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CONDENSED MATTER PHYSICS

Force Fields for Molecular Dynamics Simulation of the Deposition of a Silicon Dioxide Film

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Abstract—In this work we compare two force fields that are intended for the molecular dynamics simulation of the process of the deposition of silicon dioxide thin films. Analysis of the structural characteristics (the density and radial distribution function) of a glassy silicon dioxide cluster that was used as a substrate and a deposited film is carried out. It is shown that the DESIL force field in which the Van der Waals interaction is described by the Lennard–Jones potential turns out to be more suitable for modeling the process of deposition.

Keywords: high-performance simulation, molecular dynamics, thin film growth, deposition process, silicon dioxide force fields.

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INTRODUCTION

Multilayer optical coatings are widely used in modern optical instruments and devices. Usually, such coatings consist of alternating layers with relatively high and low refractive indexes [1]. Silicon dioxide is one of the most common materials for layers with a low refractive index.

The structural and optical properties of films are substantially dependent on the technological parameters of the process of deposition, namely the energy and angular-velocity distributions of atoms that are deposited onto the substrate, substrate temperature, pressure, gas composition in the vacuum chamber, etc. Currently, one of the most promising methods to obtain a uniform and dense film is the method of ion-beam sputtering (IBS), in which the energy of silicon atoms that are incident on the substrate and previously deposited layers of film reaches several tens of eV [2]. In terms of improving the technology of high-energy ion beam deposition, it is an urgent problem to study the dependence of the structural and optical properties of a film on the values of the technological parameters of the process of deposition. Experimental study of this dependence is difficult due to the small thickness and ordered structure of the film; thus, the use of methods of atomistic simulations in this case is appropriate.

When choosing a method of modeling one should take the fact into account that the structural heterogeneity of the film, which affects its optical properties, has characteristic dimensions on the order of several tens of nanometers. A cubic cluster of silicon dioxide with a characteristic size on the order of 100 nm contains approximately 10^8 atoms. At the moment, modeling of clusters with such a number of atoms is possible only within the framework of classical molecular dynamics (MD) and Monte Carlo (MC) modeling using parallel computing technology on supercomputer systems.

Modeling of film-growth techniques at the atomistic level has been carried out since the 1970s (see [3] and references [3–17] therein). In recent years, with the development of computational tools, especially for multiprocessor clusters, it is possible to perform simulations of clusters of a relatively large size with the use of a three-body force field, which allows one to describe chemical reactions on the surface of the film. In [4], simulation of silicon dioxide films using such force fields was conducted. The effect of increasing the film density with an increasing kinetic energy of deposited silicon atoms has been demonstrated. In [5], using the MD method, the surface properties of films of titanium dioxide with clusters that contained up to 2.4×10^4 atoms were simulated. In [6], using the MD and MS methods, the structural characteristics of the films (density, roughness, pore concentration) were investigated on the scale of approximately tens of nanometers with a number of cluster atoms of approximately 10^6.

The adequacy of MD or MC simulations, as well as their numerical efficiency, is largely determined by the force field that is selected for calculating the potential energy of the atomic interactions of the film and substrate. In [7], a fairly detailed overview of various force

fields that have been created for silicon dioxide was presented and the conclusion was made that the use of a two-particle force field with a relatively simple form is most appropriate when modeling deposition. In this case, each term in the expression of the potential energy depends on the distance between two atoms. In [7], the original DESIL force field was described. In this case, the potential energy of an atomic pair is represented by the sum of the Coulombic contribution that describes the interaction of point charges that are centered on the atoms and the Lennard–Jones potential that describes the non-electrostatic part of the interaction energy. The DESIL force field reproduces the key structural characteristics of gaseous silicon dioxide with a good accuracy (density under normal conditions, the tetrahedral motif in the structure of a continuous disordered mesh, the Si–O, Si-O-Si and O–Si–O bond angles, and the positions of the first and second peaks of the radial distribution function). At the same time, the Lennard–Jones potential energy of exchange interaction at small distances is described by a term that is proportional to $1/r^{12}$ (r is the interatomic distance) instead of a more accurate exponential function of distance. Such inaccuracy may affect the description of the kinematics of interaction of atoms that approach one another at short distances because of the large initial energy (a few tens of eV).

