Analysis of the possibility of using Cu-Au nanoclusters as bits in phase charge memory devices

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Abstract. This work analyses the potential of using copper-gold nanoalloy as a material for phase charge memory cells. For this purpose, smooth cooling of the melt of Cu-Au nanoclusters of 2.0 – 8.0 nm diameter was simulated with the molecular dynamics method, based on the modified tight-binding potential (TB-SMA). Particles of different chemical compositions were investigated. The gold content in the alloy varied from 10 to 90 percent. The authors also explored the influence of the cooling intensity on the character of the formed substructures. To reach the goal, the values of the heat removal rate were varied. As a result, nanoclusters of compositions Cu$_{90}$Au$_{10}$ and Cu$_{10}$Au$_{90}$ were found in a range of particles. Some parameters were selected for them, at which the stable development of amorphous and crystalline structures is possible.

1. Introduction
To date, the most common type of non-volatile devices is a planar flash memory built on transistors with a floating gate. However, the scaling of such cells causes some problems. So, with a decrease in the size of elements below 15 nm, leakage currents increase, which leads to the degradation of components and the loss of information. The diminution in the number of electrons stored in the cells increases the probability of stochastic effects, for example, crosstalk from neighboring elements. As a result, the device reliability deteriorates significantly. Although some manufacturers make planar flash memory using ten nanometer technologies, it is obvious that this type of storage devices has reached the limits of its technological development. Therefore, the problem of creating alternative non-volatile memory devices is still relevant.

Experts regard phase charge memory (PCM) as one of the main candidates for the role of universal memory. Its operation principle is based on the phenomenon of a sharp increase in the specific conductivity of a material during the transition from the amorphous state to the crystalline one. These storage devices have a few affirmative characteristics, such as high reading and recording speeds, significant cell scalability potential and durable service life (up to $10^{12}$ rewriting cycles).

The elementary PCM cell is a system of the control transistor and two electrodes with a layer of phase charge material (1T1R type) between them. In the process of information recording, the voltage is applied to the electrodes in the amount sufficient for the electronic breakdown of the working layer and the formation of a conducting channel. The warmth dissipated in this area heats the active area to the temperature above crystallization. The PCM material transforms into a low resistance state (SET) after the pulse termination, i.e. it crystallizes. For data cancellation it is necessary to energize a short current pulse of higher amplitude. It heats the work area to the temperature above the melting point.
After that, relatively rapid cooling is realized, due to which the cell material passes into the amorphous state (RESET).

Currently, alloys based on tellurium, for example Ge$_2$Sb$_2$Te$_5$ or Sb$_2$Te, doped with Ag/In (Ag$_5$In$_5$Sb$_{60}$Te$_{30}$) are used as the working layer of PCM memory elements [1]. However, these chalcogenide alloys have a relatively low crystallization temperature; therefore problems may occur in connection with thermal stability and data integrity in the amorphous state. In addition, tellurium has a high vapor pressure and a low melting point, which complicates the technological process of manufacturing devices. There are undesirable interactions of materials leading to inhomogeneity in the working layer composition and reduction of the cells service life. Therefore, the properties of non-chalcogenide alloys have been actively studied, for example Ge-Sb [2], Ga-Sb [3], Al-Sb [4].

This paper investigates the processes of the structure formation of copper-gold nanoalloys with the goal to analyze their potential of using them as a working layer in PCM memory devices.

2. Computer model

The operation principle of PCM memory devices determines the requirements for the working layer material of cells. Firstly, the resistance of the active elements should depend on the type of the substance substructure. Secondly, a clear distinction is needed between the parameters of the system at which the transition to the amorphous and crystalline phases occurs. Thirdly, these states should be stable, i.e. there should be no spontaneous phase transition during the process of reading the information and its long-term storage. Fourthly, trends in the improvement of nonvolatile memory devices mean an increase in the density of data recording. Therefore, small nanoclusters with diameters up to 10 nm are of interest for study.

In this work nanoclusters of Cu-Au alloy with diameters of 2.0, 4.0, 6.0, and 8.0 nm were studied with computer simulation. For this purpose the molecular dynamics method was used, which describes quite well a wide range of properties of various metals and alloys. The interatomic interaction forces were calculated with the modified tight-binding potential (TB-SMA). The average kinetic energy of atoms was defined with the rapid Verlet algorithm (time step $h = 1.0$ fs). Then, based on this, the system temperature was calculated.

The simulation was carried out with the MDNTP computer program developed by Dr. Ralf Meyer (University Duisburg, Germany).

