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Morphological instabilities of thin films during thermal relaxation: A Monte Carlo study

X. Zhou, N. Olivi-Tran *, A. Gaudon, A. Dauger

SPCTS, UMR-CNRS 6638, ENSCI, 47 Avenue Albert Thomas, 87065 Limoges Cedex, France

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Abstract

We computed by a Monte Carlo method the thermal relaxation of a polycrystalline thin film deposited on a square lattice. The thin film was modelled by a two-dimensional array of elementary domains, which have each a given height and a given crystallographic orientation. During the Monte Carlo process, the height of each of these elementary domain is allowed to change as well as their crystallographic orientation. After equilibrium is reached at a given numerical temperature, all elementary domains have changed their orientation into the same one and small islands appear. This method is a numerical approach analogous to the solid on solid model, which includes the evolution of a thin film in the vertical direction as well as parallel to the substrate. Moreover, the effects of defects, if added to the substrate, on the thin film evolution, can be easily studied.

Keywords: Ceramics; Thin films; Sol–gel processes; Computer simulations

1. Introduction

In recent years, the formation of mesoscopic structures on crystal surfaces has become a subject of intense experimental and theoretical study. Generally, for non-periodically ordered nanostructures, the increasing specific area is favorable in order to enhance the physical properties (in optics, semiconducting, etc.) owing to the increased number of active sites [1].

We will study here the evolution of a thin film deposited on a substrate with or without periodical defects. Several methods (e.g. sol–gel processing [2]) allow one to obtain, after a first heat treatment (stage I), thin films of nanometric thickness, made of a large amount nanocrystals of random orientation. At this stage, the thin film thickness is much larger than the mean size of these nanocrystals. After a second heat treatment at higher temperature (stage II), thermal annealing induces grain growth. At this stage, the size of the crystals is of the order of the thickness of the thin film. Simultaneously, the film is submitted to fragmentation into more or less interconnected islands in order to reduce the total energy and hence to reach a more stable state [3].

The computation starts at stage II of the thermal relaxation of the experimental thin film, i.e. the mono-crystals composing the thin film have the thickness of the thin film. The aim of this model, derived from the solid on solid model (SOS model) is to analyze the influence of the defects of the substrate on the resulting islands after fragmentation of the thin film occurred.

In Section 2, we present the numerical procedure. And in Section 3, results are discussed. Finally, we conclude in Section 4.

2. Numerical procedure

We modelled a thin polycrystalline film deposited on a substrate with a regular distribution of defects. Each vertex of the substrate corresponds to an elementary quantity of matter (i.e. an elementary domain) of variable height h and crystallographic orientation c, in the thin film. Each of these elementary domains has a number of neighbours equal to 4. Our model represents a thin film of 1 nm thickness. Each domain contains approximatively 500–1000 atoms; the domains are 1 nm wide.

The mechanism of mass transport during thermal annealing is surface diffusion:

$$(J(s + \mathrm{d}s) - J(s))\,\mathrm{d}t = \partial z\,\partial s \tag{1}$$

where $J(s+\mathrm{d}s) - J(s)$ is the transported mass on a small part of the surface s at time t and ∂z is the height difference in thin

* Corresponding author. Tel.: +33 555 45 2247; fax: +33 555 79 0998.
E-mail address: n_olivi-tran@ensci.fr (N. Olivi-Tran).

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film thickness, ∂s being the surface difference coming from the mass transport [4]. Our Monte Carlo process computes this mass transport in a stochastic manner proportionally to the difference in height ∂z, which is related to the induced surface difference ∂s.

Therefore, we consider here two aspects, which contribute to the energy of our thin film consisting of crystal species: the grain boundary energy (which is here equivalent to the interfacial energy between two elementary domains of different crystallographic orientations) and the surface energy (corresponding here to the height of each elementary domain). For our system of N lattice domains, the energy of this system can be written as:

$$E = \frac{1}{2}B\sum_{i=1}^{N}\sum_{j=1}^{NN}(c_i - c_j) + \frac{1}{2}D\sum_{i=1}^{N}\sum_{j=1}^{NN}(h_i - h_j) \quad (2)$$

where the first term of right hand side of the equality corresponds to the total interfacial energy including grain boundary energy and the second term corresponds to the total surface energy (see Eq. (1)). NN is the nearest neighbours of a lattice domain (equal to 4). B scales the interfacial energy between two elementary domains, the numerical values of c range from the lowest interfacial energy with respect to the substrate, to the highest.

