

# The possibility of using phase transition in Ni and Cu nanoclusters for information recording processes

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## Abstract.

The opportunity of transition metals nanoclusters' usage as a data bits in memory devices for the recording transition "order-disorder" has been analyzed. Therefore, with the help of the molecular dynamics method on the basis of TB-SMA potential the simulation of metal nanoparticles ( $D = 1.6 - 5.0$  nm) crystallization processes have been studied. Influence of various conditions of crystallization on formation of internal structure in metal nanoclusters is investigated. The stability boundaries of various crystalline isomers are analyzed. The obtained dependences are compared with the corresponding data obtained for copper and nickel nanoparticles having similar sizes. The limiting size of nanoparticles is determined, for which a structural "order-disorder" transition necessary for the data recording is still possible.

## 1. Introduction

The origin of many nanotechnologies is the natural answer to the rather limited possibility of solving some difficult technical problems to methods and approaches which are typical of microelectronics. One of these typical problems is the problem of development of technical characteristics of memory devices. Besides, from the technical view point, the most interesting decisions are those that allow multiple information rerecording. From the point of view of the data storage system development, magnetic, optical and structural-phase environment characteristics used during the recording are the most interesting ones. We will examine only one of these methods, exactly the information recording methodology with using systems that can change phase state of the carrier. The central idea is to modify the phase state of the carrier material locally, to store this phase as long as it is possible, to discover and read the recorded bit and if it is necessary to delete it many times, i.e. to return the material in the initial phase state.

The most appropriate for this phase transition is the transition from crystalline state into amorphous one, though other variants are possible too. The recording principle is the principle that some carrier is in the crystalline state; by the information recording the laser beam heats a small area with a short-time pulse to the temperature that is higher than its melting temperature. After laser action cancellation of the heated area with the typical size about 100 nm the temperature falls very fast with the heat retraction speed more than  $10^9$  K/s. At such extreme cooling rate the area is being crystallized into amorphous stage, having other in comparison with crystallized areas optical, electrical and some other properties. Thus, the recording of one data bit occurs under such conditions. It is necessary to melt this carrier area again up to the lower recrystallization temperature and wait for full transition from amorphous stage into crystallized one in order to erase this bit.

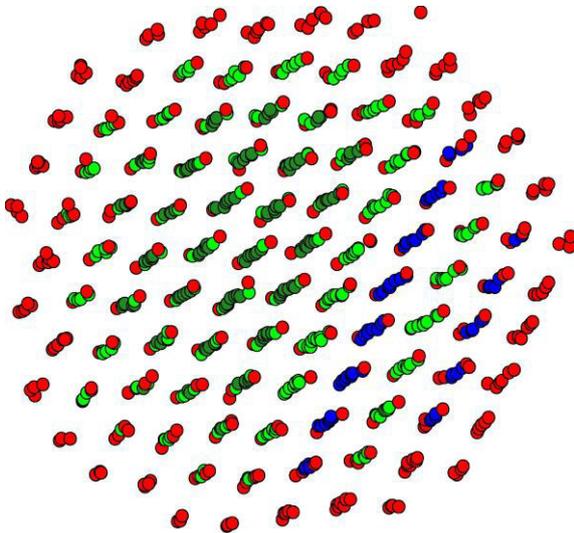
Based on the above stated, the main purpose of this work is a detailed study of possibility to use clusters of different transition metals as a single bit of information in long-term memory devices, based on principle changing of phase memory of the carrier. As the objects of this research the clusters of copper and nickel were chosen, as exactly these clusters of the given metals are successfully synthesized of different physical-chemical methods now.

## 2. The computer model

Internal structure of clusters plays an important role in understanding technology of creation of newest informational resources with phase-change memory of the carrier, however, determination of a cluster structure with the help of experimental methods deals with considerable difficulties [1]. Because of the



practically complete lack of true experimental data according to the definition of the single metal clusters structure of a small size (units of nanometers) many researchers deal with methods of computer simulation [2]. On this basis we have investigated computer simulation of structure formation processes for copper and nickel clusters conditioned upon ultrahigh-speed hardening in order to find out existing basic regularities and analysis of arising differences.