The initial spherical clusters were obtained by cutting out them from the copper lattice with the ideal FCC structure. Then a part of Cu atoms in them was randomly replaced with Au atoms in certain percentage ratios. After that all the clusters underwent the compulsory procedure of thermal relaxation at the temperature of 100 K.

3. Results and discussion

The chemical composition of binary nanoclusters as well as their size affects significantly their properties. In some cases even the addition of a single impurity atom can greatly change the particle characteristics. In case we consider these clusters from the standpoint of using them as a working layer in PCM memory devices, the cooling time of the particles of the melt is added to the first two factors since the processes of formation of amorphous and crystalline configurations are associated with a more intense or lower rate of heat removal respectively.

In this paper we investigated all the above mentioned factors. The cluster diameters varied from 2.0 to 8.0 nm. The chemical composition of the clusters was changed, namely the proportion of gold in the alloy varied from 90 to 10, 70 to 30, 50 to 50, 30 to 70, and from 10 to 90. At the first stage the simulation was carried out with the Nosé thermostat. The clusters were stepwise heated to the temperature of 1500 K (with a step of 50 K) until the complete destruction of the long-range order in them, and at each fixed value they were kept for 0.3 ns. At the second stage of the experiment the studied ensembles were smoothly cooled with the Andersen thermostat to the temperature of 300 K, with some fixed speeds corresponding to the cooling periods of 0.4, 1.0, and 4.0 ns (or the heat removal rate of $30\times10^{11}$, $12\times10^{11}$, $3\times10^{11}$ K s$^{-1}$). The simulation results are presented in table 1.
Table 1. Probabilities of the formation of amorphous and crystalline structures of Cu-Au nanoclusters of different chemical compositions with varying cluster diameters $d$ and the heat removal rate $\Delta T \Delta t^{-1}$.

| $d$ (nm) | $\left(\Delta T \Delta t^{-1}\right) \cdot 10^{11}$ (K s$^{-1}$) | Probabilities of crystalline structure formation (%) | 
| --- | --- | --- |
|   | Cu$_{90}$Au$_{10}$ | Cu$_{70}$Au$_{30}$ | Cu$_{50}$Au$_{50}$ | Cu$_{30}$Au$_{70}$ | Cu$_{10}$Au$_{90}$ |
| 2  | 30 | 70 | 40 | 0 | 0 | 0 | 10 |
|    | 12 | 100 | 40 | 0 | 0 | 0 | 0 |
|    | 3  | 100 | 90 | 30 | 40 | 100 | 0 |
| 4  | 30 | 30 | 0 | 0 | 0 | 0 | 0 |
|    | 12 | 60 | 0 | 0 | 0 | 0 | 0 |
|    | 3  | 100 | 80 | 30 | 20 | 100 | 0 |
| 6  | 30 | 0 | 0 | 0 | 0 | 0 | 0 |
|    | 12 | 60 | 0 | 0 | 0 | 0 | 0 |
|    | 3  | 90 | 70 | 20 | 0 | 100 | 0 |
| 8  | 30 | 0 | 0 | 0 | 0 | 0 | 0 |
|    | 12 | 50 | 0 | 0 | 0 | 0 | 0 |
|    | 3  | 100 | 60 | 0 | 0 | 100 | 0 |

| $d$ (nm) | $\left(\Delta T \Delta t^{-1}\right) \cdot 10^{11}$ (K s$^{-1}$) | Probabilities of amorphous structure formation (%) | 
| --- | --- | --- |
|   | Cu$_{90}$Au$_{10}$ | Cu$_{70}$Au$_{30}$ | Cu$_{50}$Au$_{50}$ | Cu$_{30}$Au$_{70}$ | Cu$_{10}$Au$_{90}$ |
| 2  | 30 | 60 | 100 | 100 | 100 | 90 |
|    | 12 | 0 | 60 | 100 | 100 | 100 |
|    | 3  | 0 | 10 | 70 | 60 | 0 |
| 4  | 30 | 70 | 100 | 100 | 100 | 100 |
|    | 12 | 40 | 100 | 100 | 100 | 100 |
|    | 3  | 0 | 20 | 70 | 80 | 0 |
| 6  | 30 | 100 | 100 | 100 | 100 | 100 |
|    | 12 | 40 | 100 | 100 | 100 | 100 |
|    | 3  | 10 | 30 | 80 | 100 | 0 |
| 8  | 30 | 100 | 100 | 100 | 100 | 100 |
|    | 12 | 50 | 100 | 100 | 100 | 100 |
|    | 3  | 0 | 40 | 100 | 100 | 0 |

