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Formation of gold nanoclusters embedded in carbon film under electron beam bombardment of pulsed-laser deposited Au-C system

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The novel technique of the formation of metal nanoclusters embedded into solid film is presented. The bombardment of the amorphous 5 nm thick two-component film formed by pulsed laser co-deposition of Au and C atoms, by fast electrons in the column of the transmission electron microscope is demonstrated to result in the nucleation and growth of Au nanoclusters embedded in carbon film. The proposed mechanism of thin film heating under the electron beam allows the evaluation of the local film temperature *T*~100 C. The growth of nanoclusters can be qualitatively described in the frames of Lifshitz-Slyozov mechanism.

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1. Introduction

Nanoclusters of metals and semiconductors embedded into thin conductive and insulating films attract an increased attention due to their potential application in nano-, opto- and radioelectronics as a material for non-volatile memory devices [1], single-electron transistors and sensors [2], protective and absorbing coatings. The manufacturing of such devices needs a technology of the formation of nanoclusters of the given size embedded into the solid matrix.

The technology of the fabrication of nanoclustered films can be based on two different approaches: the formation of nanoclusters at the surface of a substrate followed by the deposition of the cover layer, and the formation of nanoclusters directly inside the uniform multi-composite film by phase separation. The former approach includes the techniques of cluster [3] and atomic deposition with nucleation at the substrate surface [4]. The latter includes thermal annealing of multi-component layers formed by ion implantation [5], (co)-deposition of clusters' and matrix' materials [6], as well as by oxidation of matrix material [7].

Atomic and cluster deposition, as well as oxidation and annealing of multi-component systems allow clusters' size and depth control, but are limited by the applications that need a uniform clusters distribution inside the buried layer. Ion implantation, in the contrast, allows the formation of planar structures with a given morphology, but does not provide a reliable cluster size control.

In the present paper we propose a novel technique of the formation of Au nanoclusters embedded into carbon film by means of the local fast electron beam bombardment of the artificially grown two-component Au-C system. The bombardment of the amorphous film, formed by pulsed laser co-deposition of Au and C atoms, by fast electrons (E=180 keV) in the column of the transmission electron microscope was demonstrated to result in the nucleation and growth of Au nanoclusters with their size dependent on the bombardment time. The action of the electron beam is shown to be equal to the thermal annealing of the initial system. The proposed mechanism of film heating by electrons' inelastic energy loss due to plasmon excitations followed by their decay to phonons allows the evaluation of film temperature for the given electron beam parameters. The relatively slow processes of clusters formation (2-60 min) allow their in situ and on-line size control, while the local action of the electron beam that can be focused in ~1 nm^2 area provides the application of the technique in nanolithography.

2. Experimental

The samples were prepared by pulsed laser deposition (PLD) at room temperature in the UHV chamber ($p \approx 5 \cdot 10^{-7}$ Pa) of the electron spectrometer XSAM-800 [8]. The freshly cleaved NaCl(100) surface was covered by pulsed laser deposited 5 nm amorphous carbon film, that served as a substrate for the composite 5 nm Au-C layer formed by alternative laser ablation of gold and graphite targets with the ratio 1:10. The obtained structure was covered by the second carbon layer. The final sample has a sandwich-like C/Au-C/C structure formed by three layers. The thickness of layers was measured by Rutherford backscattering spectroscopy (RBS), and the chemical composition was controlled in situ by X-ray photoelectron spectroscopy. The atomic concentration of Au in the intermediate layer was $4.6 \cdot 10^{21}$ cm^{-3} with the overall film thickness h=15 nm. The NaCl being dissolved in water, the film was placed at the grid and investigated by transmission electron microscopy (TEM) at JEM 2000 EX

microscope with the electrons energy E=180 keV and the current density j=1 A/cm^2.