**Figure 1.** Ni nanocluster ( $D = 2.5$  nm) with a hcp structure.

For molecular dynamics simulation we used the modified tight-binding potential with a fixed cutoff radius corresponding to the fifth coordination shell inclusively [3] in order to calculate the interatomic forces. On the whole, when analyzing the results of various authors, we conclude that the Cleri-Rosato potentials [3] satisfactorily describe the behavior of a number of thermodynamic quantities of metallic fcc clusters on qualitative and quantitative levels. The differences between the simulation results and the data obtained by other collective potentials do not exceed 3–5%.

During simulation, the temperature was determined by the average kinetic energy of atoms calculated with the rapid Verlet algorithm at a time step  $h = 2$  fs [4]. The formation of small metallic particles from a liquid phase was studied along a constant energy  $E$  line (microcanonical ensemble).

A microcanonical ensemble was simulated by the Andersen method [5]. This molecular dynamics (MD) method is used for an isolated system with a fixed number of particles  $N$ , system pressure  $P$ , and total energy  $E$  ( $NPE$  ensemble). The advantage of this approach consists in the fact that the Andersen thermostat can imitate the technique of cooling of nanoclusters at various rates.

### 3. Results and discussion

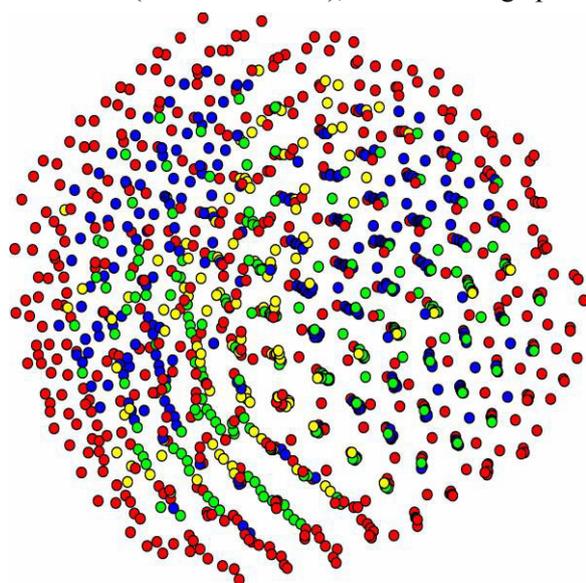
In order to study the effect of kinetics on the formation of the structure of nickel and copper clusters, the process of melting of nanoparticles with their subsequent cooling into a crystalline phase was imitated by the molecular-dynamics method. The examination of the received results we should start with nanoclusters of nickel that are already extensively used in different kinds of nanotechnological applications. The main result of simulation is that while heating of nickel nanoclusters of different diameter ( $D = 1.6 - 3.6$  nm) the melting temperature is getting higher with their following gradual cooling the process of structure formation strongly depends on the speed of the thermal energy removal.

In [6] with the help of MD simulation method the question of structural ordering has been partially investigated but only in melted polycrystalline nickel. For this purpose, the macroscopic system at temperatures corresponding to the liquid ( $T = 1850$  K) and supercooled state ( $T = 1600$  and  $1430$  K) was simulated. The analysis was conducted according to the following several characteristics: structural factor, the angular distribution relations and CNA analysis [6]. The received in [7] results show that in the molten bulk Ni, in most cases, the areas corresponding to icosahedral and distorted icosahedral phases are being formed. However, during the system supercooling the situation is getting more difficult and other structural combinations are developing.

The analysis of the received results concerning the atomic dynamics in case of nanosizes has shown that for the Ni clusters with diameter not more than 2.8 nm the following tendency is clearly seen: if cooling time  $t = 0.2$  ns; it means that icosahedral (Ih) phase is prevailed in these structures. With the increase of cooling time up to  $t = 2.0$  ns the part of the clusters with icosahedral construction of atoms will uniformly decrease. As for the contention of fcc and icosahedral (Ih) phase with reduc-

ing of cooling rate, the investigated studies have shown the influence of not only the cooling rate, but also the size effects.

Thus, the frequency of the formation of the icosahedral phase decreases continuously with increasing cluster size, being accompanied with a corresponding increase in fcc phases. And if for the clusters not more than 1.6 nm in diameter at crystallization time  $t = 2.0$  ns the fcc structure was not observed, the percentage of fcc phase for the nanoparticles with 2.54 nm in diameter reached about 40%. The occurrence probability of Ih modification if the sizes of nanoclusters are the same decreased more than two times (from 90 to 40%), as for the large particles fcc structure is the most suitable.



