deposited coating results from a complex interplay between the angular incidence distribution of the flux, the inclination history of the substrate to this flux, the atomic-scale energy barriers, the substrates surface roughness and the temperature which controls atomic migration on the surface. The many different types of vapor deposition processes each enable different combinations of these process parameters to be accessed. It is not clear what the preferred process would be for achieving a goal state pore topology. Numerous modeling approaches based upon molecular dynamics, kinetic Monte Carlo or its derivatives such as the GROWFILMS Simulator [12] could in principle be used to investigate this and the underlying controlling phenomena. Here, a kinetic Monte Carlo (KMC) method [17–19] is used to simulate the growth of coating under conditions where porosity is entrained. We selected such a method since we believe the mobility energetics of individual atoms on the growth surface is important to capture during the simulation of a problem of sufficient size that key pore morphology features are resolved. The independent roles of the angular distribution of the flux, inclination of the substrate and the homologous temperature at which deposition occurs are all then explored. The results provide an atomistic perspective of the factors that can be manipulated to produce tailored zig-zag pore topologies for a variety of applications.
2. Methodology

The kinetic Monte Carlo (KMC) simulation method has been widely used to analyze vapor deposition processes [17–19]. It has been particularly useful for investigating the relationship between the microstructure of a thin film and coating process parameters such as substrate homologous temperature, deposition rate and substrate geometry [18]. The basic underlying principle of the KMC method is that the likelihood of an atom jumping from one lattice site to another depends upon the local atomic configuration of that atom before, during and after the jump. In a KMC scheme, a characteristic activation energy for an atom’s jump transition path and a jump attempt frequency are identified and precalculated [18]. In KMC analyses of film growth, the simulation first deduces the set of jump probabilities for every allowed jump path using precalculated activation energies and then executes jumps according to their relative probabilities. After a jump is executed, time is advanced by a computational time step determined by the residence time of the system, i.e., the reciprocal of the sum of the jump rates for all the allowed jump paths of the system. This process is then repeated until the time between atom arrivals is exhausted. A new atom is added and the algorithm iterated. Atomic assembly of a film then proceeds by identifying all the available thermally activated atomic jump paths, determining their activation energy barriers and implementing a probabilistic scheme for their execution while simultaneously adding atoms to the system at a rate determined by that of deposition.

The vast number of jump paths available on a three-dimensional growth surface has made three-dimensional Monte Carlo problems involving diffusion intractably slow for the number of atoms needed to resolve the morphology of porosity in a vapor-deposited coating. Here, a two-dimensional (2D) KMC algorithm, with activation energies calculated for nickel, was used for the simulation. It enables an identification of fundamental mechanisms and an evaluation of trends as process conditions change. Details of the algorithm used here can be found in a prior publication [18]. Briefly, the simulation proceeds as follows. A 2D substrate consisting of 800 close-packed nickel atoms in width was set up with a periodic boundary condition applied in the lateral direction. Incident “atoms” were then added to this surface one at a time. The incidence angle for each arriving atom was determined from a probability distribution. Atoms were ballistically transported to the substrate. The elapsed time between the introduction of atoms above the substrate determined the rate of deposition. Upon arriving at the substrate of the film surface, the adatom was initially relaxed to the nearest cradle site with at least two nearest neighboring atoms. The incorporated atom together with all the other previously deposited atoms with available jump paths were then allowed to thermally diffuse (hop) at a rate set by the substrate temperature using the methodology described above. The two-dimensional kinetic Monte Carlo model of thermally activated diffusion considered a total of 14 jump paths and included hopping from a cradle site (with two nearest neighbors) to an adjacent cradle site with an identical number of neighbors (a 2-2 jump), jumping from/towards a step edge (3-2 and 2-3 jumps) and the jumping over a terrace edge (the Erlich–Schowbel jump path). Ref. [18] shows each of these jump paths and their activation barriers for a 2D model of nickel.

The diffusion process was modeled by identifying the binding coordination for each atom that had an available jump and then identifying the type and activation barrier for the jump. The jump probability for the \( j \)th jumping atom was \( P_j \) then deduced assuming Boltzmann statistics:

\[
P_j = v_o e^{-E_j/kT}
\]

where \( v_o \) is the effective vibration frequency (taken to be \( 5 \times 10^{12}/s \)), \( E_j \) is the activation barrier for the \( j \)th type jump, \( k \) is Boltzmann’s constant and \( T \) is the absolute temperature. The jump probability has units of inverse time. Its reciprocal is the residence time of the jumping atom in its pre-jump configuration. Since the jump probabilities for all available jumps are independent, the sum of the probabilities for all the atoms that could jump is the probability that an atom in the system will jump in unit time, and the residence time of the system before jumping is therefore its reciprocal. We randomly chose a jump from all the possible jumps weighted by their relative probability of occurrence, we computed the new atom configuration and then advanced the rate by the reciprocal of the probability of the jump. These jumps were allowed to continue until a new atom arrived whereupon the jump path loop above was reinitialized and repeated. In this way, we were able to link the deposition rate and substrate temperature to the atomic configuration for any prescribed incidence flux angular distribution.

