Structure and properties of the low-energy deposited TiO$_2$ thin films: results of the molecular dynamics simulation

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Abstract: The classical molecular dynamics simulation of the low-energy glancing angle deposition of titanium dioxide films is performed. The deposition angle varies from 60° to 80°. It is found that the film structure consists of parallel slanted columns which lead to the anisotropy of films properties. The difference between the main components of the refractive index tensor is about 0.14, which is close to the values obtained for high-energy titanium dioxide films and larger than 0.03 obtained earlier for silicon dioxide films.

Key words: molecular dynamics, thin films, titanium dioxide, refractive index, anisotropy, glancing angle deposition.

1. Introduction

Deposition at large angles, when incoming atoms move almost parallel to the substrate, leads to the formation of glancing angle deposited (GLAD) films, consisting of separated nanostructures having different dimensions and shapes [1,2]. Due to the high porosity and anisotropy of the structure, transparent dielectric GLAD films are used in various optical devices [2,3]. The properties of GLAD films essentially depend on the deposition conditions, such as deposition energy, deposition angle, substrate temperature and others. At present for the theoretical investigation of these dependencies at the initial stage of the GLAD films formation, various methods of atomistic modelling are used [4-6].

Earlier the classical full-atomicistic molecular dynamics (MD) simulation was applied to study the formation of SiO$_2$ [7, 8] and high-energy deposited TiO$_2$ [9] GLAD films. In the present work we study the formation of low-energy TiO$_2$ GLAD films. The differences in the properties of the high- and low-energy deposited GLAD films are discussed.

2. Simulation method

The simulation of the thin film deposition process is performed using the previously developed step-by-step procedure [10]. The energy of interatomic interactions is calculated using the pairwise force field [11, 12]:

$$U = q_i q_j / r_{ij} + A_{ij} / r_{ij}^{12} - B_{ij} / r_{ij}^6$$ (1),

where $q_{ij}$ is the charge of the $i$-$j$-th atom, $q_0 = -0.5q_{Ti} = -0.5q_{O} = -0.598e$, $A_{ij}$ and $B_{ij}$ are the parameters of Lennard-Jones potential, rewritten from the sigma-epsilon form to the $A$-$B$ form (Table 1).

| Interaction | $A_{ij}$ (kJ·nm$^6$/mol) | $B_{ij}$ (kJ·nm$^{12}$/mol) |
|-------------|-----------------|-----------------|
| Ti-Ti       | $5.062 \times 10^8$ | $3.1195 \times 10^8$ |
| O-O         | $3.009 \times 10^7$ | $1.735775 \times 10^8$ |
| Ti-O        | $1.4368 \times 10^7$ | $2.90927 \times 10^8$ |

At each step of the simulation procedure, titanium and oxygen atoms with stoichiometric proportion of 1:2 are inserted randomly at the top of the simulation box. The initial value of the titanium and oxygen kinetic energies is $E(Ti) = E(O) = 0.1$ eV, which corresponds to a low-energy process like e-beam evaporation [13]. At each step of the simulation procedure the NVT (constant number of particles, volume and temperature) ensemble is used. The vertical dimension of the simulation box is increased by...
0.01 nm after each injection step to compensate for the growth of film thickness. The Berendsen thermostat \[14\] is applied to keep the simulation cluster temperature, \( T = 300 \) K, constant. The duration of one injection step is 10 ps and the time step of MD modeling is 0.5 fs.

MD simulation is performed using the GROMACS package \[15\]. The simulation was carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University \[16\].

3. Results and discussion

Results of the simulations are presented in Figs. 1, 2. Deposition at low energy of incoming atoms leads to the formation of porous structures (Fig. 1). In the case of normal deposition, \( \alpha = 0 \), (Fig. 1, left side), pores of different dimensions and shapes are randomly distributed over the film volume. Pore dimensions can reach several nanometers.

\[\text{Figure 1. Structure of the deposited titanium dioxide films.} \ \alpha \ \text{is the deposition angle,} \ \beta \ \text{is the tilt angle.} \ \text{Energy of the deposited Ti atoms is equal to 0.1 eV. Substrate is colored by yellow.}\]

It is known that the deposition at large angles \( \alpha \) leads to the formation of glancing angle deposited films consisting of the separate nanostructures \[2\]. As can be seen from the Fig. 1, in the case under consideration, these nanostructures are columns with a thickness of about several nanometers.