**Figure 2.** The structure of amorphous type of Ni cluster ( $D = 2.9$  nm) with a nucleus of icosahedral phase, received during the cooling of the particle from 1500 K to 300 K during the time  $t = 0.2$  ns.

state with the least possible energy with the result that an amorphous phase begins to manifest itself to a great extent.

Thus, at  $D = 3.6$  nm under the conditions of such continuous cooling the amorphous modification was observed in 30% of the experiments performed, and the icosahedral modification, only in 10%. When, however, the time of the process reached  $t = 0.5$  ns, the amorphous phase was noted in 10% of the cases with a threefold growth of the probability of the formation of five-particle (icosahedral) symmetry. When the crystallization proceeded most slowly (cooling time  $t = 2.0$  ns), the amorphous structure was no longer realized and the icosahedral structure took place in 40% of the simulations. It is necessary to mention that many observing structures of the amorphous type had the attempt of the transition to Ih modification (Figure 2).

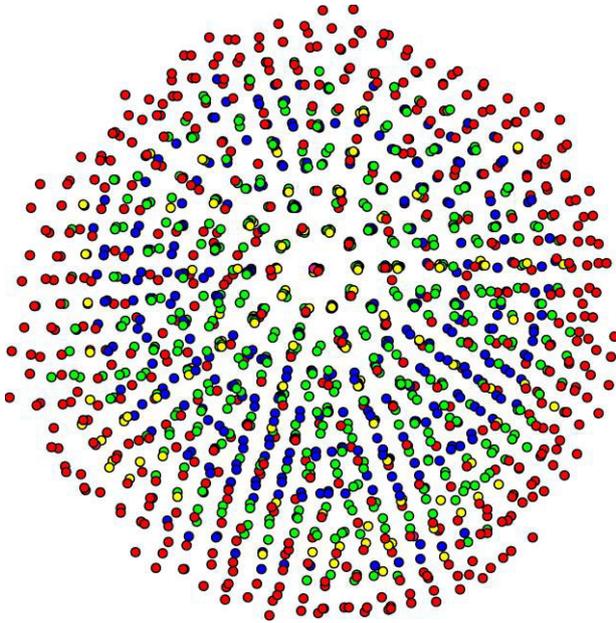
Recent MD simulations of Ni nanoclusters [8, 9] indicate that the icosahedral structure must be prevailing one to cluster sizes on the order of 1000 atoms. However, from our studies presented in this, it follows that the situation proves to be not so clear. When the real cluster structure of nickel is formed, it is necessary to take into account both thermodynamic aspects of cluster forming and kinetics of the process. On top of that, the size of the synthesized particles is of great significance.

The pointed above regularities were checked on nanoclusters of copper. Also the methodology of the gradual cooling of Cu clusters from the molten state at a room temperature  $T = 300$  K with several fixed speeds of cooling was simulated. Similarly to Ni nanoclusters the process of the structure formation depended very strongly on the cooling conditions, namely, the frequency of the formation of the icosahedral phase increased fairly uniformly with increasing rate of the process. From our data it

At high cooling rate ( $t = 0.2$  ns) for Ni clusters with  $D < 2.8$  nm only in 10% of experiments the fcc structure was being formed. Here we can observe the reconstruction of the clusters structure towards the icosahedral phase. The observing situation can be explained with the following reason: the process lead time is not enough for clusters structuring with the fcc lattice. The occurrence of hexagonal close-packed configuration was registered only once at the cooling of nanocluster with diameter 2.54 nm ( $N = 791$  atom) at a cooling time  $t = 2.0$  ns (Figure 1). Note that for all the clusters we simulated, the probability to meet the cluster with a decahedral (Dh) symmetry, that we can practically examine as intermediate between fcc and Ih, at any cooling rate fitted in a range 20 – 40%, gradually increasing with the increase of the cluster's size.

