Surface Science 606 (2012) 605–614

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Kinetic Monte-Carlo simulation of the homoepitaxial growth of MgO{001} thin films by molecular deposition

Ekaterina Antoshchenkova [a], Marc Hayoun [a,*], Fabio Finocchi [b], Grégory Geneste [c]

[a] Laboratoire des Solides Irradiés, Ecole Polytechnique, CEA-DSM, CNRS, 91128 Palaiseau, France
[b] Institut des Nanosciences de Paris, UPMC Université Paris 06, CNRS UMR 7588, 4 place Jussieu, 75005 Paris, France
[c] CEA, DAM, DIF, 91297 Arpajon, France

ARTICLE INFO

Article history:
Received 23 August 2011
Accepted 19 November 2011
Available online 3 December 2011

Keywords:
Thin films
Surface diffusion
Crystal growth
Kinetic Monte-Carlo
Clusters
Islands
Crystalline oxides
Ionic compounds

ABSTRACT

A lattice-based kinetic Monte-Carlo (KMC) code has been developed to investigate the MgO{001} crystal growth from deposition of MgO molecules, as a prototypical case of the growth of oxide thin films. The KMC approach has been designed on the basis of an extensive database including all possible diffusion mechanisms. The corresponding activation energies have been computed through first-principles calculations at zero temperature or from Arrhenius plots of the frequencies obtained by molecular dynamics simulations with empirical potentials. Crystal growth occurs layer by layer, as experimentally observed, and the diffusion of admolecules leads to a high capacity of nucleation, which is enhanced by vacancy diffusion. We have characterized the growth through surface roughness, size distribution and density of the islands, and filling ratios of the growing layers. Moreover, we have analysed the influence of each elementary mechanism on the growth. The best quality of the deposited layers is reached for temperatures larger than 700 K and for pressures smaller than 0.1 Torr. For these conditions, the simulated surface roughness is fully consistent with available experimental results.

1. Introduction

Oxide compounds are useful materials for many applications, from spintronics to sensors and actuators. In most of the devices, these systems are grown under the form of thin films that can be only a few nanometers thick or even less. Controlling both thickness and roughness is therefore a crucial issue in many cases. Techniques that allow fine tuning of the quality of the layers and provide fast enough growing films are thus highly desirable.

In order to improve the atomic-scale control during growth, numerical simulations of the growth process can be a precious tool. Predicting growth velocity, surface roughness, quantity of point defects, for various materials as a function of the macroscopic physical parameters, such as temperature, partial pressure and deposition time, would obviously be of much help in the design of ultra-thin films. Simulations of growth at the atomic scale have been proposed for simple metals and semiconductors in the recent past [1–4]. However, owing to the difficulty of using near-field microscopy with atomic resolution on insulating materials, there are less experimental studies on the growth of oxides at the atomic scale. The scarcity of experimental data on the atomic processes during the growth of oxides might also explain why this is also the case for simulations, despite the technological importance of these materials.

Growth involves a combination of elementary processes (such as adsorption, diffusion, desorption, nucleation of atoms and/or molecules, etc.) that take place at the atomic scale. Therefore, in order to build a predicting tool for understanding growth, one must start by a careful and thorough study of these elementary processes. Standard atomic-scale techniques include first-principles calculations and molecular dynamics (MD) simulations based on phenomenological interatomic potentials. The former ones are more accurate in principle, but are generally carried out at zero temperature: the diffusion mechanisms are studied by minimizing the total energy along a path that is characterized by a reaction coordinate, with respect to all the remaining degrees of freedom. The latter techniques allow much longer simulation runs, where the effects of temperature (and thus the entropic effects) on the diffusion are taken into account; the activation energies of the various elementary mechanisms are then obtained by Arrhenius plots of their frequencies.

However, deposition, diffusion and evaporation of single atomic or molecular species generally happen on much smaller time scales than macroscopic growth. Moreover, many nanostructures are formed under conditions that are far from thermodynamic equilibrium; hence

---

* Corresponding author.
E-mail address: marc.hayoun@polytechnique.edu (M. Hayoun).

0039-6028/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2011.11.026

kinetics has an impact, or even determines their growth. A multi-scale approach that combines the previous atomistic calculations and at least another technique, which enables to follow the dynamics of large systems on longer time scales, is therefore mandatory to achieve realistic descriptions of growth [5]. Kinetic Monte-Carlo (KMC) fulfils the previous requirements and allows the evolution of the system on the characteristic time scales of crystal growth to be simulated, through an efficient coarse-graining of atomic dynamics. Moreover, it gives access to out-of-equilibrium phenomena, because it provides in principle an exact numerical solution of the master equation. However, its reliability crucially depends on the quality of the underlying coarse graining, and specifically on the nature of each move and the corresponding energy barrier.

