INFLUENCE OF DEFECTS ON ADSORPTION PROCESSES IN THE NEAR-SURFACE LAYERS OF ZnO NANOCLUSTERS: MD STUDY

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We carried out molecular dynamics simulations to investigate the process of adsorption in the near-surface layers of ZnO nanoclusters. To describe the interaction between atoms, we used the reactive force field (ReaxFF). Two ZnO nanoclusters — one without defects and one with them — were the object of research. Several computer experiments with different initial conditions were performed. The study found that the defects have a significant effect on the structural and physical properties of ZnO nanoclusters, which is primarily due to the greater number of bonds in ZnO nanoclusters with defects than in pure ZnO. The adsorption process in different systems with different initial conditions occurred differently. It was found that the whole process of adsorption was divided into two stages: the first stage was characterized by a rapid increase in the number of adsorbed molecules, the second — an increase in fluctuations in the change of adsorbed molecules on the surface over time. The higher gas pressure in the system corresponds to a larger number of O_2 molecules, which diffuse into the volume of the ZnO nanocluster; therefore, the crystal structure of the surface of the ZnO nanocluster becomes amorphous. Also, it was found that the distribution of the dependence of the central symmetry parameter on the oxygen concentration in the system with a small amount of O_2 molecules was similar. The situation was completely different when the number of oxygen molecules increased: the value of the central symmetry parameter of the surface atoms was distributed more evenly, which cannot be considered as a crystalline state of the ZnO nanocluster.

Key words: nanopowders; core-shell structures; metal oxides; molecular dynamics.

I. INTRODUCTION

The development of nanotechnologies has aroused great interest in studying the properties of nanoparticles and their synthesis. The study of nanoparticles will allow a more complete understanding of the processes of phase transitions and self-organization in complex dispersed systems. Currently, the study of individual nanoparticles is one of the fastest growing areas of research in physics, chemistry and engineering. The huge scientific and practical interest in such research is the result of the unusual properties of nanoparticles, which are already or will be widely used in the future for the manufacture of miniature electronic devices and the production of new materials.

Of all the metal oxides nanomaterials that are now widely used, zinc oxide occupies a special place. ZnO is a very interesting material with a wide range of technical applications. Zinc oxide is a wide-bandgap semiconductor with band gap (E_g = 3.37 eV); it is suitable for application in optoelectronic devices with short wavelengths, such as UV light-emitting diodes and transparent field-effect transistors. It has several favorable properties, including good transparency, high electron mobility, wide bandgap, and strong room-temperature luminescence. Zinc oxide crystallizes in two main structures — hexagonal wurtzite (a = 3.24992 Å, c = 5.20658 Å) and cubic zincblende (a = 4.463 Å) [1]. Nanopowdered zinc oxide is a promising material as a working environment in lasers. Thin films and other

nanostructures based on zinc oxide can be used as sensors of gas and biological sensors [2–7].

The shape of nanoparticles depends on the method and conditions of synthesis. One of the simplest and most popular methods of obtaining nanoparticles is the gas-phase evaporation of the solid target material in an inert atmosphere, followed by condensation on the substrate surface. This method has a fairly high efficiency and is widely used on an industrial scale. The technology of this method is quite well developed for the production of a large number of powdered non-ferrous metals, such as aluminum, copper, antimony, zinc, palladium, silver. In this method, the material is evaporated by pulsed laser ablation. In recent years, pulsed laser ablation (PLA) has become a promising method for the synthesis of nanoclusters for photonics, electronics and medicine. We proposed a method for the synthesis of nanopowder of metal oxides by pulsed laser ablation of a metal target (Zn, Sn, etc.) in a chemically active environment [8]. The laser pulse heats the material of the metal target to a high temperature, and the atoms evaporate into the background gas. The inert gas reduces the kinetic energy of evaporated atoms and the formation of nanoclusters. By carefully selecting the parameters of the laser radiation and the background gas pressure, we can control the structure and the size of the particles. Understanding the physical and chemical processes that influence the evolution of nanoparticles in the presence of gas is extremely important for the further development of this technology.

