Crystallization processes in bicomponent thin film depositions: Towards a realistic kinetic Monte Carlo simulation

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ABSTRACT

The kinetic Monte Carlo (KMC) method is a powerful and simple tool to simulate the growth of thin films by deposition. However, one of its major drawbacks is the artificial order induced by the use of regular lattices. An algorithm that mimics the crystallization processes in bi-component thin film depositions via a novel KMC approach is presented in this work. This new algorithm, named GEM-CA (Geometrical Energy Modification-Crystallization Algorithm), modifies the hopping energy barrier depending on the geometrical configuration of the atoms surrounding one particular position.

The novel approach allows obtaining amorphous, crystalline and mixed structures (i.e. nanocomposites), depending solely on the synthesis parameters. In addition, we have developed a method for the analysis of deposited structures based on their degree of order. The influence of different deposition parameters such as temperature or composition is discussed in detail. GEM-CA reproduces experimentally observed trends of bi-component film deposition.

1. Introduction

The properties of most common substrates can be modified by coating deposition. In particular, thin film technology is commonly used to improve some of the optical, chemical, mechanical, tribological and other properties of some substrates for specific applications [1]. Coating technology involves several different techniques, such as physical vapour deposition (PVD), chemical vapour deposition (CVD), thermal reduction, electrochemical methods, etc. [1]. Among them, PVD, which consist on the atom evaporation from a source and its deposition on the substrate surface, is widely used.

Nowadays, experimental results are interpreted in many cases with the help of computer simulations. In fact, simulation techniques are becoming standard tools to investigate and advance the understanding of the synthesis process and the properties of materials. They are versatile and relatively cheap in comparison to the laboratory techniques; in addition, they provide information that is not accessible through direct experimentation, and allow studying the individual effect of synthesis parameters interconnected in real processes. There is a large variety of simulation methods for coating deposition, ranging from very accurate models, derived from quantum-mechanical calculations, to reactor-scale simulations [2]. In general, the former methods can reach very high levels of detail and complexity, at the expenses of reducing the time and space scales of the analysis, and vice-versa [2].

Among the different possibilities, the kinetic Monte Carlo (KMC) method has been widely used to study PVD, as it represents a balance between modest computational time (compared to quantum-mechanical calculations) and good description of the system. KMC divides PVD into two subsequent processes: i) atom deposition over the substrate, and ii) diffusion of atoms. In some cases, re-evaporation of atoms from the surface is also considered [3]. The deposition is normally simulated as a ballistic process, which can be approached with different degrees of detail, including the possibility of having a rotary system [4], the impact energy of ions and the angle of bombardment [5]. Diffusion is simulated by a model in which atoms make short jumps over a regular lattice (hopping model). Atoms on the surface jump from one site to another, by overcoming a certain energy barrier. There are several approaches found in the literature to calculate such barriers (see e.g. refs. [6–8]). A convenient choice is obtaining the values of these barriers from molecular dynamics, and simulating the growth with KMC [9,10]. The lattice geometry (cubic [7] or hexagonal [4]) and dimensions [5] (bi-dimensional or tri-dimensional) vary depending on the problem under study.

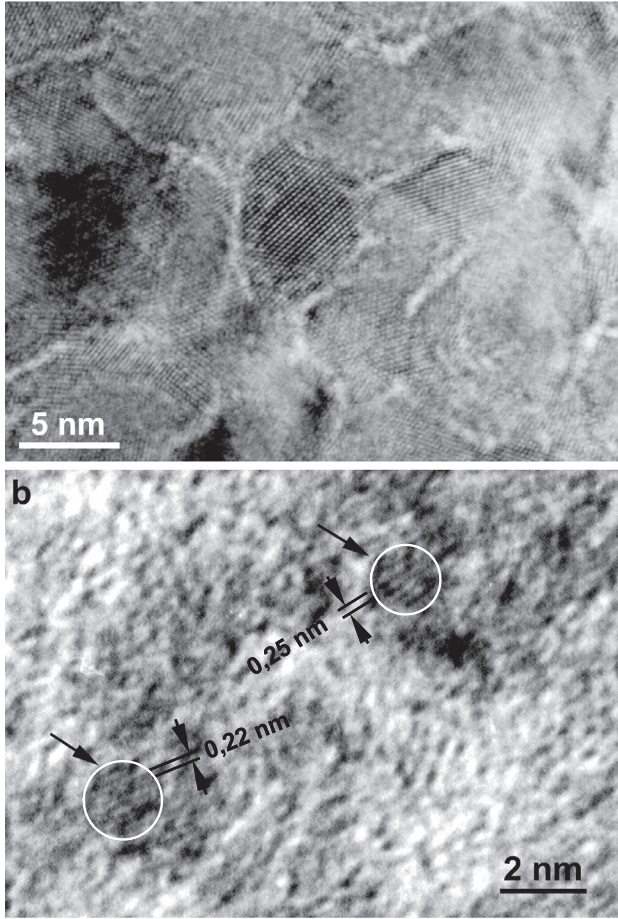Besides the obvious advantages of KMC (simplicity, flexibility and