3. Results

The TEM images of the same sample area acquired after various times of film bombardment by fast electrons in the TEM are shown in Fig.1. The initially grown sample has a uniform amorphous structure with no visible clusters (see Fig.1,a) that means that initially Au atoms do not form a condensed phase. The elongated features visible in Fig.1,a are caused by the thermal drift at the initial stages of the experiment. The irradiation of the sample by fast electrons for 2 minutes results in the nucleation of Au clusters (see Fig.1,b). The further bombardment leads to the increase of the size and the decrease of the number density of clusters (see Fig.1,c-d). The long term bombardment (more than an hour) causes the damage of the carbon film (light areas in Fig.1,d).

Assuming the spherical shape of Au clusters, the analysis of the TEM images gives the clusters size distributions (see Fig. 2,a) and their mean size <d> as a function of the bombardment time t (see Fig.2,b). The time increases, the size distribution broadens, and the clusters' mean size increases reaching its saturation value $< d >_{sat} \approx 2.8$ nm at $t \approx 100$ min.

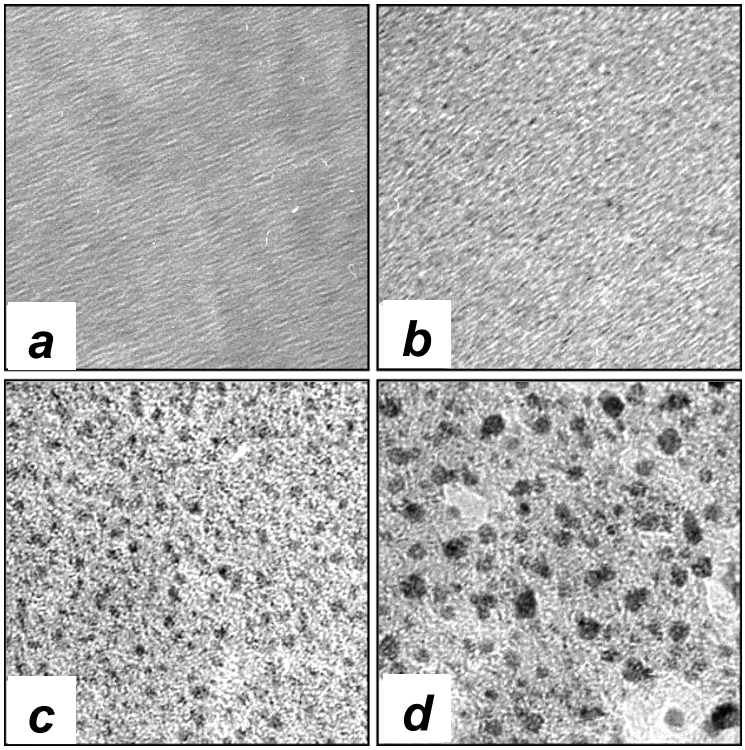

Fig. 1. The TEM images of the same C/Au-C/C sample area (50×50 nm) after 2 min (a), 12 min (b), 32 min (c) and 87 min (d) of the bombardment of the film by fast electrons.

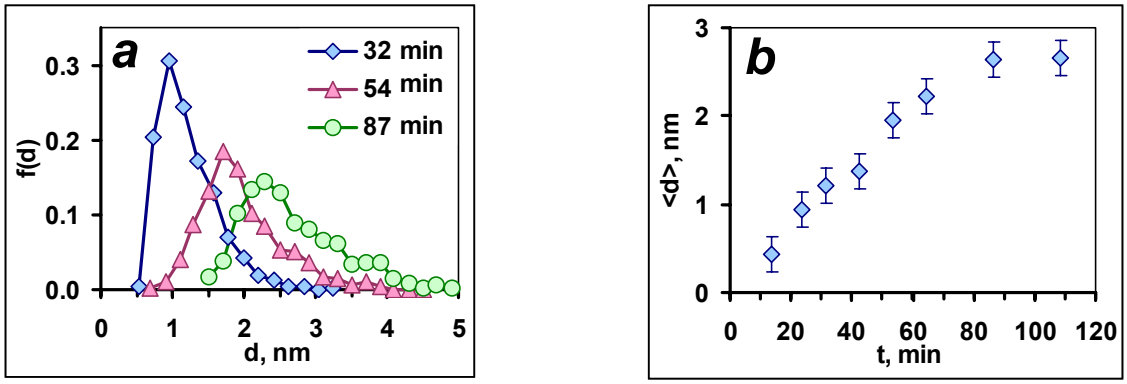

Fig.2. The size distributions f(d) of Au nanoclusters formed in carbon film under electron beam bombardment during 32, 54 and 87 min of bombardment (a); mean clusters size <d> vs. bombardment time t (b).