Using the above simulation approach, nickel layers were deposited onto nickel substrates using a range of process conditions. Approximately 500,000 nickel atoms were used for the simulations. To create zigzag morphologies, the substrate was tilted between two fixed positions for a given dwell time. The tilt angle was varied from 35° to 55°. The dwell time was altered from 2 to 200 deposited monolayers per dwell interval. Three distributions were investigated; a unidirectional (collimated) flux, a cosine flux and a \( \cos\theta \) flux angular distribution with \( \eta=3 \), 10 and 20. The various incident angle distributions are shown in Fig. 2. The deposition rate was a constant for all the simulations and corresponded to a fully dense coating growth speed of 50 nm/s. Unless otherwise specified, the homologous substrate temperature \( (T/T_m) \) was fixed at 0.2. To characterize the coatings final porosity, the relative density (packing density) has been calculated as the fraction of atoms occupying lattice sites in the deposit region. The top 200 layers were
excluded from this calculation to avoid surface roughness contributions. To improve statistics, each packing density data point represents an average of 10 simulations begun with different random number seeds.

3. Results and discussion

3.1. Zig-zag growth

Fig. 3 shows four zigzag configurations simulated by inclining the substrate intermittently under a normal flux. The oscillating amplitude $\phi$ was $\pm 45^\circ$. The incident atoms were collimated as represented by the vertical line at $0^\circ$ in Fig. 2. At each stationary position, deposition was conducted for a finite number of monolayers (or dwell time). This dwell time decreased from Fig. 3a–d. Configurations with the longer dwell times (Fig. 3a and b), resemble Fig. 1 only in that a zig-zag structure is present. However, no primary intercolumnar pore structure (indicative of growth competition between neighboring columns) is evident for this collimated incident flux. Most pores were short and elongated along the incident flux direction, but some extend almost the full length of the coating. They correspond to the secondary pores seen in Fig. 1. The hierarchical structure consisting of fine-scale columns bundled into clearly separated primary columns as seen in Fig. 1 does not occur. This type of growth is often called noncompetitive (vs. competitive growth leading to columnar cone-shaped structures) [20,21]. Decreasing the dwell time resulted in a gradual disappearance of the zig-zag structure. Instead, it was replaced by fairly straight small columns whose width varied along the length at a frequency corresponding to that of oscillation. The amplitude of the width variations also decreased with oscillation frequency (Fig. 3d).

Fig. 4 shows four configurations created using the same conditions as in Fig. 3 except that a cosine incident flux angular distribution (the broadest one in Fig. 2) was used. A totally different structural appearance can be seen in each of the four configurations. In Fig. 4a, the general zig-zag feature can still be readily identified, but a hierarchical columnar structure has now emerged. Fine columns bounded by fine pores are seen to exist with larger (primary) columns separated by primary pores. The film grew in a highly competitive mode. The circled region in Fig. 4a show an example of a growth column that became flux starved as adjacent columns outgrew it. The features seen in Fig. 4a are in good agreement with experimental observations [8,21] seen in Fig. 1. In Fig. 4b, although the hierarchical form remains, the zig-zag feature is largely suppressed. Within each primary column, the finer level columnar structure still evolved in a zig-zag format. When the stationary dwell time was decreased (Fig. 4c and d), both the zig-zag feature and the primary voids gradually disappeared and the general features of a columnar structure took over. A large domed top can be found in both Fig. 4c and d. This is a manifestation of competitive growth in a low surface mobility growth environment. The change of the incident flux angular distribution brought about a considerable structural change and consequently would change properties such as the through-thickness thermal conductivity that are dependent upon this structure.