In our simulation, we took $B = k_B T \propto 10^{-20}$ J with $T = 1800$ K. Indeed, the crystallographic orientation c is proportional to the interfacial energy due to the mismatch of crystallographic orientation between two domains. $B(c_i - c_j)$ is proportional to the interfacial energy between two elementary domains, taking into account the interplay with the substrate (the value of c with respect to the substrate for which the crystallographic orientation is constant) as well as the interplay between two elementary domains (the difference between two values of c). D scales the surface energy obtained for different heights of the elementary domains.

In our computations, we took $D = 10^{-11}$ J m^{-1} in order that $k_B T$ is of the order of $D(h_i - h_j)$ when $(h_i - h_j) = 10^{-9}$ m. $h_i - h_j$ represents the height difference between two elementary domains, hence $D(h_i - h_j)$ is the surface energy associated to the difference in height between two nearest neighbours domains. Typically $h_i - h_j$ is less than 6 nm.

For Monte Carlo simulations of single phase films, only one type of event, namely lattice domain reorientation, was considered [5]. In our model, the height of each elementary domain is also submitted to changes like in the SOS model. But, unlike traditional SOS models, a species at domain i may change its orientation with respect of its nearest neighbour.

In our model, each domain owns two states (c, h). Here, c represents the domain orientation with $c = 1$–4. By this way, only $c = 1$ crystallographic orientation will be favorable energetically, assuming that this orientation is that of the substrate and the lowest one. h has its value enclosed between 1 and 10 nm, assuming that physically, no elementary domain will have a height larger than 10 nm.

To simulate the islanding of our thin film, prior to simulation, all elementary domains were assumed to have a height of 1 nm and a random (enclosed randomly between 1 and 4) crystallographic orientation. After such initialization, the Monte Carlo algorithm works according to the classical Metropolis scheme [6]. A lattice domain is chosen at random for two independent events (crystallographic reorientation and height exchange occurring). The probability for each event is given by P in which $\Delta E = E_1 - E_2$ where E_1 and E_2 are energies given by Eq. (2), of the present configuration and the configuration which the system may reach, respectively.

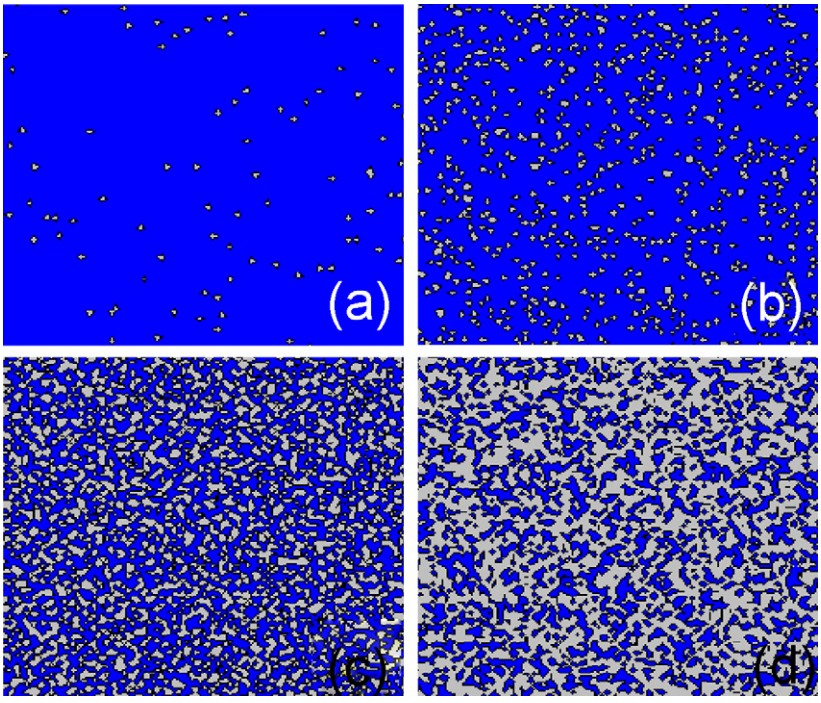

Fig. 1. Representation of the thin film evolution for $k_B T \propto 10^{-20}$ J and for four different Monte Carlo steps: (a) $t = 10^2$ MCS, (b) $t = 10^3$ MCS, (c) $t = 10^4$ MCS and (d) $t = 10^6$ MCS.