It is known that the properties of nanoparticles are

determined by their structure, and the structure — by the growth of nanoparticles. Depending on the technological features of particle synthesis, the formation processes can differ significantly. Experimental study of the mechanisms of nanoparticle formation is a technically complex and time-consuming task due to the small size of these objects. Under the conditions of experimental synthesis, it is sometimes difficult to study in detail the influence of the basic parameters of synthesis on the physical, chemical and structural properties and the external shape of the derived particles. However, computer modeling is an alternative and promising way to study the mechanisms of nanoobject formation. Modeling of molecular dynamics has made a significant contribution to improving the fundamental understanding of physical and chemical mechanisms on the nanoscale. It can be used to study many important unanswered questions concerning nanoparticles that cannot be solved directly by continuous approaches. Using the methods of computer modeling, we can investigate in detail the processes of synthesis of nanoparticles upon condensation from the gas phase, which was done in our previous work [9].

II. MODEL AND METHOD

We simulated adsorption processes on ZnO nanoparticles using the method of molecular dynamics. This method consists in the numerical solution of Newton's differential equation of motion for each atom of the system under given initial conditions. In the classical form of the method of molecular dynamics, the interaction between atoms is described by empirical force fields, and the particles that interact with each other are represented in the form of point masses [10, 11]. The defining step in creating a correct model is the choice of the potential of interatomic bonds in the system. By analyzing the nature of the formation of such nanostructures and referring to sources about the potentials of interatomic bonds, we chose the potential of Reactive Force Field (ReaxFF) [12, 13]. This potential has been developed for a wide range of chemical compounds, including ZnO, and has already been used by us in the previous work on modeling the processes of formation of ZnO nanoparticles in a chemically active environment [14–16].

ReaxFF is an empirical potential that comes from quantum mechanical calculations. The ordinal bond is directly calculated from the interatomic distances and updated with each iteration for all related interactions, including the covalent bond, valence, and torsion angles. In addition, ReaxFF describes unrelated van der Waals and Coulomb interactions. Such interactions are calculated for all pairs of atoms, and by including a shielding term, extremely close interactions can be variable. Polarization effects are also considered using a geometrically dependent charge distribution derived by the electronegativity equalization method [17]. The total interaction energy expression of the ReaxFF is broken down into several energy terms:

$$E_{system} = E_{bond} + E_{over} + E_{under}$$

$$+ E_{pen} + E_{conj} + E_{tors} \tag{1}$$

$$+ E_{val} + E_{lp} + E_{vdWaals} + E_{Coulomb}.$$

These partial contributions include bond energies (E_{bond}), under-coordination penalty energies (E_{under}), lone-pairs energies (E_{lp}), over-coordination penalty energies (E_{over}), valence angles energies (E_{val}), energy penalty for handling atoms with two double bonds (E_{pen}), torsion angles energies (E_{tors}), conjugated bonds energies (E_{conj}), and terms to handle non-bonded interactions, namely van der Waals ($E_{vdWaals}$) and Coulomb ($E_{Coulomb}$) interactions. All terms except the last two are bond-order dependent, i.e. will contribute more or less depending on the local environment of each atom [12].

For this type of task, we used the Large-scale Atomic / Molecular Massively Parallel Simulator (LAMMPS) software package developed by a research team from Sandia National Laboratory (USA). We performed calculations on the cluster of the Pidstryhach Institute for Applied Problems of Mechanics and Mathematics, based on four multi-core Intel Xeon processors in the Linux ROCKS operating environment. The dependences of the total energy of the system and the functions of radial distribution (RDF) were used to describe the adsorption processes [18], and the CSP method was used to study the surface properties [19, 20].

