Stress distribution in highly porous SiO2 films: results of the molecular dynamics simulation

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Abstract. The stress distribution over the thickness of silicon dioxide thin films is studied using simulated thin film cluster. The atomistic cluster representing the film is deposited on a glassy substrate using the full-atomistic molecular dynamic simulation. The deposition angle is equal to 80°, which leads to the growth of a highly porous anisotropic film with low refractive index. The method for calculating the stress distribution is based on the integral relationship between the thickness-averaged stress and the stress distribution. In the present work, we focus on the application of this relationship to the atomistic modeling of stresses at the initial stage of thin film growth. It is found that in the transition layer between the substrate and the film the stress distribution function corresponds to the compressive stress. With the increase in film thickness, the stress distribution function changes sign and becomes tensile. It is shown that these results correspond to experimental data.

1. Introduction
Mechanical stresses arising in growing films significantly affect the optical coatings quality [1]. These stresses depend on the deposition conditions. One of the key parameters affecting the properties of thin films is the deposition angle $\alpha$. Normal deposition corresponding to the low values of $\alpha$ leads to the formation of dense and homogeneous structures. Deposition at angles greater than approximately 60° leads to the formation of highly porous films [2]. This deposition regime is called glancing angle deposition (GLAD). Due to the low reflectance and anisotropy of the refractive index, GLAD films are interesting for various applications in optics [3].

Due to the progress in high performance computing, it is now possible to perform a full-atomistic molecular dynamic (MD) simulation of the thin film deposition process. Based on the results of this simulation, various structural and mechanical parameters of the film can be calculated. In the present work, the stresses in the GLAD silicon dioxide films are investigated in the framework of a previously developed MD approach [4-7]. High-performance parallel computing allows to achieve film thicknesses of about 50 nm which is close to the technological thickness of one layer in multilayers optical coatings.

The stress distribution function, or in-plane stress, is defined as the stress in a thin layer parallel to the substrate plane. Layer position is specified by the vertical coordinate $h$. The thickness-averaged stress for different values of film thicknesses is calculated based on the results of the MD simulation of the deposition process. The dependence of the in-plane stress on vertical coordinate is determined through
the derivative of the product of averaged stresses and film thickness with respect to the vertical coordinate [1].

2. Method

The deposition of SiO$_2$ films is simulated using the step by step MD-based procedure [4-7]. At each injection step, silicon and oxygen atoms with stoichiometric proportion of 1:2 are inserted randomly at the top of the simulation box. Energy of the interatomic interaction is calculated in the frame of the empirical pairwise DESIL force field [6]. The next functional form of this force field is used:

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

Here $q_{ij}$ is the charge of $i(j)$-th atom, $q_S = -0.5q_{Si} = -0.65e$, $A_{ij}$ and $B_{ij}$ are parameters of Lennard-Jones potential for the van der Waals interaction, $r_{ij}$ is the interatomic distance, $A_{SiO} = 4.6\times10^{-8}$ kJ·(nm)$^{-12}$/mol, $A_{SiSi} = A_{OO} = 1.5\times10^{-6}$ kJ·(nm)$^{-12}$/mol, $B_{SiO} = 4.2\times10^{-3}$ kJ·(nm)$^{-6}$/mol, $B_{SiSi} = B_{OO} = 5\times10^{-5}$ kJ·(nm)$^{-6}$/mol.

The total number of silicon and oxygen atoms per injection step is equal to 180. The initial values of the silicon and oxygen atoms velocities correspond to the deposited atoms kinetic energies $E(Si) = 10$ eV and $E(O) = 0.1$ eV. These values are typical for the high-energy deposition processes like ion beam sputtering [8].

At each injection step, the $NVT$ (constant number of particles, volume and temperature) ensemble with the periodic boundary conditions is used. The vertical dimension of the simulation box increases every injection step by $\Delta h = 0.01$ nm to compensate for the increase in film thickness. The horizontal dimensions of the box remain unchanged. The Berendsen thermostat [9] is applied to keep the simulation cluster temperature constant at $T = 300$ K. The duration of one injection step is 6 ps and the time step of MD modeling is 0.5 fs.

Before the simulation of the deposition process the fused silica substrate is prepared by the melting-quenching procedure from an alpha-quartz crystal [7]. Horizontal dimensions of substrate clusters are equal to 20 nm and 60 nm, the vertical dimension is equal to 6 nm. Horizontal dimensions of the cluster in the simulation of film deposition are the same as those of the substrate. The deposition angle is equal to 80° to obtain GLAD film.

