Effect of temperature on the structure of Cu/Si composite Janus nanoparticles

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Abstract. This work determined the effect of temperature on the formation of composite Cu/Si nanoparticles by the molecular dynamics (MD) method. For the first time, the temperature dependence of the potential energy of hybrid nanoparticles, which were single-crystal spherical clusters cut from an ideal lattice, was studied. It is shown that phase transitions and structural ordering cause a sharp change in the potential energy of composite nanoparticles. The structural arrangement of copper nanoparticles at high temperatures was found.

1. Introduction

Metal-semiconductor composite nanoparticles with a Janus-like structure are of particular interest. Firstly, the Janus-like metal/semiconductor nanoparticles created by the gas-phase method are already electronic devices-nanoscale diodes due to the contact between its components formed during the creation of the particle. Secondly, nanoscale diodes, for example, in the form of nanopowders or suspension, can have a high concentration per unit volume, promising for creating new microelectronic devices with a record high density of components. The electrophysical properties, interaction with high-frequency electromagnetic radiation of a Janus-like metal/semiconductor nanoparticle will be strongly influenced by its composition, interface, structure, shape and size, and the dielectric properties of its semiconductor part and environment [1]. When synthesizing nanoparticles, it is necessary to take into account that the formation of a set of composite nanoparticles occurs under conditions of self-organization of the substance, which may result in a greater or lesser deviation of the composition and morphology of individual nanoparticles from the certain averaged (set) values [2, 3]. To solve this problem, we can use the method of heat treatment of the resulting nanoparticles as the final synthesis stage from the gas phase. In addition, one of the known methods for producing metal nanoparticles with an oxide shell is their annealing at elevated temperatures in an oxygen-containing medium. Understanding the structure of the core created by such heat treatment is an important task.

One of the first works on studying the sintering process [4] was published in the 40s of the 20th century. In this and subsequent works, mainly macroscopic particles and, to a lesser extent, microscopic particles were studied [4-9]. The sintering mechanism of solid nanoparticles has not been fully understood despite long-term scientific research in this area. The self-preserving sintering model in [9] suggests that minimization of the agglomerate surface is the main driving force of the sintering process. Based on these studies, models of the interaction between particle fusion and agglomerate coagulation have been developed [10, 11].

In [12], for the first time, Cu nanoparticles synthesized from the gas phase and, consequently, having different sizes, shapes, and degrees of agglomeration were used to study the processes of thermal exposure. The morphology of bimetallic nanoparticles can change due to their heat treatment [13-16]. Depending on the composition and structure of the initial nanoparticles, the temperature and the duration of heating of the sample, both segregation of the components and their more uniform distribution over the particle volume is possible. It was shown that the heat treatment of electrocatalysts at 350°C leads to the destruction of the core-shell architecture and the fusion of some bimetallic nanoparticles with the formation of both
homogeneous and ordered solid solutions of PtCu, as well as to the partial reduction of copper oxides (Figure 1) [17].

In [18], the parameters of thermal stability of Cu/Si core-shell composite nanoparticles of different sizes and structures were determined using molecular dynamics calculations. However, in all the works presented above, nanoparticles were studied, monocrystalline spherical clusters were cut out of an ideal lattice. In an actual experiment, the creation of nanoparticles usually occurs under nonequilibrium conditions, which leads to the formation of various structural imperfections of the particle. This leads to twinning, agglomeration of point defects, and the appearance of lattice types that are not characteristic of matter in macroscopic states.

In our work, when studying the processes of thermal exposure, for the first time, Janus-like Cu/Si nanoparticles synthesized from the liquid phase will be used.

Accurate information on the morphological changes of the investigated particles during heating is necessary to create the most efficient heat-treatment process. For this purpose, two methods of studying the heat treatment of particles are experimentally used - differential electric mobility analyzers (DMA) and transmission electron microscopy (TEM) [19]. These methods are suitable for determining particles' concentration, diameter, and morphology before and after heat treatment. Still, they cannot provide complete information about the processes that occur during the heating of materials and the phenomena that affect the structure and shape of the processed particles. Only computer simulations can provide such information in full. Therefore, the article presents the results of modeling the heat treatment of Janus-like Cu/Si nanoparticles to study the effect of temperature on the production of particles with different, including defect-free shapes and internal structures.