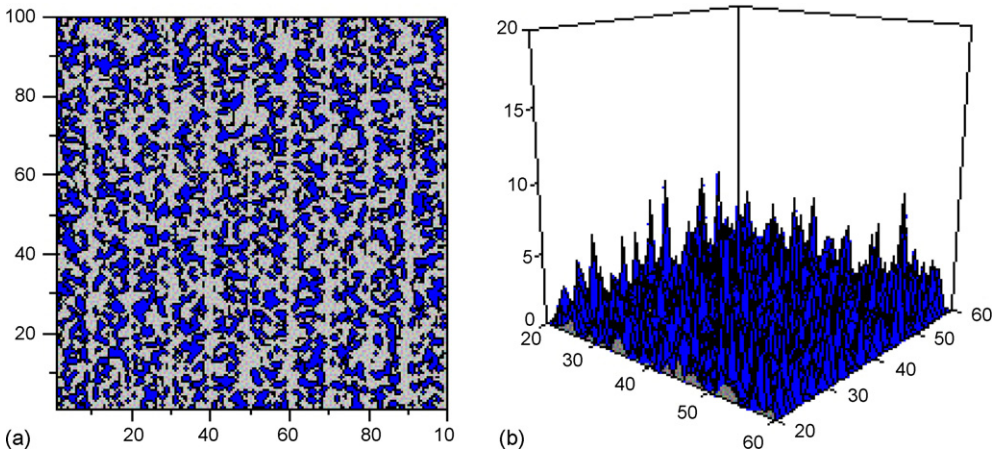

Fig. 2. Representation of the thin film for $k_B T \propto 10^{-20}$ J and for $t = 10^6$ MCS. (a) Top view and (b) perspective view.

Note that, as height exchange and crystallographic reorientation are two independent events, it may occur that a domain changes its height but not its orientation and inversely. Moreover, we used a Monte Carlo technique to study the statistical sampling of the thin film geometry, due to its surface topology.

The values of B and D are constants, only the absolute temperature T may change.

3. Results and discussion

We computed all the results presented in the following figures at a temperature $T = 1800$ K. We averaged the data over 10 different runs of our simulations. Fig. 1 shows the evolution of a thin film with no defects (top view) for four Monte Carlo times: the substrate is in dark grey while the substrate is in clear grey. Fig. 1a corresponds to $t = 10^2$ MCS (Monte Carlo steps): there are a few holes in the thin film. Fig. 1b–d shows the progressive uncovering of the substrate. For the final time $t = 10^6$ MCS (Fig. 1d) islands more or less connected appear and the substrate is partially uncovered.

Fig. 2a shows an example of thin film with stripes of defects, after 10^5 MCS. The defects are domains which are inactive, i.e. which do not change in height nor in crystallographic orientation. Fig. 2b is the same thin film in perspective view. Here again we see the partial uncovering of the substrate and the small islands, which are more or less connected.

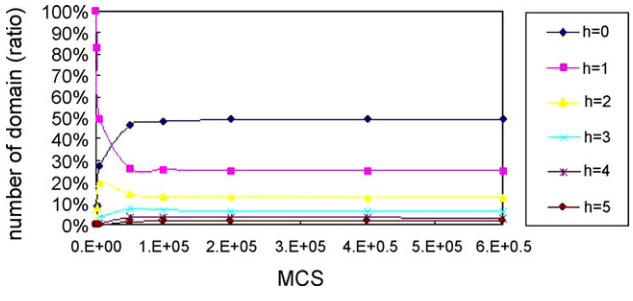

Fig. 3. Number of domains for heights $h = 1$, 2, 3, 4, and 5 nm as a function of time expressed in Monte Carlo steps for a substrate with no defects.

