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Full Length Article

Molecular dynamics study of the effect of substrate temperature and Ar ion assisted deposition on the deposition of amorphous TiO_2 films

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ABSTRACT

This paper has investigated the impact of the substrate temperature and Ar ion assisted deposition on the surface structure formation mechanism and the film properties during the amorphous TiO_2 thin film deposition process with the molecular dynamics simulation method. The results show that the reduction of the surface roughness happen when the energy of Ar ions assisted is increased or the substrate temperature rises, and also the film density on surface is changed with the increasing of Ar ions energy and substrate temperature. It is also found that the Volmer-Weber (island) growth mode of films is promoted by the lower Ar ion energy and higher substrate temperature when the substrate has an island structure. The assisted Ar ion has power of making a flat surface and increasing the local temperature. Besides, it will influence the growth mode with the change of surface atom mobility. With a high assisted Ar ion energy the Volmer-Weber (island) growth mode is inhibited, which will be conducive to the formation of more smooth film surface.

1. Introduction

Because of its interesting optical, chemical and electronic properties, the amorphous titanium dioxide (a-TiO_2) thin films have drawn wide attention over the years and have been widely used in industry [1–7]. The growth mechanism of a-TiO_2 films is very complex. The structure and morphology of a-TiO_2 films used as optical films, which could affect the optical scattering loss, are very important and are greatly influenced by the technology conditions of deposition. Therefore, it is imperative to study the relationship between the technology conditions and the structure and morphology of a-TiO_2 films. Moreover, figuring out how the deposition process impacts on the structure and morphology of a-TiO_2 films is an important theoretical research for revealing and controlling the optical properties [8].

The influences of deposition conditions on a-TiO_2 thin films growth have been widely studied, and some useful results have been obtained [9–12]. However, the growth mechanism is not clearly understood. The computer simulation method is used to study the film growth from the atomic scale. Guenther [13] have studied the impact of ion energy on the film growth with two-dimensional model, and found that the film deposition is comparable to a transient liquid film formation when the ion energy is higher than 5 eV, by which a very smooth surface of the film could be deposited. The two-dimensional model can not reveal the structure and nucleation of the growth process. The molecular dynamics method for three-dimensional simulation is used along with the development of computer technology. Baguer [14] studied the nucleation and growth of TiO_2 films on different substrates, and found the formation of a strong interface region between the substrate and the film. Vernon [15] studied the growth of TiO_2 surface following low energy atom and small cluster bombardment. Chen [16,17] studied the effect of incident Ti energy on the surface structure during the a-TiO_2 films deposition, and found that the incident energy and surface potential has important influence on the films deposition. Therefore, the three-dimensional growth process of optical films is investigated using the molecular dynamics simulation, and the influence mechanism of the substrate morphology and temperature on surface structure is unraveled during the a-TiO_2 films deposition.

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Table 1
Parameters of MA potential function [19].

Interaction	A_{ij}(kcal mol^{-1})	ρ_{ij}(Å)	C_{ij}(kcal mol^{-1}Å^6)
Ti—Ti	717653.9571	0.154	120.9967
Ti—O	391052.7442	0.194	290.3920
O—O	271718.8311	0.234	696.9407

Table 2
Parameters of LJ potential function.

Interaction	σ_{ij}(Å)	ε_{ij}(kcal mol^{-1})
Ar—Ti	3.5215	0.014019
Ar—O	3.684	0.026337
Ar—Ar	3.868	0.046246

In this paper, the molecular dynamics simulation method is proposed to study the structure and properties of a-TiO_2 films under atomic scale. Thus, how the preparation process influences the structure and morphology of the films is revealed. It could be useful to study the relationship between the optical properties and preparation parameters, which can be the foundation of designing and controlling the optical properties of films. The results show: when the energy of assisted Ar ions is increased, the surface roughness of the deposited films is reduced and the density of the films increases, the films become denser. And also the higher substrate temperature could lead to smoother surface when a-TiO_2 deposited on flat substrate, which is converse while deposited on substrate with island.

2. Computational details

In this paper, the molecular dynamics calculation has been performed with the Lammps software package [18], and a two-body potential (MA potential) proposed by Matsui and Akaogi [19] and the LJ potential have been used. Hoang, Kaur, Chen, etc. [16,20,21], who used MA potential function for the simulation of a-TiO_2, got the results which were consistent with the experiments and first principles calculation.

