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# Evolution of subsurface nanocavities in copper under argon bombardment and annealing

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ABSTRACT

The experimental and theoretical studies of evolution of nanocavities in argon-irradiated copper under annealing are presented. The subsurface argon-filled nanocavities are formed during a short annealing at a temperature around 1000 K by migration and interaction of complexes of the simplest defects created by argon irradiation at room temperature. A long-time annealing at a temperature above 1075 K leads to decomposition of nanocavities and desorption of argon from the sample. Using the X-ray photoelectron spectroscopy and scanning tunneling microscopy and spectroscopy, valuable data sets including the density of nanocavities and their size and depth distribution are obtained. A theoretical model describing the nucleation and evolution of nanocavities is developed. Computer simulations based on this model show that the nanocavities grow at elevated temperatures by absorption of argon–vacancy complexes formed during the ion irradiation. By comparison the calculations with experimental results, the migration energy of these complexes is estimated to be around 2.5–2.75 eV. Also, the value of dissociation energy of a complex, consisting of two vacancies and two argon atoms, is found to be equal to approximately 1.10–1.18 eV. The calculation of concentration of nanocavities at different annealing conditions reveals a satisfactory agreement with the experimental observations.



## 1. Introduction

Cavity formation in metals under irradiation has been studied for a long time (see, e.g. [1–5]). Usually, the cavities have large sizes, up to micrometers, and appear in the bulk. Recently, the studies of nano-scaled cavities (radius of about 5–20 nm) in subsurface layers [6–12] were reported. These nanocavities induced by radiation affect structural, electronic and quantum properties of materials. Therefore, investigations of the evolution of subsurface nanocavities after ion irradiation are necessary for technological applications.

Besides, by analyzing experimental data and combining them with theoretical approach and simulation results, some basic aspects of physical process in metals under irradiation [13–17] can be elucidated. An adequate modeling of nanocavities nucleation under annealing, which takes into account the nature and structure of defects, is able to predict the concentration of the simple defects as well as the resulting density and size of the nanocavities at various growth conditions. Also, by comparison of simulated and experimental results one can find the values of undefined physical parameters such as migration and dissociation energies of defect complexes which determine the kinetics of the defects and cavities formation.

In this paper, the methods of the scanning tunnel microscopy and spectroscopy (STM/STS) along with the X-ray photoelectron spectroscopy (XPS) are used for the studies of copper samples which were irradiated with Ar ions and then annealed. The experimental values of subsurface nanocavity concentration, nanocavity distributions on sizes and depths are obtained. Then, using our kinetic model, the migration and binding energies for complexes of vacancies and argon atoms are calculated by a computer simulation. The values of these energies determine the processes of cavities nucleation and growth in a wide temperature range.

## 2. Experiment

For nanocavities growth we used copper single crystals with two different surface orientation: the (1 1 0) and (1 0 0). After the irradiation by argon at room temperature, the copper samples were annealed. Afterwards they were studied by the STM and STS and XPS techniques. The argon irradiation (irradiation time is 1800 s, ion flux is $1.4 \times 10^{14}\,cm^{-2}\,s^{-1}$ and energy is 5 keV) leads to the sputtering of the copper surface as well as to the ion implantation

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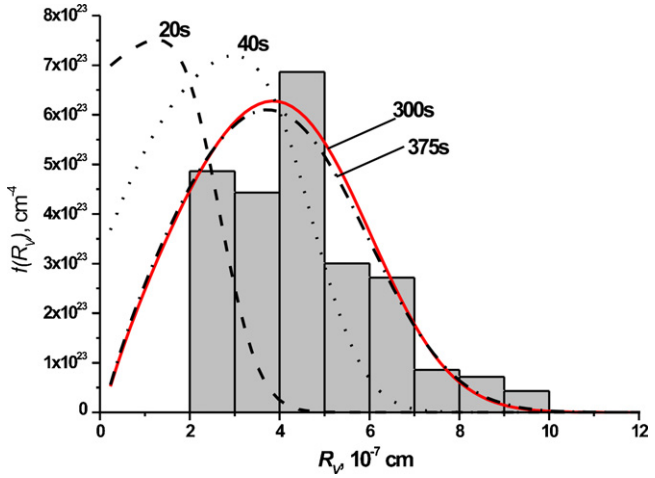


**Fig. 1.** Distribution functions of nanocavities $f_V(R_V,t)$ after annealing at the temperature 1050 K for different annealing times. Function $f_V(R_V,t)$ for 300 s annealing (solid curve) fits the experimental histogram.

on the depth of about 10 nm resulting in the point defects below the surface. The irradiated samples were annealed at the temperatures of 1000–1050 K for 300 s resulting in the formation of subsurface nanocavities. Then the additional annealing was done at the temperatures of 1075–1150 K for 1200 s. This annealing leads to dissociation of nanocavities accompanied by decreasing the argon concentration in the sample due to diffusion of the argon away from the copper crystal through its surface. After each annealing stage the samples were analyzed by the XPS method in order to indicate argon content in copper. The annealed samples were examined by the STM/STS method as well. Usage of this only surface-sensitive method to analyze subsurface objects becomes possible due to quantum resonances originated from a backscattering on the nanocavity interface. These resonances are observed as the local changes of differential conductivity on the sample surface. By this method it is possible not only to find the location of the subsurface cavities and to determine their mean concentration per a surface unit but also to define their size and depth distributions. This method is described in details elsewhere [8–11]. The Cu(1 1 0) samples are more suitable for this method than the Cu (0 0 1) ones due to the electron propagation in copper favoring the [1 1 0] direction. Therefore the STM/STS data presented in this publication are obtained mainly on the Cu(1 1 0) samples. However, according to our observations, there is no significant difference in the STM/STS data of corresponding characteristics obtained with both the Cu(0 0 1) and Cu(1 1 0) samples.