In the present work, the DESIL_B force field is presented, within which the Buckingham potential [8], which contains an exponential term for calculating the exchange interaction, is used to describe the non-electrostatic potential energy of the interatomic interaction. According to the results from modeling clusters of various sizes, the structural characteristics of glassy silicon dioxide were obtained within DESIL_B. The advantages and disadvantages of the DESIL and DESIL_B force fields are discussed.

1. SIMULATION METHOD

Modeling was carried out using classical MD. The procedure of spraying (injection of silicon and oxygen atoms, distribution of their initial positions and velocities, boundary conditions, restrictions on the movement of substrate atoms) as implemented in the original KUVALDA program was described in detail in [7]. For the molecular-kinetic part of this procedure, the GROMACS program [9] is used as an external procedure.

Simulation was performed at Moscow State University using the LOMONOSOV supercomputing complex [10].

2. RESULTS AND DISCUSSION

The potential energy of the interatomic interaction pair is approximated by the Buckingham potential of the form

$$U_B = \frac{q_i q_j}{r_{ij}} + A_{ij}\exp(-b_{ij}r_{ij}) - \frac{c_{ij}}{r_{ij}^6}. \quad (1)$$

The force field of silicon dioxide with the functional form (1) was proposed in [11]. The parameters of the potential were determined from the results of quantum chemical modeling of small molecular clusters; this allowed the reproduction of their geometric characteristics. However, when modeling the process of sputtering, the force field must reproduce the bulk structural properties, such as the radial distribution function and density (RDF). The parameters in [11]

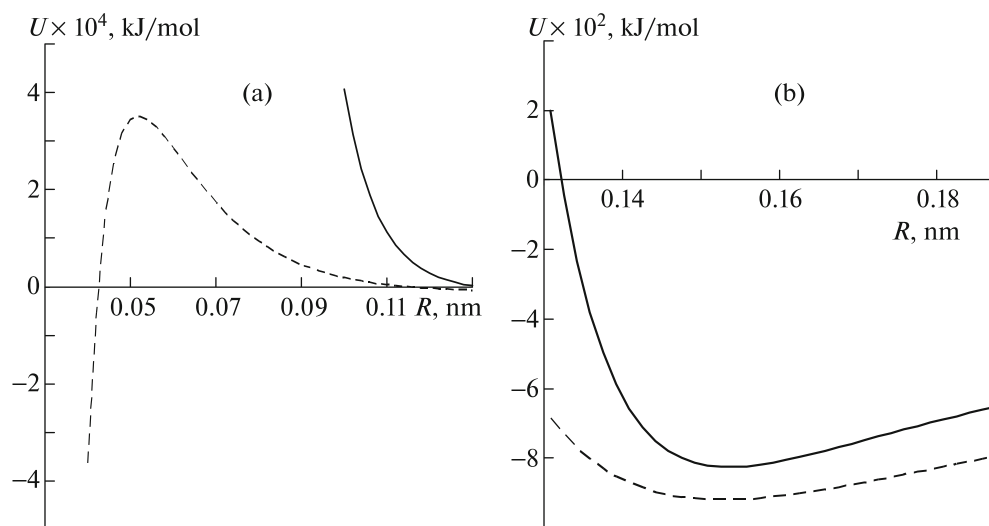

Fig. 1. The potential energy of the interaction of the silicon and oxygen atoms, U (kJ/mol), depending on the distance, R, between them in nm; the solid line is the DESIL force field with the Lennard–Jones potential, the dashed line is the DESIL_B force field with (1).

were taken as the primary ones and then changed in order to satisfy these requirements. The fitting procedure for determining parameters was described in [3].

The potential energy of the interaction between silicon and oxygen atoms depending on the distance is shown in Fig. 1a and 1b. It can be seen (Fig. 1a) that at small distances the Buckingham potential has a non-physical behavior due to the fact that the sharp increase of the term is inversely proportional to the sixth power of distance. With regard to the problem of thin-film deposition, such non-physical behavior poses difficulties, since at an energy of ~10–100 eV the atoms that are incident on the film may come closer at a short distance. The barrier in the Buckingham potential should be large enough so that the interatomic distances could not reach the values that correspond to this nonphysical behavior during the interaction of energetic silicon atoms with the substrate and the previously deposited layers of the film. The energy of 100 eV corresponds to 9.65×10^3 kJ/mol, which is less than one-third of the barrier height, viz., on the order of 3.5×10^4 kJ/mol (Fig. 1a). As subsequent modeling has shown, this is enough to escape the region with the nonphysical Buckingham's potential. Table 1 shows the calculated DESIL_B force field and parameters of potential (1) known from [11]. The charges in the DESIL_B model are considerably less than in [11], while the value of coefficient c_{ij} for the Si–O pair is significantly higher. Within the DESIL-B force field, the Buckingham potential decreases faster than in [11] due to the larger value of the parameter b_{ij}. The parameters of the DESIL_B force field with a Lennard–Jones potential are given in Table 2.

