Journal of Non-Crystalline Solids 448 (2016) 1–5

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Full-atomistic nanoscale modeling of the ion beam sputtering deposition of SiO_2 thin films

F.V. Grigoriev *, A.V. Sulimov, E.V. Katkova, I.V. Kochikov, O.A. Kondakova, V.B. Sulimov, A.V. Tikhonravov

RCC M.V. Lomonosov MSU, Russian Federation

ARTICLE INFO

Article history:
Received 16 April 2016
Received in revised form 8 June 2016
Accepted 25 June 2016
Available online 5 July 2016

Keywords:
Optical films
Ion beam sputtering
Deposition
Molecular dynamics
Silica glass

ABSTRACT

The previously developed high-performance parallel method of the atomistic simulation of the ion beam sputtering deposition process is applied to the SiO_2 thin films. Structural properties of deposited films such as density, concentration of point defects, ring statistics, as well as effects arising from the interaction of high energy sputtered Si atoms with the growing film are discussed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Modern optical coatings typically consist of layers with low and high refractive indices. Silicon dioxide (SiO_2) is widely used as a low-index material, while several other metal oxides are used as high-index materials. For this reason, a special attention has been given to the investigation of structural properties of oxide films and specifically of SiO_2 films produced by the ion beam sputtering (IBS) process [1].

The understanding of influence of IBS parameters on structural and optical properties of SiO_2 and other oxide films is important for improving of the currently used deposition technologies. Existing experimental techniques are focused on studying integral film structural and optical properties, such as density, refractive index, etc. At the same time, the tremendous progress in high-performance computing enables one to investigate a deposition process at the atomistic level. Previously, we offered the molecular dynamics (MD) approach developed for the full-atomistic simulation of the deposition of thin films with thicknesses of $10 \div 100$ nm [2]. The approach is based on the original computationally efficient force field and on the parallelization of the simulation process at the model level. In the present paper, we apply the developed approach to the investigation of structural properties of deposited silica films: geometry of interatomic bonds, density profiles, concentration of point defects, and ring statistics. The dependence of these characteristics on the energy of deposited atoms is discussed.

* Corresponding author.
E-mail address: fedor.grigoriev@gmail.com (F.V. Grigoriev).

http://dx.doi.org/10.1016/j.jnoncrysol.2016.06.032
0022-3093/© 2016 Elsevier B.V. All rights reserved.

2. Simulation method

The MD simulation of deposition process is organized as a step-by-step procedure as described in Ref. [2]. The simulation procedure duration is proportional to $N^2 \ln N$ [2], where N is the number of deposited atoms. It is also dependent on the force field (FF), which is used for calculation of potential energy of interatomic interactions. Therefore, a computational efficiency of the FF plays an important role for modeling of clusters consisting of about 10^6 atoms. For this reason, the pair-wise (two-body) FF with a simple expression for the potential energy of interatomic interactions appears to be suitable for modeling of large clusters. Until today, a number of pair-wise potentials for SiO_2 have been elaborated [3–7]. Unfortunately, most of these potentials feature unphysical properties at small interatomic distances r due to presence of the uncompensated $-C/r^6$ term in their expressions. For the well-established BKS (Beet, Kramer, van Santen [7]) force field, the barrier between physical and unphysical parts of the potential for the Si—O pair is 5000 K (0.45 eV) [4]. High-energy Si atoms can easily get over this barrier. The pair-wise Morse potential (MP) without $-C/r^6$ term was also used for SiO_2 MD simulations [3]. However, the simulation of nanoparticles with MP showed that their density achieved 3.0 g/cm^3 [8]. In our simulation experiments with MP, the 2.7 g/cm^3 density of deposited SiO_2 films was obtained. These values substantially exceed the experimental density of silica glass, which is equal to 2.20 g/cm^3.

Taking into account the above-mentioned problems, we elaborated the original DESIL (Deposited films of SILica) FF for simulation of the IBS process. The potential energy of interatomic interactions in DESIL

Table 1
Parameters of the Lennard–Jones potential of the DESIL force field.

	Si—O	Si—Si	O—O
C_{12}, kJ·nm^{12}/mol	$4.6 \cdot 10^{-8}$		$1.5 \cdot 10^{-6}$
C_6, kJ·nm^6/mol	$4.2 \cdot 10^{-3}$		$5.0 \cdot 10^{-5}$

FF is expressed as:

$$U = \frac{q_i q_j}{r_{ij}} + \frac{C_{12(ij)}}{r_{ij}^{12}} - \frac{C_{6(ij)}}{r_{ij}^{6}}, \tag{1}$$

where q_i and q_j are charges of ith and jth atoms, $C_{12(\mathrm{ij})}$, $C_{6(\mathrm{ij})}$ are parameters of the Lennard–Jones (LJ) potential, and r_{ij} is an interatomic distance. The particle mesh Ewald (PME) method [9] is used for the electrostatic interaction, and the cutoff radius for LJ potential is chosen equal to 1 nm.

The LJ potential provides a reasonable accuracy of description of the non-polar part of interatomic interactions in a wide interval of interatomic distances, which is important for the simulation of the IBS process. Initially, the LJ potential was developed for noble elements, but later it was used in FF for organic compounds (see OPLS [10], AMBER [11]) and in the universal FF [12].