Fig. 1. High-resolution transmission electron images of thin films composed by Ti and C. a) Polycrystalline TiC. b) Nanocomposite formed by small TiC grains surrounded by an a-C matrix [11].

wide scales of time and length reachable), the main problem it faces for simulating PVD is the use of a regular lattice with fixed positions. That lattice imposes an artificial degree of order over atoms deposited on the surface, finally resulting in an ordered system (monocrystal), while different types of structures (e.g. amorphous, polycrystal, etc.) are observed in real processes. For instance, Fig. 1 shows high-resolution transmission electron microscopy of a polycrystalline TiC (Fig. 1a) and a nanocomposite formed by TiC nanoparticles embedded in an a-C matrix (Fig. 1b) prepared by co-sputtering [11]. It is not possible to obtain these structures by conventional KMC since ordered and disordered structures are indistinguishable with the classical KMC approach.

Some attempts to overcome this difficulty have been already made by some authors. For instance, Wang and Levine [12] introduced artificial grain boundaries on the system, and Bruschi [13] and Ono [14] divided the surface into misoriented cells. However, in these cases, the polycrystal nature is introduced in the simulation instead of being a result of it, which biases the obtained results.

The aim of the present work is to provide a new KMC simulation algorithm that allows obtaining structures similar to those observed in Fig. 1, i.e. to study the formation and growth of polycrystals or nanocomposites, as well as the influence of several parameters in these processes. For this purpose, a novel crystallization algorithm that modifies the energy-hopping barrier depending on spatial arrangements has been developed, the Geometrical Energy Modification-Crystallization Algorithm (hereafter referred as GEM-CA). The use of two different atoms during the deposition allows the introduction of occupational order and disorder, even in the presence of a regular substrate

lattice.

2. Description of the model

2.1. Background

The model presented here is based on the work of Helin et al. [8] and Tan et al. [15], being an extension of them. The coating growth is a process consisting of a random vertical ballistic deposition of atoms and subsequent diffusion on the surface. The atoms are deposited on a bi-dimensional square lattice (same number of sites in vertical and horizontal directions) with a compact hexagonal packaging, chosen due to its higher symmetry. The deposition process is characterized by the deposition rate (monolayers/s) and time (s); the percentage of surface coverage and the time between depositions of atoms are inferred from these values.

The diffusion is controlled by atoms hopping over the surface, using periodic boundary conditions. The time consumed by a diffusion process (t_{diff}) depends on its rate (ν_{diff}):

$$t_{diff} = \frac{1}{\nu_{diff}} \tag{1}$$

The diffusion rate is calculated by an Arrhenius-type expression:

$$\nu_{diff} = \frac{2kT}{h} \exp\left(-\frac{E_B}{kT}\right) \tag{2}$$

where k and h are the Boltzmann's and Planck's constants, respectively, T is the absolute temperature and E_B is the activation barrier. The latter term is composed of different contributions:

$$E_B = E_S + \beta E_L + (\Delta\alpha)E_D + \Delta E_N \tag{3}$$

where Δ is an operator which represents the difference between the final and initial states, E_S is the energy of interaction of the atoms with the substrate (in other words, an energy barrier always present in a diffusion event). E_D is the substrate defect energy, which has to be taken into account for atoms next to substrate defects, and α is the number of defects next to a given atom. These defects are often introduced in KMC, and serve as seeds for grain nucleation. The number of substrate defects on the surface is introduced as an input variable, and they are distributed randomly over the surface at the beginning of the calculations. E_L is the "ladder energy", an energy barrier that accounts for the presence of obstacles (atoms or defects) along the diffusion path (see Fig. 2a). β represents the number of these obstacles, with possible values 0, 1 or 2. E_N is the energy of the neighbour atoms, and it is calculated by a Morse potential, at the beginning and at the end of the diffusion event. According to [8,14], E_N is calculated considering Next Neighbours (NN) and Next Nearest Neighbours (NNN) atoms, allowing 18 neighbours per position (see Fig. 1b). For a site i on the lattice the expression is as follows:

$$E_N(i) = \sum_{j=1}^{NN, NNN} E_{ji}, \quad E_{ji} = V_0\left[\exp\left(-2a\frac{r_{ij}-r_0}{r_0}\right) - 2\exp\left(-a\frac{r_{ij}-r_0}{r_0}\right)\right] \tag{4}$$

where V_0 is the energy interaction between NN, a is a constant that controls the width of the curve, and r_0 and r_{ij} are the distance between NN and i and j atoms, respectively, expressed in atomic units. The values of E_S, E_B, E_L, V_0 and a have been taken from the work of Helin et al. [8] and Tan et al.[15], following the work of Voter [16]. They are summarized in Table 1 for completeness. Since only NN and NNN are checked, just three values of r_{ij} and E_{ij} are possible, as indicated in Fig. 2b. Therefore, Eq. (4) can be reduced to:

$$E_N = n_{NN}E_{NN} + n_{NNN1}E_{NNN1} + n_{NNN2}E_{NNN2} \tag{5}$$

where n_{NN}, n_{NNN1}, and n_{NNN2} are the number of NN, NNN1 and NNN2 occupied positions respectively (see Fig. 2b). Then, by substituting E_N