Differences in the properties of fused silica and silicon dioxide films: results of the atomistic simulation

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Abstract. The previously developed atomistic method of the thin film deposition simulation is used to study the differences of the structural and mechanical properties of silicon dioxide thin films and fused silica. It's found that the bulk modulus, Young modulus and Poisson’s ratio are higher for high-energy deposited film than for low-energy deposited film and fused silica. All calculated values are in accordance with experimental data. The excess of the high-energy deposited film density above density of low-energy deposited film and fused silica in discussed in terms of the radial distribution function and cumulative number function.

1. Introduction

The study of differences in the structural and mechanical properties of the substrate and the growing on this substrate film is important for improving the technology of optical coatings production, in particular, for reducing mechanical stresses in the coatings. Experimental study of these differences may be still a great challenge. At the same time, up today the structure and properties of the deposited films are widely studied using the classical atomistic simulation methods [1-3]. Due to the progress in high performance computing, it is possible to perform the atomistic simulation of thin films deposition process on the length of about a several tens nanometers that is close to the technologically sensible thicknesses.

In the present work the previously developed method of molecular dynamic simulation of the thin film deposition process [4-6], is used to study structural and mechanical properties of deposited silicon dioxide thin films and fused silica which is often used as a substrate. Structural properties are analyzed using the radial distribution function and cumulative number function. Mechanical properties are analyzed using the calculation of the bulk modulus, Young modulus and Poisson’s ratio of the high- and low-energy deposited films and fused silica. The obtained values are compared with experimental ones.

2. Simulation method

Simulation of the thin films deposition is performed using the classical molecular dynamics approach and is organized as a step-by-step procedure [4-6]. The fused silica cluster is used as the substrate. Both film and substrate are described the DESIL force filed [4]. At every deposition step the periodic boundary conditions with \(NVT\) ensemble (constant number of atoms, volume and temperature) are applied with the following MD parameters: 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 SiO2 groups per one injection cycle is 25. The Berendsen thermostat [7] is used to keep the simulation box temperature constant. Horizontal sizes of the substrate are 9 nm and 10 nm, substrate thickness is equal to 5.7 nm. MD simulation is performed using the GROMACS package [8]. The electrostatic part of the interatomic energy is calculated using the Particle Mesh Ewald [9] method, pme_order parameter is equal 8.

Simulation is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University [10].

3. Results and discussion
Radial distribution functions (RDF) $g(R)$ are calculated using the standard GROMACS facilities [8]. To obtain the film cluster for RDF calculation, the next steps should be performed:

1. Simulation of the SiO$_2$ thin films deposition process as described in Sec. 2. The film thickness achieved in the present simulation is about 40 nm.
2. Preparation of the thin film cluster from the deposited structure. To avoid the surface effects, RDFs are calculated for the cluster inside the deposited film (black square in Fig. 1). For the correct treatment of the electrostatic interactions the total charge of the prepared cluster should be equal to zero.
3. Relaxation of the prepared cluster. The atomistic structure in the top and bottom areas of the cluster should be equilibrated due to changes in the structure surrounding the cluster outside their bottom and top boundaries. Asymmetric NPT ensemble (constant number of atoms, pressure and temperature) providing independent changes in vertical and horizontal sizes of the cluster is applied.
4. Simulation of the relaxed cluster in symmetric NPT ensemble during 200 ps and calculating of the Si-O, Si-Si and O-O RDF’s.

All of RDF’s simulation steps are shown schematically in Fig. 1.

*Figure 1. To the description of the radial distribution function calculation. See the text for the details.*
Additional structural information is provided by the cumulative number function, \( n(R) \) [8], which is defined as average number of particles within a distance \( R \) with respect to the reference atom, Si or O. In accordance with the definition, \( n(R) \) is proportional to the integral of \( g(R) \) in the range from zero to \( R \).

Results are shown in Figs. 2, 3.

**Figure 2.** Radial distribution functions \( g(R) \) of fused silica (black solid curves) and film (black dotted curves) and cumulative number function \( n(R) \) of fused silica (green solid curves) and film (green dotted curves). The secondary axis for \( n(R) \) is on right side of graphs. Energy of deposited Si atoms is equal 10 eV.

Fig. 2 shows that for the high-energy deposited film the RDF’s peaks are lower and wider than for the fused silica. The peak positions for film and fused silica differ insignificantly. This corresponds to the practically identical values of the averaged distances in the first coordination sphere for film and fused silica (Tab. 1). At the same time the film density exceeds the fused silica density for the value 0.16 g/cm\(^3\) (right column in Tab.1). This result is in accordance with known from the previous simulations [3,5].