The deposition energy noticeably affects the structure of the GLAD TiO\(_2\) films. According to \[9\], in the case of high-energy deposited films, the tilt angle \( \beta \) is greater than in the case of low-energy deposited films (Fig. 1) at the same values of the deposition angle \( \alpha \). The relationship between deposition angle \( \alpha \) and tilt angle \( \beta \), \( 2\tan\beta = \tan\alpha \) predicted by the ballistic model \[4\], performs better for high-energy deposition. This can be explained as follows. Within the framework of the ballistic model, it is assumed that the deposited atoms move along straight lines up to the moment when they reach the film \[4\]. This assumption performs better in the case of the high values of the kinetic energy of incoming atoms. Indeed, with the reduction of the deposition energy the influence of the interatomic interaction on the atomic trajectories grows. This leads to deviations of these trajectories from straight lines near the films.

The density profiles of the deposited films and dependence of the film porosity on the deposition angle are shown in Fig. 2. The profiles for the high-energy deposited films shown in this figure were calculated using the results from \[9\]. Fluctuations in the density profiles are caused by the formation of slanted columns in GLAD films. In the case of low-energy deposition, the largest fluctuations are observed in the case of \( \alpha = 60^\circ \). The thickness of the transition layer between film and vacuum is approximately 2-3 nm for all deposited films.

The film porosity \( f(\alpha) \) is calculated as follows:

\[ f(\alpha) = 1 - \rho(\alpha)/\rho(0) \quad (2), \]
where $\rho(0) = 3.9 \text{ g/cm}^3$ is the density of the normally deposited film, $\rho(\alpha)$ is the density of the film deposited at an angle $\alpha$. The porosity of high-energy deposited films increases by approximately threefold with an increase in the deposition angle from 60° to 80°. At the same time the porosity of low-energy deposited films varies insignificantly with increase of $\alpha$.

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The structure of low-energy deposited TiO$_2$ film looks more ordered than the structure of low-energy SiO$_2$ GLAD films, as follows from a comparison with the results presented in [7, 8]. Growing SiO$_2$ GLAD films have a tree-like structure rather than a set of separated columns, as in the case of TiO$_2$.

The structural anisotropy of the GLAD TiO$_2$ films results in optical anisotropy. The difference $\Delta n$ between the main components of the refractive index tensor is calculated in the frame of the Bruggeman effective medium approach [17] for the GLAD structures shown in Fig. 1. It is found that the maximum value of $\Delta n$ reaches 0.14 and depends insignificantly on the deposition angle in the interval from 60° to 80°. This value is close to $\Delta n = 0.13$ obtained for high-energy deposited TiO$_2$ films at a deposition angle of 70° [9]. In contrast to low-energy deposition, the $\Delta n$ value at high-energy deposition reduces significantly when the deposition angle is decreased from 70° to 60°. The $\Delta n$ for the low-energy GLAD SiO$_2$ films simulated in [7, 8] is about 0.03 [18]. There are the following reasons for the large difference in $\Delta n$ values between TiO$_2$ and SiO$_2$ low-energy GLAD films. First, the $\Delta n$ value increases with an increase in the average value of the refractive index, $n = 1.49$ for SiO$_2$ [19] and $n = 2.5$ for TiO$_2$ [20]. Second, the TiO$_2$ films consist of the parallel separated columns (Fig. 1), which provides the anisotropy of properties, while the structure of low-energy SiO$_2$ GLAD films is more homogeneous [7,8].

4. Conclusion

The classical MD simulation of the low-energy GLAD TiO$_2$ films is performed. It is revealed that deposition at angles varying from 60° to 80° leads to the formation of anisotropic structures consisting of separated parallel columns having thickness of about 5 nm. The porosity of these films is about 0.3 and changes insignificantly when the deposition angle increases from 60° to 80°. The difference $\Delta n$ of the main components of the refractive index tensor calculated using the Bruggeman effective medium approach, is about 0.14, which is close to $\Delta n = 0.13$, obtained in the case of high-energy TiO$_2$ films deposited at an angle of 70°. For the low-energy GLAD SiO$_2$ films the calculated value of $\Delta n$ is about 0.03.

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