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Short communication

The algorithm of Monte Carlo growth simulation of $PbTiO_3$ thin film

G.L. Yu, J.G. Zhu, W. Lu, D.Q. Xiao *

Department of Materials Science, Sichuan University, Chengdu 610064, China

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Abstract

An algorithm for the simulation of the growth of $PbTiO_3$ (abbreviated as PTO) thin film is presented in this paper, in which the active energy of different atoms is not only related to the local configuration, but related to the kind of the atoms of the configuration as well. The active energy was considered from the interactions between the ions, which are calculated by Coulombic potential. A pack of simulation software for PTO was developed. From the simulation it is obtained that the rate and temperature of deposition play a very important role in the initial process of the growth of PTO thin film, and with the rising of deposition temperature and the decreasing of deposition rate the size of the initial nucleuses gets larger and the number of them gets less.

Keywords: Monte Carlo simulation; Thin film growth; $PbTiO_3$; Oxides

1. Introduction

The researches on the growth mechanism of thin films have attracted much attention in the past decades, in which both the theoretical and experimental methods are adopted. Computer simulation is one of the theoretical methods, which can give some detailed information on the microstructure of thin film growth.

At present, much simulation is about the homoexpitaxial and the heteroexpitaxial thin film growth of metal or semi-conductive materials with only one or two kinds of elements. Molecular dynamics [1], Monte Carlo simulation [2–4], and transmit state theory (TST) [5] methods have been applied. Witten [6,7] developed diffusion-limited aggregation simulation (DLA) to explain the shape of two-dimensional islands at the initial stage of thin film growth. The direct experimental observation of the shape of the islands of Au/Ru(0001) thin film being deposited at 300 K confirm the result of the DLA [8,9]. Huang et al. [10–13] developed a kind of three-dimensional atomistic simulators to simulate the texture competition of aluminum thin films. And the three-dimensional simulation of Cu thin film, which is used as electrode in integrated circuit (IC) has also been reported [14].

Multiple-element oxide thin films, such as ferroelectric $PbTiO_3$–$PbZrO_3$ thin films, have an increasingly wide range of technological applications including optical wave guides, ferroelectric random-access memories, sensors and actuators, and infrared detectors and detector arrays because of their excellent properties. However, the simulation of the growth of multiple-element oxide thin films is far from understanding. Although, a few papers on oxide growth simulation have been published [15], but they are almost about oxide crystals and not related to oxide thin films.

The purpose of present work is to develop a three-dimensional simulation algorithm based on Monte Carlo method and also to develop a pack of simulation software for the growth of multiple-element oxide thin films. In this paper, an algorithm for the simulation of the growth of $PbTiO_3$ (abbreviated as PTO) thin film

* Corresponding author. Tel.: +86 28 85412415; fax: +86 28 85415045.
E-mail address: nic0402@scu.edu.cn (D.Q. Xiao).

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is presented. The active energy is calculated by Coulombic potential from the interactions between the ions, which is not only related to the local configuration, but related to the kind of the atoms of the configuration. From the simulation it is obtained that the deposition rate and temperature play a very important role in the initial process of the growth of PTO thin film, and with the rising of deposition temperature and the decreasing of deposition rate the size of the initial nucleuses gets larger and the number of them gets less.

2. Monte Carlo algorithm

$PbTiO_3$ is a material with perovskite structure, which was modeled as eight cubic bulks in present study as illustrated in Fig. 1, because there are atoms in the face center and bulk center of the molecular cells. It is assumed that the length of one side of each of eight cubes illustrated in Fig. 1 is 2 Å, which is almost equal to the half of the lattice constant of $PbTiO_3$. The lattice space for atoms' movement in the Monte Carlo simulation is determined by the number of the cubic bulks of $N \times N \times H$, where N and H are the length (also the width) and the height of this lattice space, respectively. N equals to 100 in present work, and H is related to the thickness of the film and varies with the total atoms being simulated. In this model, the periodic boundary condition is applied, which means that the atom enters the lattice space from the right edge after it moves out of the left edge of lattice space, or enters from the left edge after it moves out the right edge of lattice space. The model of fabrication process of $PbTiO_3$ thin films is considered as follows:

(1) Deposition of atoms

The kind of deposition atoms is determined according to the ration of Pb:Ti:O = 1:1:3 (as the atom ratio of $PbTiO_3$) by a stochastic number generated by computer. Such consideration is based on the fact that the kind of an atom being deposited at one moment is randomly selected, but the ratio of atoms is 1:1:3 for the whole $PbTiO_3$ thin films. The initial position of the deposited atom (x_0, y_0, z_0) on the substrate is chosen randomly by a series of stochastic numbers generated by computer.

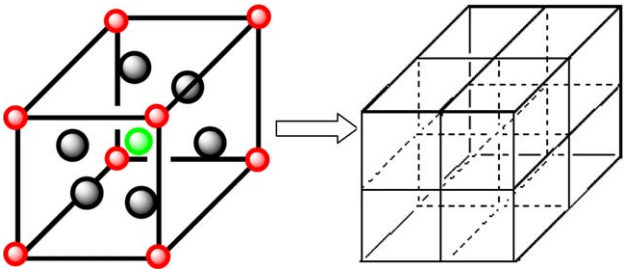

Fig. 1. The Monte Carlo lattice model of $PbTiO_3$ structure.

(2) Diffusion of atoms

The diffusion probability P_i of an atom in the direction i being considered can be calculated by the formulae

$$P_i = \Gamma_i / \sum \Gamma_i, \tag{1}$$

where Γ_i is the hopping frequency in the direction i which depends on the active energy.

$$\Gamma_i = \Gamma_0 \exp(-\Delta E_d^i / k_B T), \tag{2}$$

where Γ_0 is a hopping frequency constant (10^{12}–10^{13}), $\Delta E_d{}^i$ is the diffusion activation energy in the direction i, which will be described in detailed in the following section; k_B is the Boltzmann constant; and T is the deposition temperature.

In this model, it is supposed that an atom can only diffuse to four nearest neighbor lattice sites such as $(x_0 + 1, y_0)$, $(x_0 - 1, y_0)$, $(x_0, y_0 + 1)$, and $(x_0, y_0 - 1)$ in the same plane. And $(x_0, y_0, z_0 - 1)$ can also be allowed to diffuse to if the site is not in the substrate. If there are atoms in these sites, the diffusion to sites is prohibited. A stochastic number ρ generated by computer is used to decide the site which an atom can diffuse to. The diffusion time Δt needed can be calculated by

$$\Delta t = 1 / \left(\rho \sum \Gamma_i \right). \tag{3}$$

(3) Re-evaporation of atoms

Whether an atom re-evaporates depends on the height of the energy barrier which should be covered.

Under these considerations the Monte Carlo events in present model consist of the deposition event, the diffusion event, and the re-evaporation event. At one moment, one Monte Carlo event can occur. The deposition rate is assumed as V_{dep}, whose unit is layers/second and can be converted to nm per second by multiplying 0.2 nm/layer. The occurring frequency of the deposition events can be expressed as $V_{dep} \cdot N^2$. In present study, V_{dep} is a small number in the range of 10^{-2}–10^3, and $V_{dep} \cdot N^2$ is below 10^5 and relatively far small to Γ_0 (10^{12}–10^{13}). Therefore in most time of fabrication processes, the Monte Carlo events are dominated by diffusion events.

(4) Relations of the events of deposition, diffusion and re-evaporation

An atom will deposit at random position (x, y), and above the atom have being deposited (z), and on the substrate when there are no atoms being deposited above the substrate. Then the atom begins to diffuse. The total time of diffusion events being allowed to occur for an atom is given as $1/(V_{dep} \cdot N^2)$. During this time the diffuse event is allowed. And one step diffusion time can be calculated by formulae (3). When the total diffusion time ($\sum \Delta t$, summary of time spent by all diffusion