To further explore the effect of the incident flux distribution upon pore morphology, the flux distribution was systematically varied, keeping the dwell time fixed. Representative configurations are shown in Fig. 5 corresponding to $\cos(\theta)$, $\cos^3(\theta)$, $\cos^{10}(\theta)$ and $\cos^{20}(\theta)$ distributions shown in Fig. 2. Several trends are evident. The hierarchical pore structure seen with a cosine distribution steadily becomes homogenized in going from Fig. 5a to d, i.e., as the flux distribution becomes narrower. The tendency is maximized when the incidence is unidirectional as seen in Fig. 3a. In other words, as more of the flux begins to become parallel to the surface normal, the growth becomes increasingly noncompetitive. This process can be further manipulated by varying the substrate inclination. Fig. 6 shows configurations generated with $\phi$ increasing from $\pm 45^\circ$ to $\pm 60^\circ$ while keeping the other process parameters the same as in Fig. 5a. The increased oscillation amplitude leads to well separated hierarchical columnar structures for all four flux distributions. The two relatively homogeneous structures under smaller zig-zag oscillation amplitude growth now open up considerably (Fig. 6c and d). The most uniformly separated structure is seen in Fig. 6c, which is a result of using an intermediate flux distribution of $\cos^{10}(\theta)$ along with the larger oscillation amplitude. The results also indicate that the tangent rate is
followed when \( n=20 \) or higher, but as \( n \) is decreased, the rule becomes less well obeyed (Figs. 3–5). The interplay of flux distribution and oblique deposition angle together determine if a well-separated hierarchical columnar structure emerges.

Examination of the results above also indicate significant changes in coating density. Fig. 7 shows the effect of the dwell time on film density for various angular flux distributions. The relative density at first decreases with the dwell time for all three distributions but then becomes independent of dwell time in the long dwell time limit. Figs. 3 and 4 indicate that the higher oscillation frequencies lead to a higher relative density. It can also be seen that the decrease is larger for the more narrowly distributed fluxes. For a fixed dwell time, the relative density increased with collimation of the flux.
Fig. 8 plots the effect of dwell time on relative density as the maximum oscillation angle is varied. Inclining the substrate promotes shadowing, and so the coatings relative density decreases as the inclination angle is increased. It can also be seen that adjusting the dwell interval and inclination angle (between 0° and 55°) enables the coating’s relative density to be manipulated between 0.79 and 0.65 for $T/T_m=0.22$.

Fig. 9 shows the effect of flux angular distribution on packing density for different deposition temperatures. It shows that the coating becomes denser as the flux distribution is narrowed (collimated) and that a modest increase of substrate temperature from $T/T_m=0.2$ to 0.26 can reduce the trapping of pores across the entire range of flux angular distributions.

In this model material and deposition system, the morphology we have been able to show and the volume fraction of porosity can be sensitively controlled by modifying the incidence flux angular distribution by changing the substrate temperature/deposition rate and by adjusting the angle/dwell time for substrate tilting. We note that the relatively small length scale of the modelled system does not incorporate long length scale features, and the sensitivity to the process variables in the modelled system may therefore be greater than a real material system that contains a pore hierarchy. The results
The above phenomena are most germane for the finest length-scale pores in such structures. It should also be pointed out that the model does not address phenomena associated with energetic deposition where processes other than thermally activated diffusion can provide mechanisms for atom movement. In processes that utilize assisting ion fluxes or where the atoms are created by sputtering at low pressures, the high kinetic energy of the arriving atoms/assisting ions can lead to densification of films at much lower temperatures than is achievable with the thermalized flux analyzed here. An extensive atomistic analysis of these hyperthermal effects can be found in Refs. [22–25]. It is also worth noting that the simulations above apply only to cases where the flux is atomically dispersed. In many deposition processes, gas phase nucleation of small clusters can occur, and in such situations, a quite different mode of growth can occur.

### 3.2. Competitive vs. noncompetitive growth

Columnar structures, a result of competitive growth, are [26] a universal phenomena observed in vapor deposited coatings grown under low adatom mobility and low atom energy conditions. The results above indicate that these phenomena disappear when the flux becomes narrowly distributed. In Fig. 3 where a unidirectional (collimated) flux was used, many features of noncompetitiveness (i.e., a high fraction of growth columns that