Provided the visible Au clusters are uniformly distributed inside the Au-C 5 nm thick layer, the dependence of the clusters' number density $N(t)$ can be obtained (see Fig.3,a). It decreases reaching the saturation $N_{sat} = 2.9 \cdot 10^{20}$ cm^{-3} at $t \approx 100$ min.

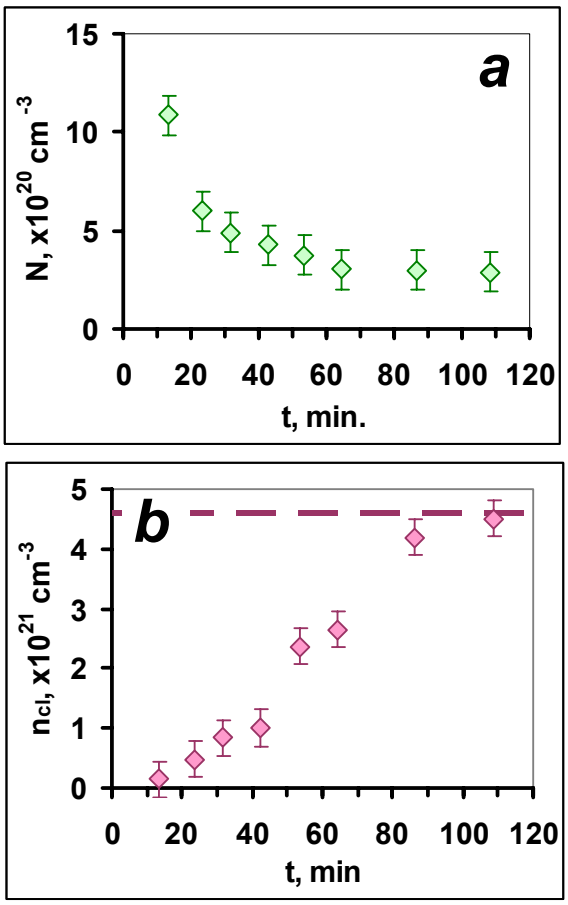

Fig. 3. The clusters number density N (a) and the concentration n_{cl} of Au atoms in clusters (b) plotted as a function of the time t of the sample bombardment by fast electrons. The dotted line shows the overall concentration of Au atoms in the sample as measured by RBS.

The TEM image (see Fig.1,a) evidences the absence of Au clusters in the initially grown film. The concentration n_{cl} of Au atoms condensed in clusters can be estimated as

$$n_{cl} = \frac{\pi}{6} < d >^3 N / v_0, \qquad (1)$$

where $v_0 \approx 0.01$ nm^3 is the Au atom volume. The function $n_{cl}(t)$ obtained from the experimental $N(t)$ and $< d(t) >$ plots using Equation (1) is presented in Fig.3,b. It is seen that the number of Au atoms condensed in clusters monotonically increases with the bombardment time reaching its saturation value $n_{cl}^{sat} \approx (4.3 \pm 0.3) \cdot 10^{21}$ cm^{-3} at $t \approx 100$ min. This value is in a good agreement with the overall number of the deposited Au atoms ($n = 4.6 \cdot 10^{21}$ cm^{-3}) measured by RBS. It indicates that at these times almost all Au atoms are condensed in clusters.

It is known that one of the means of the formation of nanoclusters embedded into the solid matrix is a thermal annealing of the initially grown multi-component system resulting in the phase separation [5-6]. In order to compare the results of the electron beam bombardment and the thermal annealing, the initial C/Au-C/C sample was annealed in vacuum at $T = 200$ °C for $t = 5$ min. Fig.4,a shows the TEM image of the annealed film. It is seen that the thermal annealing results in the nucleation of Au clusters in the amorphous carbon film with the mean cluster size $< d > \sim 0.4$ nm that is equivalent to the action of the electron beam with the energy $E_0 = 180$ keV and the current density $j = 1$ A/cm^2 for 12 min (see Fig.4,b). Therefore, it can be concluded that the bombardment of the sample by fast electrons is an alternative to the thermal annealing.