The procedure of adjusting parameters of DESIL FF is organized as follows. As in Ref. [3], the charges of silicon and oxygen atoms are taken equal to $q(\mathrm{Si}) = 1.3e$ and $q(\mathrm{O}) = -0.65e$, where e is the elementary charge. Initial values of LJ parameters are chosen so as to fit the general curves of the BKS potential. The α-quartz structure is used as an initial geometry of SiO_2 cluster. The silica glass structure was then obtained from the crystalline structure using the MD melting-quenching procedure [2]. Initial LJ parameters are modified using iterative fitting procedure so as to satisfy the following conditions:

1. To preserve the α-quartz structure after a local optimization.
2. To reproduce silica glass density (2.20 g/cm^3) using the MD simulation in the NPT (constant number of the particles, pressure, and temperature) ensemble.
3. To reproduce the radial distribution function (RDF) and the SiO_4 tetrahedrons network of the obtained silica glass structure.

The final set of adjusted parameters is presented in Table 1.

All simulation experiments were performed on the supercomputer 'Lomonosov' of the Supercomputing Center of Lomonosov Moscow State University [13]).

3. Results and discussion

3.1. Interaction of a single sputtered Si atom with the substrate

For the description of substrate and film temperature relaxation in the vicinity of a deposition event, we introduce the averaged local temperature function T_L:

$$T_L(R, \Delta\mathrm{R}, t, \Delta\mathrm{t}, N) = \frac{1}{N\Delta t} \sum_{i=1}^{N} \int_{t}^{t+\Delta\mathrm{t}} T_i(R, \Delta\mathrm{R}, \tau) d\tau, \tag{2}$$

where t is the time passed since the collision of the sputtered Si atom, Δt is the averaging time interval, R is the radius of a half-spherical layer around the sputtered atom (Fig. 1, right side), ΔR is the layer thickness, $R = 0$ corresponds to the collision point, T_i (R,ΔR,τ) is the temperature at the moment τ, i is the MD trajectory number, and N is the number of MD trajectories. For the dependencies shown in Fig. 1, the next parameters are taken: $\Delta t = 1$ ps, $\Delta R = 0.1$ nm, $N = 100$, t varied from 0 to 10 ps with the step of 1 ps, and R varied from 0.2 nm to 1 nm with the step of 0.1 nm.

For the Si atom with the kinetic energy of 100 eV, the averaged local temperature monotonically decreases with time and approaches the substrate temperature in the time interval of about 10 ps after the collision instant (Fig. 1, right side). This time interval substantially exceeds the thermalization time of the sputtered atom that was found to be about 1 ÷ 2 ps [2,14]. Substantial increase of the substrate/film local temperature is observed at distances $R < 1$ nm (Fig. 1, left side). T_L is well above the softening point of silica glass (1600 °C) in the local area with the characteristic size ≈0.5 nm around the collision point. We refer to this effect as to the "local melting (LM)" effect. Similar dependencies are obtained for sputtered Si atom with energy $E = 10$ eV, but in this case, T_L is less than in the case of $E = 100$ eV.

We believe that the LM effect can facilitate relaxations of the substrate and growing film structures. As a result of collisions of high-energy Si atoms with the surface, point defects can be formed, e.g., non-bridging oxygen atoms, oxygen vacancies, and threefold- and twofold-coordinated silicon atoms. The relaxation of structural defects requires heating of the produced films that leads to breaking chemical bonds in local defects and forming Si—O bonds. To ensure this relaxation in practice, deposited films are often subjected to the annealing procedure [15]. With respect to influence on the film structure, the LM effect and the annealing procedure are analogous but with essential differences. The LM effect is a sequence of short-term local events while annealing procedure may have duration of up to several days and involves structure

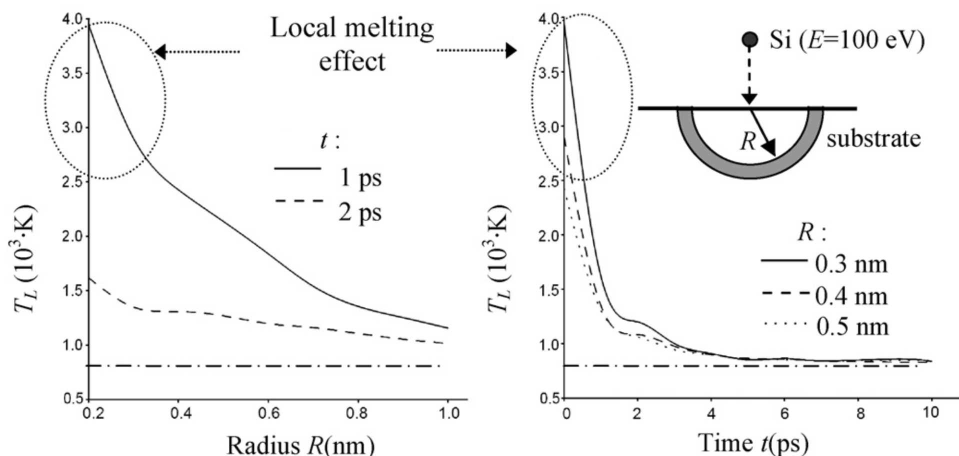

Fig. 1. Dependencies of averaged local temperature T_L on time (right side) and on the radius of a half-sphere around collision point (left side). Horizontal line corresponds to the substrate temperature (800 K), E—initial kinetic energy of the sputtered silicon atoms.

Download English Version:

https://daneshyari.com/en/article/1480264

Download Persian Version:

https://daneshyari.com/article/1480264

Daneshyari.com