Within the DESIL_B force field, the geometry of a cluster with an initial α-quartz structure remains mainly unchanged upon local optimization with periodic boundary conditions (Fig. 2). Some distortions

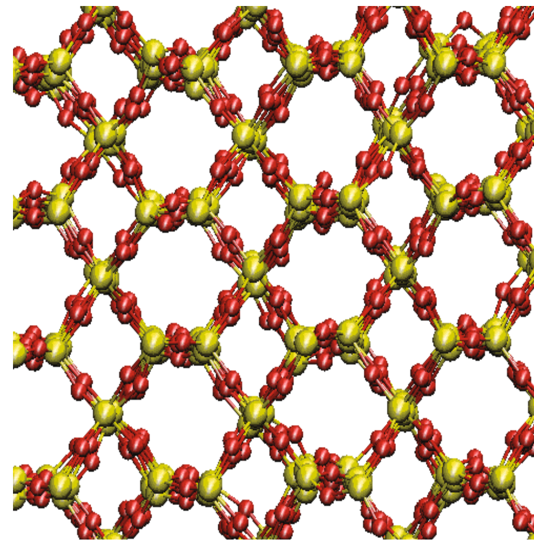

Fig. 2. The atomic structure of crystalline silicon dioxide within the DESIL-B force field.

are due to the fact that the Si–O bond length that corresponds to the minimum potential energy of the cluster is equal to 0.168 nm, which is 0.004 nm higher than the experimental value. Upon local optimization, the density does not change and equals 2.65 g/cm^3, i.e., it corresponds to a crystalline modification of α-quartz.

The substrate structure of glassy silicon dioxide was obtained using the DESIL_B force field and the MD procedure described in [7, 12]. The cluster of a substrate with a thickness of 2 nm contains 9×10^4 atoms and has horizontal dimensions of 26 × 23 nm.

The radial distribution function of substrate atoms is shown in Fig. 3. When using the Buckingham potential (the DESIL_B force field), the height of the first peak of the RDF is nearly two times less than for

Table 1. The parameters of the DESIL_B [11] force fields. The Buckingham's potential (1) is used to describe the Van der Waals interaction

i–j	A_{ij}, kJ/mol		b_{ij}, 1/nm		c_{ij}, kJ nm^6/mol		Atomic charges (e)	
	DESIL_B	[10]	DESIL_B	[10]	DESIL_B	[10]	DESIL_B	[10]
O–O	5×10^5	1.34×10^5	37.0	27.6	0	1.69×10^{-2}	1.6 (Si)	2.4 (Si)
Si–Si	6×10^5	–	38.0	–	0	–	–0.8 (O)	–1.2 (O)
Si–O	2.1×10^6	1.737×10^6	60.8	48.73	2.0×10^{-3}	1.29×10^{-2}		

Table 2. The parameters of the DESIL force fields [7]. The Lennard–Jones potential is used to describe the Van der Waals interaction

	Si–O	Si–Si , O–O	Atomic charges (e)
c_{12}, kJ nm^{12}/mol	4.6×10^{-8}	1.5×10^{-6}	$q_{Si} = 1.3$
c_6, kJ nm^6/mol	4.2×10^{-3}	5.0×10^{-5}	$q_O = -0.65$