2. Results of Simulation and Discussion
One of the main features of the synthesis is the significant heterogeneity of the internal structure and external shape of the resulting nanoparticles. Therefore, depending on the parameters of the evaporation-condensation process, up to 90% of particles with a pronounced non-spherical shape and different internal structures can be formed in the system. However, the polydispersity of the resulting particles does not always negatively affect the further technological application of this material. Recently, such free particles have been effectively used in various chemical reactions due to their high catalytic activity.

Creating the most efficient heat treatment process requires accurate information on the morphological changes of the particles under study during heating. Modeling of thermal effects on Cu/Si particles of various sizes was carried out by the molecular dynamics method in the LAMMPS software package (Large-scale Atomic / Molecular Massively Parallel Simulator). The modified many-particle potential of the embedded atom MEAM (Modified Embedded Atom Method) was used in these calculations [20]. The number of atoms in the cluster is 1800.

\[
U_i = \sum_i F_i (\rho_{h,i}) + \frac{1}{2} \sum_i \sum_{j \neq i} u_{ij}(r_{ij})
\]

(1)

where \(\rho_{h,i}\) is the electron density at the node of atom \(i\); \(F_i\) is the energy of "embedded" of atom \(i\) in the electron density of the medium; \(u_{ij}\) is the central potential of the pair interaction between atoms \(i\) and \(j\) located at a distance of \(r_{ij}\) from each other.

The "embedded" function:

\[
F(\rho_i) = AE_c \frac{\rho_i}{\rho_i^0} \ln \left( \frac{\rho_i}{\rho_i^0} \right)
\]

(2)

where \(A\) is the fitting parameter, \(E_c\) is the cohesion energy, and \(\rho_i^0\) is the background electron density for the node of atom \(i\) in its reference (usually equilibrium) lattice.

Figure 1 shows a graph of the temperature dependence of the potential energy of a janus-like Cu/Si particle during heating in the temperature range of \(T = 300\, K\) to \(T = 1600\, K\) during the time \(t = 10\, ns\). Figure 2 also shows the evolution of the particle structure under heating as a function of temperature. Moreover, I is the view of the particle from the side from which the copper (black) and silicon (gray) parts of the nanoparticle are visible; II, III, IV are the view of the particle from the copper side at \(T = 300\, K, 850\, K, 1400\, K\), respectively. From the graph and images of the particles, it is seen that no significant changes occur in the amorphous particle in the temperature range from \(100\, K\) to \(600\, K\). At \(T = 650\, K\), a decrease in energy is observed due to the course of an exothermic reaction and caused by the ordering of copper with the formation of crystal structures. This change is not observed when a copper nanoparticle (created from the gas phase) melts in the case of a non-
defective lattice [12]. When the temperature reaches 850 K (particle III), there is a sharp increase in energy due to the melting process of copper. The silicon atoms begin to envelop the copper. When the program runs repeatedly, the copper comes to the surface, forming a dendritic structure.

![Graph of the temperature dependence of the potential energy of a janus-like Cu/Si particle during heating in the temperature range of T = 300 K to T = 1600 K during the time t = 20 ns. I - view of the particle with the visible copper (black) and silicon (gray) parts of the nanoparticle are visible, II, III, IV- particle at T = 300 K, 850 K, 1400 K, respectively.](image)

In the case of very slow heating up to 800K for 20 ns the copper formed a defective icosahedral structure. Appearance of a Janus-like nanoparticle Cu/Si to and after thermal exposure is shown in Fig.2.

![Appearance of the janus-like Cu/Si nanoparticle before - (a) and after thermal exposure - (b)](image)

The described evolution of the structure with temperature changes is confirmed by the radial distribution function of the Cu/Si nanocluster atoms. Figure 3 shows graphs of the radial distribution function of the atoms of a janus-like particle nanocluster at two temperatures. At a temperature of T= 300 K, copper and silicon are in an amorphous state after cooling from the liquid phase (Figure 3a). In Figure 3b, for copper, temperature T= 800 K, the appearance of the second and third peaks is noticeable, while silicon continues to be in an amorphous state.
3. Conclusion
The temperature dependence of the structure of Janus-like metal/dielectric Cu/Si nanoparticles was determined by the numerical method of molecular dynamics using the potential of an embedded atom. The temperature dependence of the potential energy of composite nanoparticles, which are single-crystal spherical clusters cut from an ideal lattice, is investigated. At T = 650 K, an exothermic process occurs, caused by the ordering of copper with the formation of crystal structures. When the temperature reaches 850 K, an endothermic process occurs due to the melting of copper.

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