The sizes of the studied nanoclusters varied between 2–5 nm and had a hexagonal wurtzite structure. The directions of the initial velocities for O_2 molecules were chosen randomly, the values of the initial velocities were set in accordance with the system temperature. The temperature in the studied volume was maintained at a certain fixed value ($T = 300$ K). The key point of the simulation is the connection of the system with the thermostat to maintain a specific system temperature. Since a significant amount of energy was released during the adsorption of molecules on the nanoclusters, such a connection is necessary in order to avoid additional temperature increases. In real experiments, this bond is provided by an inert or reactive gas. In our computer simulation, temperature control was provided using the Beredsen thermostat method [21, 22]. This method is widely used for modeling systems with a large number of degrees of freedom within the molecular dynamics approach. To maintain the temperature, the system is connected to an external thermostat with a fixed temperature. The speeds are calibrated at each step so that the change in the temperature speed is proportional to the temperature difference between the system and the thermostat.

III. RESULTS AND DISCUSSION

Two ZnO nanoclusters — one without defects and one with them − were the object of the research. In

the course of the study, it was found that the defects have a significant effect on the structural and physical properties of ZnO nanoclusters; this is primarily due to the greater number of bonds in ZnO nanoclusters with defects. The adsorption process in different systems, with different initial conditions, occurred differently. Figure 1 shows the system at the initial time of the simulation. Figure 2 shows the dependences of the number of adsorbed O_2 molecules on the simulation time for different nanoclusters. In this case, only molecular adsorption was taken into account. All curves show a general trend of sharp growth at the beginning of the simulation, and a slowdown in growth thereafter. This behavior can be explained by a decrease in gas pressure in the system. The figure shows that over time the number of adsorbed molecules increases, both for nanoclusters without defects and with defects. However, the number of O_2 molecules on the surface of a defective cluster is greater than on pure clusters. This is due to the fact that nanoclusters with defects have more free bonds. The surface energy of nanoparticles decreases with an increase in the nanoparticle size, decreasing the surface to volume ratio. As a result, the average coordination number may increase as the structure changes. The figure shows that the amount of adsorbed state O decreases with an increase in the cluster size.
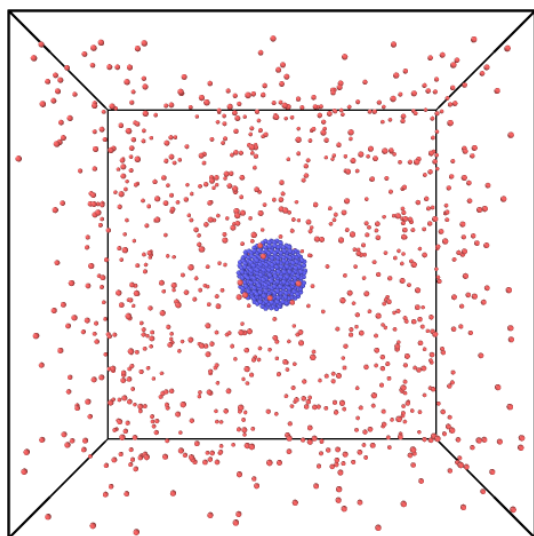

Fig. 1. Image of the system at the initial time of the simulation (Zn — blue dots, O — red dots, $V = 8000$ nm^3, $n = 10^{19}$ cm^{-3})

Analyzing the change in the potential energy of nanoclusters over time (Fig. 3), we can conclude that under the same conditions, defective nanoclusters and pure nanoclusters have a common tendency to decrease exponentially due to a decrease in free near-surface bonds. However, the values of potential energy are large for nanoclusters in which there is a large number of defects. We performed calculations of the central symmetry parameter (CSP) for the near-surface layers of nanoclusters. This parameter is calculated using the

formula:

$$CSP = \sum_{i=1}^{N/2} |\mathbf{R}_i + \mathbf{R}_{i+N/2}|^2 \qquad (2)$$

where N are the nearest neighboring atoms of the i-th atom, $\mathbf{R}_i$ and $\mathbf{R}_{i+N/2}$ are vectors from the central atom to a specific pair of nearest neighbors. In solid-state systems, CSP is a useful characteristic of the local arrangement of the lattice around the atom, and can be used to determine whether an atom is part of an ideal lattice, or a local defect, or it is simply on the surface. For a cubic face-centered lattice, when the CSP value is 0, it means that the atom is surrounded by neighboring atoms on the ideal lattice, and the larger the value of the central symmetry parameter, the more the structure deviates from the ideal. Figure 4 shows the results of CSP calculations for pure nanoclusters.
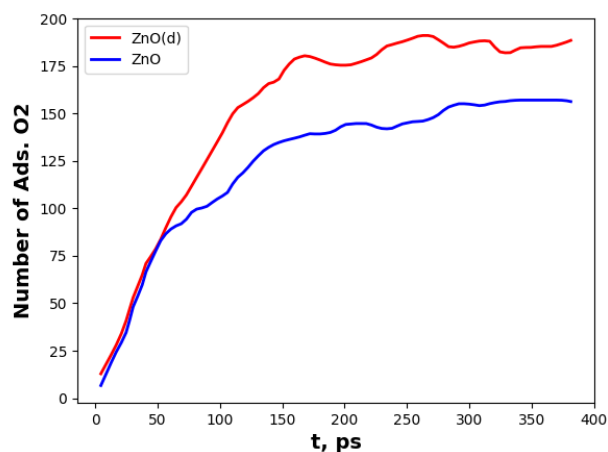

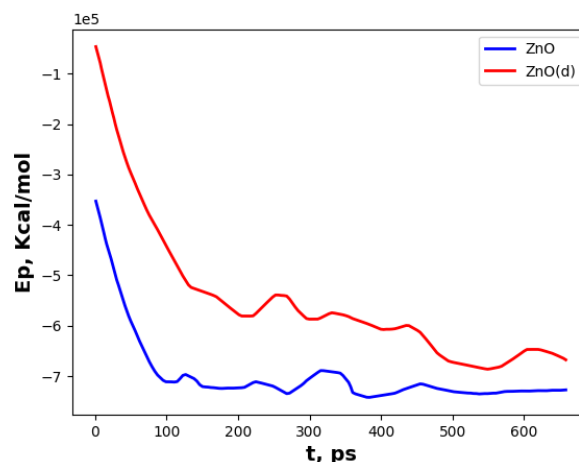Fig. 2. Change in the number of adsorbed O_2 molecules on the surfaces of nanoclusters over time

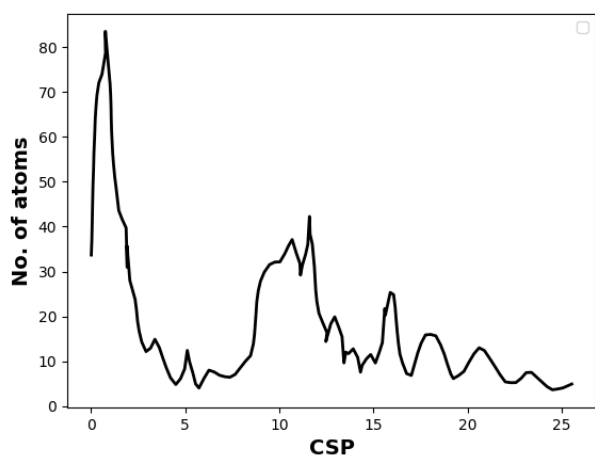Fig. 3. Dependence of potential energy with time for different systems

Fig. 4. CSP analysis of the near-surface layers of the ZnO nanocluster

Fig. 5. CSP analysis of near-surface layers of ZnO nanocluster with defects

It is established that the tendencies of distribution of the dependence of the central symmetry parameter for nanoclusters without defects have a pronounced peak in the range 0–3 Å, which indicates that after the adsorption processes on the surface of nanoclusters, they still retain a relatively crystalline structure. In turn, the value of the parameter of central symmetry (Fig. 5) of surface atoms of the nanoclusters with defects is distributed more evenly and there is one obvious peak of about 14 Å. This kind of dependence allows us to claim that the structure in such nanoclusters loses crystallinity. Based on the above analysis, our assumption is reasonable. Also, it was found that the dominant types of defects were oxygen vacancies and interstitial zinc atoms.

