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Modeling and simulation of the deposition/relaxation processes of polycrystalline diatomic structures of metallic nitride films

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ABSTRACT

This work develops a model that mimics the growth of diatomic, polycrystalline thin films by artificially splitting the growth into deposition and relaxation processes including two stages: (1) a grain-based stochastic method (grains orientation randomly chosen) is considered and by means of the Kinetic Monte Carlo method employing a non-standard version, known as Constant Time Stepping, the deposition is simulated. The adsorption of adatoms is accepted or rejected depending on the neighborhood conditions; furthermore, the desorption process is not included in the simulation and (2) the Monte Carlo method combined with the metropolis algorithm is used to simulate the diffusion. The model was developed by accounting for parameters that determine the morphology of the film, such as the growth temperature, the interacting atomic species, the binding energy and the material crystal structure. The modeled samples exhibited an FCC structure with grain formation with orientations in the family planes of ⟨111⟩, ⟨200⟩ and ⟨220⟩. The grain size and film roughness were analyzed. By construction, the grain size decreased, and the roughness increased, as the growth temperature increased. Although, during the growth process of real materials, the deposition and relaxation occurs simultaneously, this method may perhaps be valid to build realistic polycrystalline samples.

1. Introduction

Thin films have been applied in many industrial devices, including microelectronics, optoelectronics, detectors, sensors, micro-electro-mechanical systems, and, recently, nano-electro-mechanical systems [1]. Thin films have become important forms of material due to their unique characteristics, including their optical, electrical and mechanical properties [2]. Transition metal nitrides, such as ZrN, HfN and VN, have many technological applications because of their high melting points, chemical stability, and corrosion resistance [3–5].

Regarding the technological applications of thin films, it is important to optimize and control the film characteristics, such as roughness, strength, friction resistance, and adhesion to the substrate [6]. Extensive studies of the correlation between the film structure and deposition parameters have recently been performed to understand the film formation process [7]. A great deal of attention has been devoted to grain growth in polycrystalline materials. Nevertheless, this process is difficult to study by means of analytical models [8], although it can be modeled in a simplified form despite the complexity of the phenomena using several models of crystal growth processes [9,10].

Particular interest has arisen in the use of atomic-level computer simulations based on energy-minimization, molecular dynamics (MD) and Monte Carlo (MC) methods [11]. Kinetic Monte Carlo (KMC) simulations have emerged as one of the fundamental tools for studying the growth of thin films and have been used to elucidate the physics of the growth process. This technique was first adopted in the early 1970s [12,13] and has bifurcated in numerous directions. Furthermore, the kinetic Monte Carlo method is useful for simulating processes that require a high number of iterations because it is not limited by the vibrational period of the atom, as is the case for the molecular dynamics method. The application of kinetic Monte Carlo modeling to alloy systems has not been extensively investigated due to the complexity of these systems [14]. Anderson et al. [15,16] proposed the most widely known and used theory for computer modeling and simulation of grain growth, the KMC method. Schulze [17] and Xiao [18] developed a hybrid scheme for simulating epitaxial growth with KMC simulations. This researcher included the use of a more conventional KMC model and some improvements regarding the handling of the boundary condition between the KMC and continuum regions. The method is used to examine unstable step-flow with direct comparison to the KMC simulations. Liu et al. [19] presented

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two-dimensional cross-sectional KMC simulations of electrodeposition processes of single crystal copper on an atomically even surface, observing the evolution of the microstructure. Bentz et al. [14] performed a KMC study on the spin-one Ising model with diffusion to examine the surface roughening of a binary alloy of A and B atoms. Fursenko et al. [20] developed a software program that predicts the parameters of the deposited films and determines the optimal arrangement of the sputtering systems for the growth of a thin film with the desired properties. Edwards and Wilkinson [21] introduced a simple model that describes the surface growth; this model is more compact than those based on ballistic deposition. Wolf and Villain [22] used different rules for particle hopping, resulting in different behavior. More recently, Esen and Ozdemir [23] studied the growth and equilibration of an initially V-shaped surface consisting of monolayer height steps separated by terraces using the Kinetic Monte Carlo (KMC) method. Some of the processes that are considered are attachment and/or detachment of particles to/from steps, freely diffusing atoms on the surface, and the movement of particles along the step or cluster edges.

Although the literature contains reports on the simulation of thin film growth, polyatomic and polycrystalline films require further study because of their technological importance. This study performed simulations using the kinetic Monte Carlo method to understand the behavior of the film morphology. This method was applied to thin films of zirconium nitride (ZrN), vanadium nitride (VN) and hafnium nitride (HfN). In addition, an approach was developed to estimate and control the surface roughness of thin film growth using KMC models. The model presented in this work mimics the atomic adsorption, and surface migration processes that were considered to be the three most important processes controlling the micro-structure of the film.