Fig. 5. Effect of flux angular distribution on atom configuration using an intermittently oscillated substrate with \( \phi \) of \( \pm 45^\circ \). The power index \( n \) in the \( \cos^n \theta \) flux distribution was (a) 1, (b) 3, (c) 10 and (d) 20, respectively. The dwell time measured in monolayers per dwell interval was fixed at 200. The normalized substrate temperature was 0.2, the deposition rate=3 \( \mu m/min \) and the substrate had a width of 800 nickel atoms.
persist through the film thickness and a growth surface whose roughness does not change appreciatively with thickness) emerge for all configurations (Fig. 3a–d) even though the substrate was inclined intermittently to the flux. The number of fine film columns is fairly stable from the bottom to the top of each of the four films. There is no noticeable change in column width, and no domed features can be identified. This is not the case in Fig. 4a–d where a cosine flux distribution was used. The effect of just changing the flux incidence angle distribution (defined by $n$ in a $\cos^n\theta$ distributed flux) is most vividly shown in Fig. 5 where a cosine flux was used to grow the film shown in Fig. 5a and a collimated one was used in Fig. 5d. The most pronounced features of competitive growth quickly emerge as the flux distribution is allowed to broaden.

An even better way to show the difference between competitive growth and noncompetitive growth is to use simpler model setups to those investigated above by allowing no substrate motion during deposition, Fig. 10. The four commonly encountered columnar structures were generated by combinations of unidirectional and cosine flux with normal and oblique incidence conditions. In Fig. 10a where each atom’s incident direction is perpendicular to the substrate, the structure is rather dense and uniform with no coarse growth columns. The growth surface was flat and did not rapidly lose its flatness as growth progressed. Almost no clear dome-topped and/or coarse growth column

Fig. 6. Effect of flux angular distribution on atom configuration using an intermittently oscillated substrate with $\phi$ of $\pm 60^\circ$. The power index $n$ in the $\cos^n\theta$ flux distribution was (a) 1, (b) 3, (c) 10 and (d) 20, respectively. The dwell time measured in monolayers per dwell interval was fixed at 200. The normalized substrate temperature was 0.2, the deposition rate=3 nm/min and the substrate had a width of 800 nickel atoms.
structures can be identified. This is better delineated in Fig. 10b, where the same unidirectional flux is deposited at an oblique angle of 45° to the substrate. Coarse growth columns have now appeared. However, the columns are now clearly parallel to each other and persist from the bottom to the top of the coating and have an inclination that approximately satisfies the tangent rule [27]. The neighboring columns in this coating do not compete with each other for the flux.

When a broad cosine distribution was used, Fig. 10c and d, a smaller number of growth islands propagated upwards from the substrate, and only a few were able to survive. Those that did were then poised to dominate the growth field. In Fig. 10c, a close examination of the growth evolution shows that three to four columns survive to eventually form domed tops (each dome representing a single cluster propagating from the initial nucleation stage). In Fig. 10d, competition for flux is even more intense and related process occurring within the growth column. Interestingly, the pores do not obey the tangent rule. The pores become aligned at the flux orientation angle, not its tangent value, as the distribution broadens. We believe this arises because of flux filtering by both near and far removed growth features.

In sum, these four configurations suggest that a unidirectional incidence flux promotes a noncompetitive growth mode, whereas a broad distribution leads to competitive growth. Moreover, an oblique deposition reinforces these tendencies and acts to amplify the effect of the flux distribution.

The simulation of coating growth under various deposition setups have revealed two growth patterns, the widely observed competitive and the less commonly observed noncompetitive growth mode. The KMC simulations indicate that these two extremum modes of growth result in quite different morphologies. The simulations also reveal the roles of various process parameters in determining the eventual film morphology and point towards growth envi-
4. Conclusions

A kinetic Monte Carlo method has been used to simulate void evolution during physical vapor deposition. It has revealed that the orientation of voids in a columnar thin film structure can be readily manipulated by the process variables provided the adatoms have limited surface mobility. By inclining a substrate alternatively in between symmetric, oblique stationary positions, a zigzag columnar growth configuration has been shown to develop. The internal structure of such zigzag configurations strongly depends on the incident flux distribution. As the flux incidence angle distribution changes from unidirectional (collimated) to a broad cosine distribution, the growth

Fig. 10. Common configurations of physical vapor phase growth deposited with (a) stationary substrate under unidirectional flux, (b) stationary substrate under oblique unidirectional flux, (c) stationary substrate under cosine flux distribution and (d) stationary substrate under oblique cosine flux distribution. The normalized substrate temperature was 0.2, and the deposition rate was 3 μm/min. The substrate had a width of 800 nickel atoms.
morphology changes from a uniform columnar structure to a bundled hierarchical structure in which many scales of porosity are exhibited. The multiple-scale structure is reinforced by increasing the substrate oscillation angle. Collimating the flux helps to create denser films. The simulations have also revealed that the widely observed competitive mode of growth requires a broad incident flux distribution and is amplified by oblique deposition conditions.

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