The calculation of the thickness-averaged stresses is organized as follows:

1. Simulation of the silicon dioxide film deposition. The number of injection steps is $N_i = 500$. This ensures a growth of layer with the thickness of approximately 5 nm.
2. Simulation of the deposited cluster in the $NVT$ ensemble and calculation of the pressure tensor components $p_{ex}(yy)$. The initial state for the simulation is the final state after the completion of $N_i$ injection steps. The length of the MD trajectory for averaging of $p_{ex}(yy)$ values is taken equal to 100 ps. The thickness-averaged stress tensor components are calculated as follows:

$$ \sigma_{ex(yy)} = -p_{ex(yy)}(L/H) $$

where $L$ and $H$ are the vertical dimension of the simulation box and film thickness, respectively (Fig. 1). The multiplier $(L/H)$ in Eq (2) provides a pressure correction taking into account the empty volume at the top of the box.
3. Stages 1-2 are repeated until the film thickness achieves a specified value. Achieving the thickness of about 40 nm requires approximately 4000 injection steps. Total number of atoms in the final cluster is about two million.
The stress distribution function (in-plane stress) $\sigma_{h,xx}(h)$ throughout the vertical coordinate $h$ is related to thickness-averaged stress $\sigma_{xx}(H)$ by the following equation [1]:

$$\sigma_{xx}(H) = \frac{1}{H} \int_0^H \sigma_{h,xx}(h) \, dh$$  \hspace{1cm} (3)

where $H$ is the thickness of the deposited film, $h < H$. Multiplying both parts of the Eq (3) by $H$ and differentiating with respect to $H$ we obtain the relationship between the thickness-averaged stress and the in-plane stress:

$$\frac{d}{dH} (H\sigma_{xx}(H)) = \sigma_{h,xx}(H)$$  \hspace{1cm} (4)

MD simulation is performed using the GROMACS package [10]. Components of the pressure tensor are calculated using the kinetic energy and virial tensors [10]. For visual analysis of the atomistic structures the Visual Molecular Dynamic (VMD) package is used [11]. The simulation is carried out using equipment at the shared research facilities of high performance computing resources at Lomonosov Moscow State University [12].

3. Results and discussion
The resulting deposited structure is shown in the central part of Fig. 2.

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The deposition under the angle $\alpha = 80^\circ$ leads to the formation of a high porous anisotropic structure. The density profile (right side of Fig. 2) shows a significant decrease in the density of GLAD film compared to the density of the normally deposited film, equal to 2.4 g/cm$^3$. This structure is typical for the deposition under large values of $\alpha$ [1,2].

The results of the average stress calculations are shown in Fig. 3. At the initial stage of film deposition the stress in compressive. With an increase in the film thickness, a shadow effect [1] appears, which leads to the formation of separated slanted columns and voids between these columns in the film structure (Fig. 2, central part). The voids absorb stresses arising in the film due to interaction with deposited high-energy Si atoms. This leads to a decrease in the absolute values of the stress and a change in the sign of stress of $\sigma_{yy}$ component. The of $\sigma_{xx}$ remains compressive in the studied interval of film thickness.

![Film thickness, $H$(nm)](image)

**Figure 3.** Dependencies of the thickness-averaged stress tensor components $\sigma_{xx}(yy)$ on the film thickness.

The components of the in-plane stress tensor are calculated using Eq (4). The results are shown in Fig. 4.

![Vertical coordinate, $h$(nm)](image)

**Figure 4.** Dependencies of the in-plane stress tensor components on the vertical coordinate $h$, $\alpha$ is the deposition angle. The total thickness of the deposited film and substrate is 45 nm.
If the vertical coordinate is less than 15 nm, both components of the stress tensor are compressive. The transition layer between the substrate and film makes a significant contribution to the volume-averaged film stress. With further vertical coordinate growth, the stress becomes tensile for both components. The change of the stress sign with growth of vertical coordinate was observed in the experiments [1].

The difference in the values of $\sigma_{h,xx}$ and $\sigma_{h,yy}$ indicates the anisotropy of the GLAD film properties. This is due to the anisotropy of the film structure, see the central part of Fig. 3.

4. Conclusion

The distribution of the in-plane stress in the GLAD silicon dioxide film has been studied using thin film clusters simulated by the previously developed MD based method. The method of the in-plane stress calculation is based on the integral relationship between the thickness-averaged stress and the in-plane stress.

It is shown that the in-plane stress in the transition layer between the substrate and the film is compressive. The stress changes sign and becomes tensile when the thickness of the deposited layer exceeds approximately fifteen nanometers. This result is in agreement with the available experimental data.

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