2. Method description

Monte Carlo simulations of most spatially distributed systems are plagued by several problems, namely, execution of one process at a time, large separation of time scales of various processes, and large length scales. Recently, methods as coarse-grained Monte Carlo were introduced in order to capture large length scales at reasonable computational times. These method and others similar are frequently reported in the literature [24–26]; the assumption that a group of atoms is first deposited within different grains and then they are relaxed is an approximation; nevertheless, there are experimental proofs that allow to split growth processes into a single deposition stage and a single diffusion/relaxation stage [27]. In this document, although the growth process is modeled with several approximations, the final structure of the polycrystalline material is obtained, similar to a real growth, achieving this by considering the deposition and diffusion stages as separated processes. With this procedure, a polycrystalline system that represents the coatings structure was developed.

A model of diatomic and polycrystalline thin film growth was developed using the Monte Carlo method and the solid-on-solid method with nearest-neighbor interactions. The KMC method in the grain growth simulation is based on the thermodynamics of atomic interactions and is both simple and fascinating [9].

Fig. 1 presents flowcharts describing the algorithm implemented. Fig. 1(a) presents the flowchart of the program starting, the variables input, and the initialization; Fig. 1(b) shows the flowchart of the deposition, including the adsorption and nucleation processes, and Fig. 1 (c) represents the flowchart of the diffusion process. Film growth requires both deposition and diffusion processes. The deposition process considers the adsorption of atoms from the gas phase to the surface, which can include the acceptation or rejection of atoms [28], the nucleation of three-dimensional islands [29], and the growth of the polycrystalline films [30]. The diffusion process includes the migration of atoms on the surface [28] and grain boundary diffusion [31]. Some of the parameters used in the simulations are: the size of the sample; the space in which the material growth occurs $L \times L$, with $L = 100\,a$, where a is the lattice parameter; the deposition temperature (T); the equilibrium binding energy of the interacting atomic species depending on the material (γ); the number of atoms per pulse or the flow of atoms (N); the number of pulses (pls); the initial height (z_0); and the number of relaxation steps (RS), which controls the mobility of the adsorbed atoms. The relaxation process is directly related to the ionic energy, and it depends on the working pressure and the polarization [32]. All of the parameters used in these simulations are listed in Table 1, and values of the lattice parameter and the binding energy for each material simulated are listed in Table 2.

For stable conditions, the theory predicts that the nucleation rate J (in $\text{s}^{-1}\text{cm}^{-3}$) can be represented as $J = N_m B \exp(-G/k_B T)$, where N_m is the number of molecules per unit volume of the liquid, B is a kinetic factor, and k_B is the Boltzmann constant and T is the temperature. Considering the orders of magnitude, $N_m \approx 10^{22}\ \text{cm}^{-3}$ and $B \approx 10^{10}\ \text{s}^{-1}$. The thermodynamic factor of the Gibbs free energy formation (ΔG) plays an important role in the kinetics of the nucleation [37]. The average grain size GS is inversely proportional to the nucleation rate and is described by:

$$GS \approx (1/N_m B)\exp(\Delta G/k_B T) \qquad (1)$$

In our case, ΔG took values according to the literature; the values of ΔG for different materials are presented in Table 2.

2.1. Deposition process

The starting point of the simulation is a neutral substrate that does not bias the film orientation; thus, the substrate interactions are chosen so that clusters nucleate without preference for either of the orientations [18]. The substrate is represented by atoms in a lattice [31] with $f(x,y,z) = 1$ in $z = 0$, where neither vacancies nor overhangs are permitted [37]. These sites are filled by a solid substrate material [38] with a flat surface [30], whereas the rest of the lattice is empty ($f(x,y,z) = 0$) [11]. Before the deposition begins, the substrate is totally occupied. To simplify the calculations, a reference lattice is created as a matrix with L^3 number of positions to be filled for each atom [31].

At each step of the simulation, the x -and y-coordinates where the atom will be placed are chosen randomly, and the atom begins to fall down from an initial height z_0 high enough to find the lowest empty site of z corresponding to the previously selected (x, y) point. Each randomly chosen lattice point on the substrate surface, which is labeled by an integer number [1], must be an empty substitutional position on the surface [39]. When the deposition begins, a fixed flux of atoms N is sent to the substrate surface. This flux consists of a pulse of $5L^2$ atoms [40]. The total flux of atoms during the simulation is $pls \times N$ that can take values between N and $5\,N$. Two possible types of atoms $t(x,y,z)$, which are named as A and B for a metallic ion M^- (V, Zr, or Hf) and N^+, respectively, can arrive at the surface, and the type of the deposited atom is randomly assigned with a probability of 0.5. Because the materials studied here (VN, ZrN and HfN) are diatomic systems with a rock-salt type FCC structure, each metallic ion must have only nitrogen as its nearest neighbors. The occupancy is characterized by the function $f(x,y,z) = 0$ if the position is empty or $f(x,y,z) = 1$ if is occupied [11]. According to these considerations, implicitly there are two extreme vales for the absorption rate: (1) an infinitely large value, if the site is empty and the neighborhood is correct (A requires B neighbors, B requires A neighbors); then the atom is adsorbed and (2) zero, if the site is