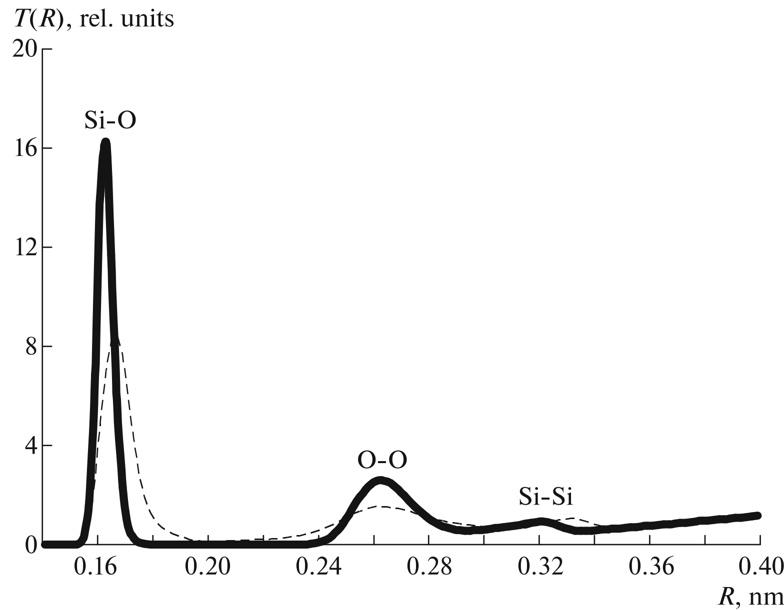

Fig. 3. The radial-distribution function $T(R)$ (relative units) for glassy silicon dioxide depending on the distance, R (nm), between the atoms. The solid line is the DESIL force field, the dashed line is the DESIL_B force field.

the RDF with the use of the Lennard–Jones potential (the DESIL_B force field) and its position is shifted by approximately 0.004 nm to the right. At the same time, the height of the second peak in DESIL_B is significantly lower, while their positions nearly coincide. Both the first and second peaks of the RDF in the case of the Buckingham's potential are more blurred, which points to the great fluctuations in the Si–O bond lengths (first peak) and the distances between the nearest oxygen atoms (second peak). For both potentials, the areas under the first peak of the RDF are the same. This means that the concentration of tetra-coordinated silicon atoms is same, as it should be. The positions of the second peak coincide with the experimental ones [13], while the position of the first RDF peak with Lennard–Jones potential is closer to the experimental one.

Modeling the process of thin-film deposition was carried out in correspondence with the methodology in [7]. Groups of silicon and oxygen atoms were injected into the area of modeling every 6 ps, while the substrate temperature was kept constant at 500 K. The energy of the deposited silicon atoms is 10 eV and the energy of the oxygen atoms corresponds to a temperature of 1000 K.

Figure 4 shows the film density that depends on the total thickness of the substrate and film. In the case of the DESIL force field, the dependence is close to the one that was obtained earlier in [7]: the film density does not exceed 2.5 g/cm^3, the thickness of the substrate–film and film–vacuum transition layers is approximately 1.5 nm. For the dependence that was obtained using the DESIL_B force field the film density significantly exceeds the substrate density (by 1 g/cm^3).

As the structural analysis shows, this excess is caused by the occurrence of a large number of penta-coordinated silicon atoms (up to 40% of the full number). Moreover, the average value of the Si–O bond length increases from 0.168 to 0.178 nm. The presence of silicon atoms with such Si–O bond characteristics has no experimental confirmation. It is likely an artifact of the force field. Perhaps the formation of configurations with penta-coordinated Si atoms and great concentration is associated with the flat shape of the Buckingham potential near the minimum of interaction energy of oxygen and silicon atoms (Fig. 1b). This leads to a greater variety in the geometry of the short-range order of a deposited film as compared to the glassy state. It is worth noting that when modeling deposition using the Lennard–Jones potential, the concentration of penta-coordinated silicon atoms is less than a quarter of a percent. The concentration of one-coordinated oxygen atoms and three-coordinated silicon atoms are several times lower with the use of Lennard–Jones potential as compared to the use of the Buckingham potential.

Thus, the DESIL force field seems to be preferable in modeling deposition of SiO_2 thin films, whereas both fields can be used in modeling the bulk samples of glassy SiO_2.

We carried out a comparison of the numerical effectiveness of the DESIL_B force field with the Lennard–Jones potential and the DESIL_B force field with Buckingham's potential. The results are shown in Fig. 5. The trajectory length from the MD