IV. CONCLUSIONS

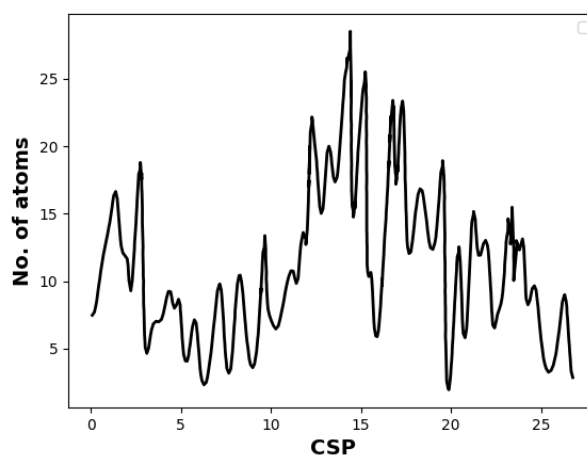We carried out modeling using the method of molecular dynamics of adsorption processes of O_2 molecules on ZnO nanocluster in different initial conditions. It is established that the whole process of adsorption can be divided into two stages: the first stage is characterized by a rapid increase in the number of adsorbed molecules, the second — an increase in fluctuations in the change of adsorbed molecules over time. The study found that the defects have a significant effect on the structural and physical properties of ZnO nanoclusters, which is primarily due to the greater number of bonds in ZnO nanoclusters. It was established that the tendencies of distribution of the dependence of the central symmetry parameter for nanoclusters without defects have a pronounced peak in the range 0–3 Å, which indicates that after the adsorption processes on the surface of nanoclusters they still retain a relatively crystalline structure. Also, the value of the central symmetry parameter of surface atoms of nanoclusters with defects is distributed more evenly and there is one obvious peak of about 14 Å. This dependence suggests that the structure in such nanoclusters loses crystallinity.

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ВПЛИВ ДЕФЕКТІВ НА ПРОЦЕСИ АДСОРБЦІЇ В ПРИПОВЕРХНЕВИХ ШАРАХ НАНОКЛАСТЕРІВ ZnO: МД ДОСЛІДЖЕННЯ

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Ми провели моделювання методом молекулярної динаміки, щоб дослідити адсорбцію в приповерхневих шарах нанокластерів ZnO. Для опису взаємодії між атомами використовували міжатомний потенціал реактивної сили (ReaxFF). Об'єктами дослідження були два нанокластери ZnO — перший нанокластер без дефектів, другий із ними. Проведено кілька комп'ютерних експериментів із різними початковими умовами. Дослідження показало, що дефекти мають великий вплив на структурні та фізичні властивості нанокластерів ZnO, що пояснюємо передусім більшою кількістю зв'язків у нанокластерах ZnO. Адсорбція для різних систем із неоднаковими початковими умовами відбувалася по-різному. Встановлено, що весь процес адсорбції поділяється на дві стадії: перша характеризувалася швидким збільшенням кількості адсорбованих молекул, друга — збільшенням коливань зміни адсорбованих молекул на поверхні з плином часу. Вищий тиск газу в системі відповідає більшій кількості молекул O_2, що дифундує в об'єм нанокластера ZnO, отже, кристалічна структура поверхні нанокластера ZnO стає аморфною. Також виявлено, що тенденції розподілу залежності центрального параметра симетрії від концентрації кисню в системі з невеликою кількістю молекул O_2 були подібними. Зовсім інша ситуація, коли кількість молекул кисню збільшилася: значення центрального параметра симетрії поверхневих атомів розподілено рівномірніше, що не можна розглядати це як кристалічний стан нанокластера ZnO.

Ключові слова: нанопорошки, структури "ядро–оболонка", металооксиди, молекулярна динаміка.