In the present work, we have addressed the homoepitaxial growth of magnesium oxide {001} as a prototypical example of the growth of binary charge-transfer insulating oxides. We have focused on the growth via a flux of MgO molecules impinging the surface; therefore the growing system is always stoichiometric. The growth via combined Mg and O_2 fluxes is chemically much more complex and will be investigated in the future. Indeed, as both Mg and O_2 are volatile species at usual growth temperatures, the identification of the adsorption-controller species is delicate [6]. However, even in this case, growth implies the nucleation of MgO admolecules and clusters on the surface. Hence the study of stoichiometric MgO is a necessary step to address growth under non-stoichiometric conditions or other more complex oxides. Most elementary mechanisms at the atomic scale have been obtained in previous studies by density-functional calculations and MD simulations using phenomenological potentials [7–10]. This large database, which includes activation energies for a variety of distinct mechanisms, has been used as input of a KMC code especially developed for the MgO homoepitaxial growth. We have studied the surface morphology at various pressures and temperatures and analysed the relative contribution of each atomic process on the growth. In this paper, we introduce the KMC model briefly and recall the main atomic processes that are responsible for atomic diffusion in MgO; then we discuss the numerical results: morphology and number of growing layers, nucleation and size distribution of adclusters, influence of temperature and pressure on the quality of the film.

2. Kinetic Monte-Carlo: the model

2.1. Modelling kinetics

The KMC approach on a rigid lattice [11–13] is well suited to simulate and study growth of crystals or thin films and catalytic reactions at surfaces. A major issue in simulations of crystal growth is to deal with fast diffusion events (on the ns scale) and slow deposition events (on the s scale) at the same time. The Bortz, Kalos and Lebowitz [11] method allows bridging this time-scale gap. This efficient algorithm keeps a list of all possible events (whatever the time scale is) and the simulation proceeds by selecting one of them at each KMC step. All along the simulation, the possible events happen on average with their own frequency, which must be provided as an input. These data can be taken from experiments, theoretical models or be estimated through other numerical methods, such as MD simulations or first-principles calculations.

One way to obtain these frequencies, Γ, is to use the activation energies, E_a, associated to the events through the transition state theory [14,15]:

$$\Gamma = \Gamma_0 \exp(-E_a/k_BT) \qquad (1)$$

where k_B and T are the Boltzmann constant and the temperature. MD simulations at different temperatures can provide both activation energy and prefactor, Γ_0, via an Arrhenius plot. On the contrary, the prefactor cannot be obtained from *ab initio* calculations at $T=0$ K (except in an approximate way through the so-called harmonic transition state theory). In the present work, we have combined *ab initio* and MD data. For consistency sake, we have chosen to replace the prefactor Γ_0, for all data, by a universal frequency that depends only on temperature:

$$\Gamma_0 = \frac{k_BT}{h} \qquad (2)$$

where h is the Planck constant.

The deposition rate by a MgO molecular beam can be obtained via the kinetic theory of gases, which provides the amount of gas hitting the unit area of a surface per unit time [16]:

$$Z = \frac{bP}{\sqrt{M_rT}} \qquad (3)$$

where P is the gas pressure above the surface, M_r is the relative molecular mass of the gas, and b is a constant (3.51 10^{26}molecules $m^{-2}\,s^{-1}\,K^{1/2}\,Torr^{-1}$). We assume that the sticking coefficient is equal to unity, that is, each molecule that hits the surface is adsorbed. This choice is motivated by the fact that the computed desorption energy for a MgO admolecule from the flat surface is at least equal to 2.48 eV, that is, the opposite of the adsorption enthalpy, calculated within DFT-GGA [7]. When the admolecule binds to a step edge or to other low-coordinated surface sites, the adsorption enthalpy is even more negative, since more chemical bonds are formed. All desorption barrier heights are therefore much larger and imply that the corresponding events are unlikely in the range of temperatures and pressures considered in the present work. They are thus neglected.

2.2. Elements of the KMC model: diffusion of admolecules

Once adsorbed on the surface, we consider that the MgO admolecule can diffuse but cannot dissociate. This is because its dissociation implies a static energy barrier of about 2.8 eV within DFT-GGA [8] on flat {001} terraces [27]. The incorporation of the diffusion processes in the KMC code requires the knowledge of all possible diffusion mechanisms and their associated frequencies.

Four different mechanisms of a MgO molecule diffusing on a flat MgO{001} surface have been evidenced in previous studies [9,17]. They are: (i) Mg rotation: the admolecule rotates by 90° around its O ion through an intermediate configuration at 45°, where the molecular axis is roughly parallel to the surface plane (Fig. 1(a)). (ii) O rotation: the molecule rotates by 90° around its Mg ion through an intermediate configuration at 45°, where its axis is roughly parallel to the surface plane (Fig. 1(b)). (iii) Exchange of Mg: Mg turns around O, reaching the same intermediate configuration as during the Mg rotation, and pushes the Mg ion below O off the surface plane. Then, the Mg adatom replaces the Mg that was originally beneath; this one then binds to the O adatom (Fig. 1(c)). (iv) Simultaneous jumps of both ions towards new sites, referred to hereafter as a ‘molecular diffusion’ (Fig. 1(d)). These four mechanisms and their activation energies, given in Table 1, correspond to the possible movements of an isolated admolecule on a flat {001} terrace. The most complex mechanism, namely the Mg exchange, has the lowest activation energy, hence is the most frequent one.

During growth, <100> steps appear spontaneously. At the edges of such steps, the admolecule can execute another mechanism called downward diffusion and described in Fig. 1(e). In this case, the molecule falls down from the upper terrace onto the lower one, with no activation barrier [7]. This behavior implies that not only the Ehrlich–Schwoebel barrier is negative [7], but that the migration of a MgO admolecule above the step edge leads to a progression of the edge itself, without any activation energy. In the KMC model, we thus consider that an admolecule at the edge of a step or an adcluster automatically falls down on the terrace below and will never cross the edge backward.