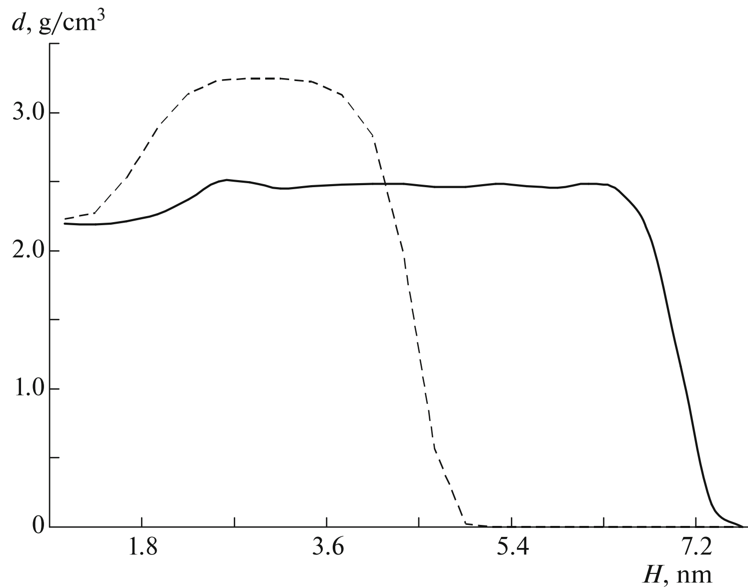

Fig. 4. The density, d (g/cm^3), of the deposited film with allowance for the substrate (an initial depth of 2 nm) depending on the distance, H (nm), from the bottom of the film. The solid line is the DESIL force field, the dashed line is the DESIL_B force field.

simulation of a substrate cluster that contains 9×10^4 atoms was equal to 500 ps with a step of 1 fs. The simulation was performed using the GROMACS program and the NPT ensemble with a constant particle number, pressure, temperature, and periodic boundary conditions.

As one can see from the dependences in Fig. 5 (ceteris paribus), the calculation time with Buckingham's potential is approximately two times greater than the calculation time with the Lennard–Jones potential. Such a result is quite expected, since the calculation of an exponential function needs more time than the calculation of a power function. The numerical effectiveness that is calculated by the formula $a(N) = \frac{T(16) \cdot 16}{T(N) \cdot N}$ for the Buckingham potential decreases from $a(16) = 1$ to 0.7 at $N = 32$ and then remains at nearly the same level. For the Lennard–Jones potential, $a(32) = 0.8$ and the effectiveness decreases further in the limits of 0.05 with an increase in the number of nuclei to 128.

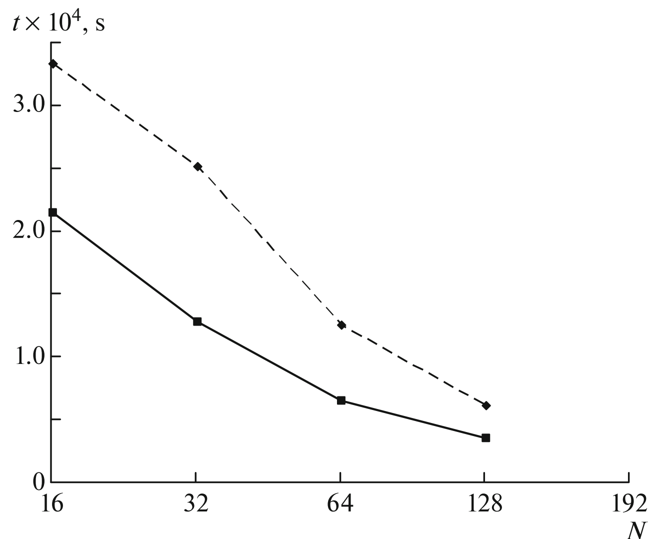

Fig. 5. The time of substrate modeling, t (s), depending on the number of nuclei, N. The solid line is the DESIL force field, the dashed line is the DESIL_B force field.

CONCLUSIONS

In this paper we compare two force fields for the atomistic simulation of the deposition of thin silicon-dioxide films. In describing the Van der Waals interaction we used the previously obtained DESIL [7] force field that was calculated using the Lennard–Jones potential, along with the DESIL_B force field that is presented in this work that was calculated on the base of Buckingham's potential with an exponential dependence on the interatomic distance. It is shown that both force fields reproduce the structure (the bond length, SiO_4 tetrahedrons, and the density and positions of the first maxima of the RDF) reasonably well for glassy silicon dioxide. When modeling thin-film deposition using the DESIL-B force field, the film density was found to be 3.2 g/cm^3, which exceeds the experimental values of 2.1–2.4 g/cm^3. The analysis of the structure revealed that this increase in the density

is due to a high share of penta-coordinated silicon atoms (up to 40%).

Thus, despite the fact that the DESIL_B force field reproduces the structure of glassy silicon well, the DESIL force field with the Lennard–Jones potential turns out to be preferable when modeling the process of deposition.

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