Glancing angle deposition of optical coatings: results of the full-atomistic simulation

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Abstract. The earlier developed molecular dynamics approach is used to simulate the thin film glancing angle deposition. The deposition at glancing angles is used for the production of optical thin films with low refractive indices. Both low-energy and high-energy deposition processes are considered for the case of silicon dioxide thin films. It is revealed that glancing angle low-energy deposition forms silicon dioxide films with low densities of about 1.5 g/cm³ and low refractive indices. Density profiles of growing films essentially depend on the initial conditions of the deposition process. The density of high-energy deposited films achieves 2.4 g/cm³. This value is close to that obtained before in the case of normal incidence deposition.

1. Introduction

Glancing angle deposition (GLAD) is the promising technique for the production of optical thin films with low refractive indices [1]. In this technique angles between the directions of particles flow and the normal to the substrate exceed 80° so the deposited particles move almost parallel to the substrate. This leads to the formation of separated nanostructures which shapes depend on the deposition conditions [2]. These so-called “sculptured thin films” (STF) [3] have low densities and therefore have low refractive indices which ensure also low reflectance of the produced films [4].

Structural, mechanical and optical properties of GLAD-grown STF essentially depend on the deposition conditions: density of deposited particles flow, particle energy distribution, substrate temperature, and so on [1-4]. In the present work the earlier developed method for the full-atomistic simulation of thin film deposition process [5-7] is applied to study the GLAD-grown SiO₂ films structural properties. Film density profiles are obtained for the cases of high-energy and low-energy deposition. The porosity and morphology of simulated nanostructures are studied qualitatively using visualization techniques. It was found that in the case of low energy of deposited silicon atoms structural properties of the GLAD-grown and normal deposition grown SiO₂ films differ essentially. In particular density of the GLAD deposited films reduces noticeably compared with the normal deposited films. This density reduction is accompanied by the increase of concentration of pores having dimensions of up to several nanometers.

2. Simulation method

The simulation of thin films deposition is performed using the classical molecular dynamic (MD) method. DESIL force filed [5-7] is used for the calculation of the potential energy of interatomic interaction. Deposition process is organized as a step-by-step procedure described in [5]. At every
deposition step the MD simulation is performed using periodic boundary conditions with $NVT$ ensemble (constant number of atoms, volume and temperature). In the present work the following MD parameters are used: the deposition temperature is $T = 300$ K, the duration of one deposition cycle is 6 ps, the time step of MD modeling is 0.5 fs, the number of injected SiO$_2$ groups per one injection cycle is 25. Berendsen thermostat [8] is used to keep the simulation box temperature constant. Horizontal dimensions of the substrate are 10 nm and 11 nm, maximum value of film thickness is about 40 nm. Density and thickness of the substrate are 2.14 g/cm$^3$ and 4.5 nm, respectively. The electrostatic component of the interatomic energy is calculated using the Particle Mesh Ewald [9] method. MD simulation is performed using the GROMACS package [10]. The visual analysis is performed using Visual Molecular Dynamic (VMD) [11] program facilities.

All calculations have been performed using the supercomputers ‘Lomonosov’ and ‘Lomonosov-2’ of the Supercomputing Center of Lomonosov Moscow State University [12].

3. Results and discussion

Initial values of the deposited Si atoms velocities are specified as follows:

$$v_z = -v_0 \cos \alpha; \quad v_x = v_0 \sin \alpha \sin \beta; \quad v_y = v_0 \sin \alpha \cos \beta$$

(1),

where $\alpha$ is the glancing angle (see Fig. 1), $\beta$ angle is chosen in the interval from 0º to 90º, $v_0$ denotes the initial value of the Si atoms kinetic energy, that is 10 eV for high-energy deposition and 0.1 eV for low-energy deposition. Coordinate axes are directed as shown in the right part of Fig. 2. Initial coordinates of the deposited silicon and oxygen atoms are specified as described in [5].

Results of the simulation are shown in Figs. 1, 2.

![Figure 1](image_url)

**Figure 1.** Density profiles of deposited films for the low- and high-energy deposition processes, $\rho$ (g/cm$^3$) is the film density, $H$(nm) is the film thickness, $\alpha$(grad) is the glancing deposition angle. The four curves at the left part and two curves at the right part differ by sets of random values of initial coordinates of silicon and oxygen atoms. The vertical dashed line denotes the upper boundary of the substrate, the horizontal dashed line denotes the experimental value of glassy SiO$_2$ density, that is 2.2 g/cm$^3$.

The density of the film fabricated using high-energy deposition is essentially higher than the density of low-energy deposited film. This density fluctuates near the average value of 2.4 g/cm$^3$ (the
right part of Fig.1) which is close to the density of the film deposited at normal flux incidence\(^{\circ}\) [7]. The low-energy deposition process produces films having fluctuating profiles (the left part of Fig.1). The profiles noticeably depend on the initial coordinates of deposited silicon and oxygen atoms. In contrary, in the case of high-energy deposition the two curves corresponding to different sets of initial coordinates are practically identical. The average value of density of low-energy deposited film is equal to 1,5 g/cm\(^3\) which is much lower than the density of the film deposited at normal flux incidence [7]. The decrease of thin film refractive index as compared to that of fused silica can be estimated using the Gladstone–Dale equation \([13]\) in the form of \(\Delta n = 0,21 \cdot \Delta \rho\), where \(\Delta \rho\) is the difference between film and glassy density. In our case \(\Delta \rho = -0,7\) g/cm\(^3\). So the variation of the refractive index in the case of low-energy deposition achieves \(\Delta n = -0,14\). It is worth noting that the empirical character of the Gladstone–Dale equation limits it in the prediction of relationships between density and refractive index of structures with high porosity.

The atomistic structure of deposited films is shown in Fig. 2. Substrate atoms are painted as yellow (Si) and red (O), deposited atoms are painted as grey (Si) and blue (O). The constant density surface is shown in Fig. 2. Density at a certain point is calculated as a sum of atomic contributions exponentially reducing with the growth of distances between atoms and this point.

Accordingly to the density profiles (Fig. 1) the porosity of deposited films is higher in the case of deposition with \(\alpha = 5^\circ\) than in the case of normal incidence deposition. There are no pores in the film obtained using the high-energy deposition (Fig. 1, right part).

**Figure 2.** Atomistic structure of deposited films, \(\alpha\) (grad) is the glancing deposition angle. The 3D film structure is shown at the left. Layers of atoms with x coordinates in the interval 4,5 nm < \(x\) < 5,5 nm are shown at the center and right side of the figure. Layers denoted as a) and b) differ by the initial sets of coordinates of deposited atoms.
4. Conclusions
The full-atomistic classical simulation of the glancing angle deposition of silicon dioxide films has been performed. Both low-energy and high-energy deposition processes are studied. Glancing angle deposition with low energy produces films with low density of about 1.5 g/cm$^3$ and with refractive index 1.32. Density profiles and visual representation of the low-energy deposited films show the essential dependence of their microscopic structure on deposition conditions.

The density of high-energy deposited films achieves 2.4 g/cm$^3$. This value is the same as that obtained earlier for the case of deposition with the atomic flux in the direction perpendicular to the substrate plane.

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