The experiment with pure substances has shown that the process of the structure formation of Cu and Au is very much dependent on the cooling conditions [5]. The crystalline modifications predominate at a low rate of heat removal. The amorphous structures prevail with intensive cooling. Moreover, the increase of the cluster diameter stabilizes the formation of the crystal structure of both copper and gold. Here arise the problems of obtaining the probability of amorphous modification necessary for the functioning of PCM materials. To achieve these parameters by increasing the cooling rate is not rational because of a number of serious difficulties in their technical implementation. Therefore, the purpose of simulating Cu-Au nanoclusters was to search for the configurations where the appearance of amorphous structures becomes stable with the increase in the heat removal rate, while at the same time there are sound indicators of the formation of crystalline modifications during slow cooling.

The analysis of the results shows that the amorphous configuration is preferable for Cu$_{50}$Au$_{50}$ and Cu$_{30}$Au$_{70}$ nanoclusters, regardless of the heat removal rate. Moreover, the increase in the particle diameter makes this dependence more pronounced. Alloy Cu$_{70}$Au$_{30}$ generally shows similar results. Thus, at the heat removal rate of $\Delta T \Delta t^{-1} = 3 \cdot 10^{11}$ K s$^{-1}$ the proportion of the crystalline structures decreases from 90% to 60% when the cluster size is growing. Cu$_{90}$Au$_{10}$ particles show a wider range of values. Here, $\Delta T \Delta t^{-1} = 30 \cdot 10^{11}$ K s$^{-1}$ the amorphous configuration prevails (it is stabilized at
$d = 6.0 \text{ nm}$, while at $\Delta T \Delta r^{-1} = 3 \cdot 10^{11} \text{ K s}^{-1}$ the crystalline one predominates (the maximum is reached at $d = 8.0 \text{ nm}$). However, the most interesting is the configuration of Cu$_{90}$Au$_{10}$. In this case, the particle substructure type doesn't depend on the cluster diameter being determined by the heat removal rate. The crystalline structures are formed during slow cooling (100% of all the cases), the amorphous compositions being shaped at high and average cooling rates (90 – 100%). Figure 1 shows typical structural configurations of Cu$_{10}$Au$_{90}$ nanocluster with the diameter of 2.0 nm.

![Cu$_{10}$Au$_{90}$ nanocluster](image)

**Figure 1.** The typical structural configurations of Cu$_{10}$Au$_{90}$ nanocluster with the diameter of 2.0 nm: (a) amorphous ($\Delta T \Delta r^{-1} = 30 \cdot 10^{11} \text{ K s}^{-1}$); (b) icosahedral ($\Delta T \Delta r^{-1} = 3 \cdot 10^{11} \text{ K s}^{-1}$); (c) decahedral ($\Delta T \Delta r^{-1} = 3 \cdot 10^{11} \text{ K s}^{-1}$).

Thus, according to the research results, it can be concluded that Cu$_{90}$Au$_{10}$ and Cu$_{10}$Au$_{90}$ alloys can act as the PCM memory cell material when the cluster size is at least 8.0 nm in the first case and 4.0 nm in the second one.

4. Conclusion

The improvement of phase charge memory devices is associated with researches of the properties of different tellurium-based alloys and non-chalcogenide compounds of germanium, hafnium and plumbum as well as with the investigation of new materials for the active layer of cells. The metal nanoclusters are of particular interest for study. This is primarily due to their relatively low cost and high probability of obtaining particles with the required size distribution during the synthesis process.

This work investigated the potential of using Cu-Au nanoclusters as a working layer of PCM memory cells. The smooth cooling of the melt of Cu-Au nanoclusters of 2.0 – 8.0 nm diameter was simulated with the molecular dynamics’ method, using the modified tight-binding potential (TB-SMA). As a result of this, we identified two nanoalloys – Cu$_{90}$Au$_{10}$ and Cu$_{10}$Au$_{90}$. The first alloy has demonstrated a significant influence on the size effects. The formation of the amorphous structure is stabilized with the increase in the cluster diameter. Thus, the application of Cu$_{90}$Au$_{10}$ and Cu$_{10}$Au$_{90}$ nanoalloys as bits in PCM memory devices is possible; though there are limitations on the minimum cluster size of 8.0 and 4.0 nm, respectively.

To understand the nature of the structural transitions of copper-gold alloy nanoclusters, it is necessary to study a wider range of cooling rates and conduct a more detailed structural analysis of the particles.

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