MA potential function is presented as following equation:

$$U(r_{ij}) = A_{ij}\exp(-\frac{r_{ij}}{\rho_{ij}}) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}} \quad (1)$$

Where $U(r_{ij})$ is the molecular potential, r_{ij}- is the distance. The atomic charge of the Ti and O are +2.196e and −1.098e in several, and the parameters A_{ij}, ρ_{ij}, and C_{ij} are shown in Table 1. The coulomb interaction, the third part of the MA potential function, is a long-range force which the wolf's method [22]. is used to deal with, and the others are short-range forces for which a truncation radius treatment method is used, and the truncation radius is 8 Å.

The LJ potential function is presented as following equation:

$$U(r_{ij}) = 4\varepsilon_{ij}[^{12} - (\frac{\sigma_{ij}}{r_{ij}})^6], r < r_c$$
$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (2)$$
$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

Where $U(r_{ij})$ is the LJ potential, $r_{ij}$are the distance, $r_c$is the cut off, ε_i is the dielectric constant, and the other parameters are shown in Table 2.

During the simulations of a-TiO_2, the periodic boundary condition is used on the X-Y plane, and the free boundary condition is used in the Z direction. The cell size of a-TiO_2 on the X-Y plane is 45.9 Å × 45.9 Å. In the process of molecular dynamics simulation, the Nose's temperature control method is used. The time step is 1 fs.

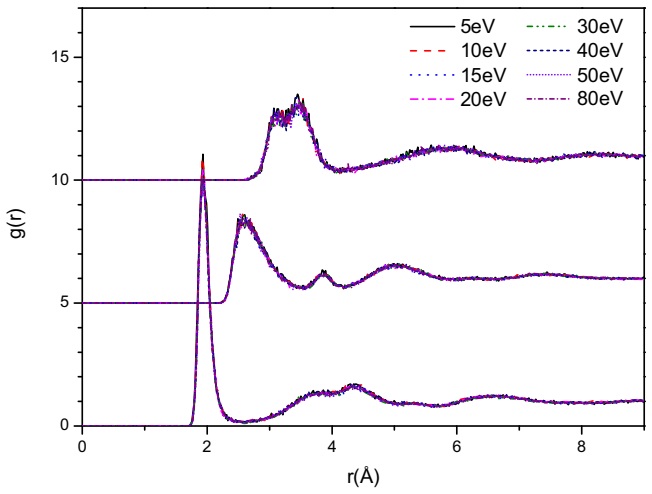

Fig. 1. The radial distribution function (RDF) of a-TiO_2 deposited in different incident ion energy at 500 K.

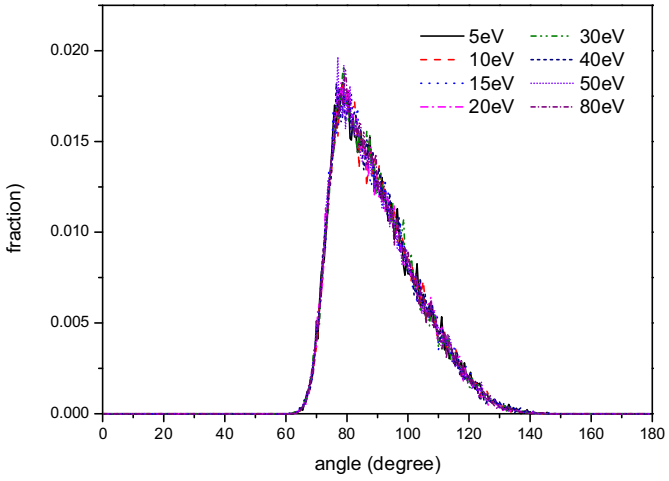

Fig. 2. The angular distribution function of the O—Ti—O bond angle in a-TiO_2 deposited in different incident energy at the temperature of 500 K.

In the actual process of thin film deposition, the incident particles have an energy distribution which depends on the deposition conditions. This paper studied the impact of substrate temperature and morphology on the thin film deposition under different incident ion energy. The energy of the incident titanium ions is respectively selected as 5 eV, 10 eV, 15 eV, 20 eV, 30 eV, 50 eV and 80 eV, while the incident oxygen ions energy is selected as 4 eV. The substrate temperature is at 300 K and 500 K. The energy of assisted Ar ions is respectively selected as 50 eV, 80 eV, 100 eV, 150 eV, 200 eV. In every deposition process, there are 2000 titanium ions and plenty of oxygen ions deposited within 10 nanoseconds, and the structure and morphology of the deposited a-TiO_2 films are analyzed.

3. Results

3.1. Structural properties of deposited a-TiO_2

The radial distribution function (RDF) and the angular distribution function of the O—Ti—O bond angle of the TiO_2 deposited in different conditions at the temperature of 500 K are obtained, as shown in Figs. 1 and 2.

As Fig. 1 shows, there is only short-range order but no long-range order in all of the deposited TiO_2 films. In Fig. 2, the O—Ti—O