A quantitative description is necessary in order to study the process of thin films islanding. One of the principal characteristics of the islands is the distribution of the heights of the domains. Fig. 3 shows this distribution for numerical thin films deposited on a substrate without defects. We see that, at the beginning of thermal annealing, the number of domains with height equal to one decreases while the number of domains with height equal to two increases very rapidly. After this first stage, the uncovering of the substrate continues and 47% of the substrate is uncovered after 5×10^4 MCS. The distribution of the heights of the domains reaches a dynamical equilibrium after 2×10^5 MCS.

Fig. 4 shows the evolution of the uncovering ratio of the thin film. Three curves are plotted here: uncovering ratio for a substrate without defects, with stripes of defects every 20 domains and with stripes of defects every 10 domains. The uncovering ratio reaches a stationary value after 2×10^5 MCS. This value is about 50% for a substrate without defects, 52% with defects spaced of 10 domains and 55% with defects spaced of 10 domains. Knowing that the presence of defects induces to an initial uncovering ratio of 5% (for stripes of defects spaced of 20 domains) and 10% (for stripes of defects spaced of 10 domains), the uncovering ratio related to the growth of islands is then 50%, 49.5% and 50% for substrates with no defects, defects spaced of 20 domains and defects spaced of 10 domains, respectively.

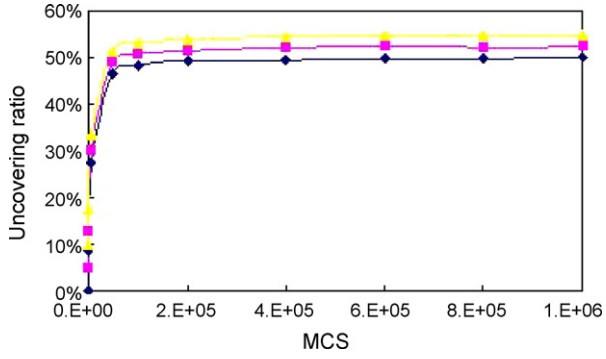

Fig. 4. Uncovering ratio of the thin film for a substrate without defects (triangles), with defects spaced of 20 domains (squares) and with defects spaced of 10 domains (diamonds) as function of time in MCS.

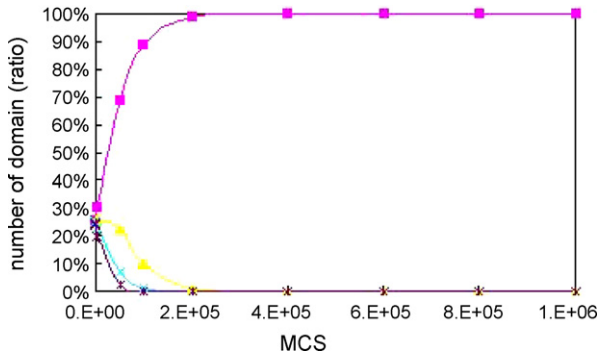

Fig. 5. Evolution of the number of domains with crystallographic orientation $c = 1$ (squares), $c = 2$ (triangles), $c = 3$ (stars) and $c = 4$ (crosses) as a function of time in MCS.

Fig. 5 shows the evolution of the number of domains with crystallographic orientations equal to 1, 2, 3 and 4, respectively, as a function of time expressed in MCS. This curves show clearly that the number of domains with orientation equal to 1 increases to the detriment of the number of domains with higher value of the crystallographic orientations (i.e. 2, 3 and 4). After $t = 2 \times 10^5$ MCS all domains have an orientation corresponding to the lowest interfacial energy: the thin film is composed of epitaxial islands on the substrate.

4. Conclusion

In this work, the thermal annealing of a polycrystalline thin film deposited on a monocrystalline substrate was studied. We used a model similar to the solid on solid model but the crystallographic reorientation of the thin film has been added in our model. The results of simulations show that the islanding phenomenon is associated to a strong morphological instability of the initial thin film. Moreover, the presence of periodical defects on the substrate limits the randomness of the distribution of the resulting islands just by a confinement effect.

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