The \( n(R) \) functions explain why the noticeable difference of fused silica and film density is consistent with practically identical values of average distances between nearest atoms. All \( n(R) \) functions for the film (dotted curves) exceed \( n(R) \) for fused silica (solid curves) if the \( R \) value is more than the distance corresponding to the first RDF peak (Fig. 2). Since the cumulative function \( n(R)/R^{3*3} \) is proportional to the density in the limit \( R \to \infty \), the difference in the film and fused silica density is due to the changes in the third and subsequent coordination spheres, that can be described in terms of torsion angles Si-O-Si-O, orientation of the structural tetrahedrons and so on. At the same time parameters of the first and second coordination spheres (Si-O bond length and valence angles or nearest Si-Si and O-O distances) are the same for films and fused silica.

**Table 1.** Structural parameters of the fused silica and high-energy deposited silicon dioxide film. Average distances correspond to the first peak positions of RDF’s in Fig. 2.

|               | \( R \) (Si-O), nm | \( R \) (O-O), nm | \( R \) (Si-Si), nm | Si-O–Si angle,° | Density, g/cm\(^3\) |
|---------------|-------------------|------------------|-------------------|-----------------|-----------------|
| Film          | 0.164             | 0.268            | 0.309             | 145             | 2.36            |
| Fused silica  | 0.164             | 0.269            | 0.310             | 145             | 2.20            |

The influence of the annealing to the structural properties of the deposited films is demonstrated in Fig. 3. The simulation of the post-deposited annealing is organized as described in [11], annealing temperature is equal 1300 K. As shown in Fig. 3 annealing results in reducing of the \( n(R) \). This correlates with reducing of the film density known from the previous simulations [11]. Average values of \( R \) (Si-O), \( R \) (O-O) and \( R \) (Si-Si) practically do not change under the annealing.
Figure 3. Radial distribution functions $g(r)$ of “as deposited” film (black solid curves) and annealed film (black dotted curves) and cumulative number function $n(r)$ of “as deposited” film (green solid curves) and annealed film (green dotted curves). See the text for the details.

To study mechanical properties, the bulk modulus, Young modulus and Poisson’s ratio are calculated. The bulk modulus $K$ is calculated as follows [12]:

$$K = -V \left( \frac{\partial P}{\partial V} \right)_T \tag{1},$$

where $V$ is the volume of the simulation cluster, $\partial P$ is the variation of the external pressure applying to the cluster surface, $\partial V$ is the variation of the cluster volume due to the applied pressure.

Two expressions were used for the Young modulus calculation. First of them is based on the relationship between $K$ and $E$ [12]:

$$E = 3K (1-2\beta) \tag{2},$$

where $E$ is the Young modulus and $\beta$ is the Poisson’s ratio for silicon dioxide glassy, see Eq. (4) below. The second way for the $E$ calculation is based on the Young modulus definition [12]:

$$E = P/(\Delta L/L_0) \tag{3},$$

where $P$ is the pressure applied to the vertical direction of the cluster, $L_0$ and $\Delta L$ are the initial vertical dimension of the cluster and its variation, respectively.

Poisson’s ratio is calculated as the ratio of transverse contraction strain to longitudinal extension strain in the direction of stretching force [12]:

$$\beta = -(\Delta d/d)/(\Delta L/L) \tag{4},$$

where $d$ and $\Delta d$ are the transverse size and its variation, $L$ and $\Delta L$ are the longitudinal size and its variation. Stretching force is applied in the longitudinal direction.

Results of the calculation are presented on Fig. 4.
As shown in Fig.4 values of bulk modulus, Young modulus and Poisson ratio for the high-energy deposited film are higher than for the low-energy deposited film and fused silica. Values of Young modulus calculated using Eq. (3) are higher than for the case of using Eq. (2). Experimental value of Young modulus of dense silicon dioxide films and fused silica are equal to 74 GPa [13] and 69 GPa [14] respectively. So Eq. (3) overestimates $E$ approximately for 30 GPa while Eq. (2) gives the value of $E$ that is close to the experimental one. Reduction of the energy of deposited Si atoms results in the decrease of films density and decrease of the values of all modulus (Fig. 4). This result is in accordance with the experiment [13]. Experimental values of Poisson's ratio $\beta$ of SiO2 films and fused silica are equal to 0.19 [15] and 0.17 [16]. Calculated values of $\beta$ (Fig. 4) are higher than experimental ones, but the excess of the film's Poisson's ratio values over the fused silica ones is in accordance with experiment.

4. Conclusions
Differences in the structural and mechanical properties of silicon dioxide films and fused silica are analyzed using the classical molecular dynamic approach. It is found that the excess of the density of high-energy deposited silicon dioxide film over the fused silica density is explained by differences in the structure in the third and subsequent coordination spheres. At the same time such parameters of the first coordination sphere as bond lengths, valence angles are almost the same for the film and for the fused silica. Bulk modulus, Young modulus and Poisson's ratio are higher for the high-energy deposited film than for the low-energy deposited film and fused silica. The calculated values of structural parameters and bulk modulus are in accordance with experimental results.
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