The observed tendency was violated only for clusters with a diameter more than 2.8 nm. Clusters of such size at the high rate of crystallization corresponding to the time of cooling from 1500 to 300K for 0.2 ns frequently have no time to properly reorganize the atomic surroundings for attainment of a

can be seen that at a cooling time of  $t = 0.2$  ns the face-centered cubic structure is formed in 5–10% of the performed experiments and the icosahedral structure is formed in 60–70% of the experiments (Figure 3). As the cooling time increases to  $t = 2.0$  ns, the frequency of occurrence of the face-centered cubic modification increases to 30–40%, whereas the frequency of occurrence of the icosahedral modification decreases by a factor of 2, i.e., to 30%.



**Figure 3.** Cu nanocluster ( $D = 3.2$  nm) with an icosahedral structure.

are being formed, in case of quick cooling the icosahedral phase is mainly being formed. At high cooling rate the prevail structure of Cu and Ni clusters with diameter more than 3.5–3.7 nm will be amorphous one.

Our results are in agreement with the data obtained by Liu et al. [10], who also used the Cleri-Rosato many-body potential in the study of the sample containing 500 copper atoms distributed in the cubic cell with periodic boundary conditions. In [10], the authors investigated the influence of the cooling rate on the formation of different structural modifications. Although the simulated cooling rate  $Q$  in [10] differed by two orders of magnitude ( $Q_0 = 8.05 \cdot 10^{13}$  K/s,  $Q_5 = 3.62 \cdot 10^{11}$  K/s), the chosen cooling rates seem to be unreasonably high and cannot be reached using available technical methods. Nonetheless, the performed simulation clearly confirmed the role of the cooling conditions in the formation of a specific structure.

In particular, the data obtained in [10] make it possible to draw a similar conclusion that the face-centered cubic phase is predominantly formed at a low cooling rate and that the rapid crystallization leads to a considerable increase in the content of the icosahedral structural modification. Moreover, the sample simulated in [10] at a high cooling rate is characterized by a high percentage of amorphous and defect structures. In [10], the authors did not uniquely determine the role of the cooling rate in the development of the hexagonal close-packed modification; however, it was noted that the face-centered cubic and hexagonal close-packed modifications are frequently observed in combination and form a mixed structures.

#### 4. Conclusions

In this represented work that deals with molecular dynamics method on basis of modifying potential of tight binding, the processes of internal structure in nanoclusters of copper and nickel on conditions of

The above tendency is violated only for clusters with diameters larger than 3.5 nm. The clusters of this size at a high crystallization rate ( $t = 0.2$  ns) have no time to form a regular structure, and, hence, the amorphous structure is dominant. In particular, the clusters at  $D = 3.7$  nm upon smooth cooling have the amorphous structure in 60% of cases and the icosahedral structure in only 20% of cases, whereas the face-centered cubic structure is not formed at all. However, when the cooling time increases to  $t = 0.5$  ns, the amorphous phase is formed in only 30% of experiments. At the cooling time  $t = 2.0$  ns, the amorphous structure is not observed.

The model of gradual cooling (NPE ensemble) of small metal particles allows to compare the results of MD simulation for Ni clusters with data for Cu nanoparticles, researched in the same conditions. The comparative analysis of computer experiments results shows the presence of the same regularities in formation of inner clusters structure: at slow passing process of crystallization the close-packed structures

ultrahigh-speed hardening typical of memory devices with phase-change memory of the carrier have been studied. To analyze the formation processes, we used the structureless clusters formed upon melting of primary fcc nanoparticles and cooled them to room temperature. Various structural modifications were shown to form in cooling from a liquid phase, and some criteria of their stability were determined. In simulating, we revealed the role of the size factor and the heat removal rate in the structure formation in metallic clusters.

The comparative analysis of computer experiments results shows the presence of the same regularities in formation of clusters structure of copper and nickel: during the passing process of crystallization within several nanoseconds the close-packed structures are being formed, in case of quick cooling the icosahedral phase is mainly being formed. Let's notice, that such clusters in overwhelming majority of cases had quite regular forms. If we increase the cooling rate in 10 times the prevail structure of Cu and Ni clusters with diameter more than 3.5-3.7 nm will be amorphous one.

It is necessary to take into consideration all these peculiarities when using small nanoclusters Ni or Cu in devices with phase-change memory of the carrier. From the technical view point the transition from crystallized condition into amorphous one is more appropriate, but the use of transition of the FCC - icosahedrons type is also possible that is more reasonable at sizes of one bit metal domain to 3 nm. The structural transition "order-disorder" with the particle size of more than 3.5 nm for a data recording can be applied.

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