The study by the aforementioned experimental techniques reveals the following results. During the irradiation of copper at room temperature the Ar ions are implanted under copper surface and do not create nanocavities yet. However, the annealing of the irradiated samples at a temperature about 1000–1070 K for 300 s leads to the nanocavities formation. Their average density is about $4.4 \times 10^{11}$ cm$^{-2}$. The mean depth of the cavities location is about 10 nm and their size distribution is represented by the histogram shown in Fig. 1. During further annealing at a temperature about 1075–1150 K for 1800 s the nanocavities disappear and argon leaves copper due to diffusion through the surface. Thus, the process of the nanocavity evolution can be divided into three main stages: (i) argon implantation and radiation defect formation at room temperature, (ii) nanocavities formation under subsequent annealing at elevated temperatures (1000–1070 K) and (iii) nanocavity decomposition and argon depletion under further annealing at higher temperatures (1075–1150 K).

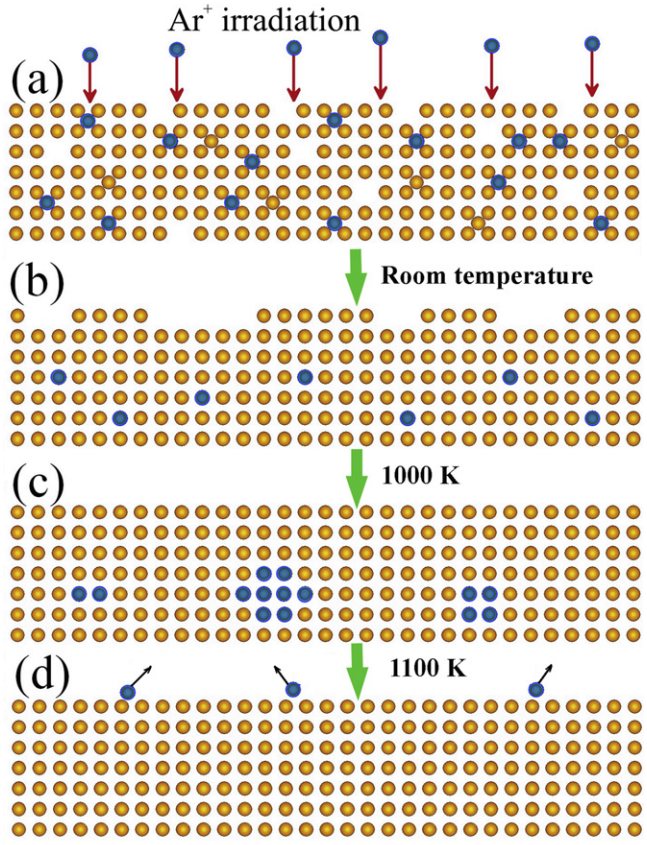


**Fig. 2.** Schematic presentation of the main processes taking place at different annealing temperatures: (a) Ar irradiation leads to point defects formation (copper vacancies and interstitials, Ar interstiatials); (b) during irradiation at room temperatures the vacancy argon complex are formed due to vacancy and Ar diffusion; (c) annealing at 1000–1070 K stimulates the nanocavity formation; (d) annealing at 1075–1150 K leads to dissociation of the nanocavities and losses of argon.

## 3. Simulation

We developed a physical model describing the nanocavity formation and evolution. This model also serves for determining the values of some physical parameters such as the migration and binding energies of Ar complexes in copper. The model of cavities evolution is divided in three stages (i–iii) by presenting three different sets of kinetic equations corresponding to the temperature intervals in the experiment. The stages of the model describe the following processes (see Fig. 2 for schematic presentation):

(i) Under Ar irradiation at room temperature for 1800 s, vacancies and copper interstitials are created in a copper crystal (see Fig. 2(a) and (b)). The vacancies and interstitials may diffuse to the surface, which is considered as a sink for all the defects. Alternatively, the copper interstitials may recombine with the vacancies. The implanted Ar atoms initially occupy the interstitial sites. The interstitial argon also interacts with vacancies or may diffuse to the surface and leave the sample. By interacting with the interstitial Ar, the vacancies may form point vacancy–argon complexes ($vAr$), i.e. an argon atom in a copper vacancy. These complexes are stable and do not diffuse during irradiation at the room temperature since the binding energy of argon and vacancy in copper is about 2.9 eV [18].

(ii) At the next stage (annealing at temperatures 1000–1070 K for 300 s), the vacancy–argon complexes, which have been formed on the irradiation stage, become mobile (see Fig. 2(c)). They can diffuse and interact with each other forming the clusters of two