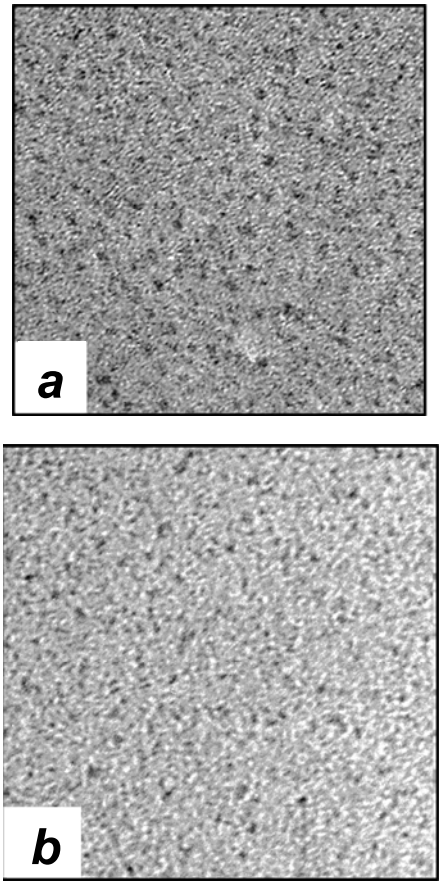

Fig. 4. The TEM images (50×50 nm) of Au nanoclusters in carbon film formed by thermal annealing of the initial Au-C system in vacuum at $T = 200$ °C for 5 min (a) and by electron bombardment with energy $E_0 = 180$ keV and current density $j = 1$ A/cm^2 for 12 min (b).

4. Discussion

Let us consider the mechanism of the local sample heating by fast electrons in order to explain the observed formation of Au nanoclusters in the carbon film under the electron bombardment. The local temperature of the film heated by the electron beam can be estimated using the balance equation for the thermal power Q transmitted to the film by the characteristic energy losses of the primary electrons, and that emitted by the heated part of the film due to its heat conductivity and thermal radiation from the surface:

$$Q = \kappa \frac{T}{S} V + S \sigma_{SB} T^4, \qquad (2)$$

where $\kappa = 1.6 \cdot 10^{-2}$ W/K·cm is the heat conductivity of carbon, $\sigma_{SB} = 5.8 \cdot 10^{-12}$ W/K^{4}cm^2 is the Stephan-Boltzmann constant, $S = 5 \cdot 10^{-10}$ cm^2 is the irradiated film area determined by the diameter of the electron beam, $V = S \cdot h = 7.5 \cdot 10^{-16}$ cm^3 is the volume of the irradiated part of the film.

The power Q, transmitted to the film at the early stage of the bombardment by fast electrons is determined by the characteristic energy losses of the primary electrons in the amorphous film and can be expressed as:

$$Q = \sum_i E_i j \sigma_i n V / e, \qquad (3)$$

where $j = 1$ A/cm^2 is the primary electrons current density, $n \approx 1 \cdot 10^{23}$ cm^{-3} is the atomic concentration in the film, E_i and σ_i are the energy loss and the cross-section for the inelastic processes responsible for the film heating.

The processes of the inelastic interaction of fast 180 keV electrons with the solid film include the core and valence shells ionization, the excitation of plasmons, phonons, as well as the emission of the characteristic X-ray radiation. The electron shell ionization is followed by the recombination processes resulted in the emission of slow (SSE) and fast (FSE) secondary electrons, Auger-electrons (AE), and the characteristic X-ray radiation (XR), that in turn initiate the cascade processes of the electron shells ionization and plasmon excitations [9]. The cross-sections of the abovementioned processes for the primary 180 keV electrons are given in Table 1 [9-10]. There are also the values of the power density Q_i / S transmitted to the film by primary electrons, calculated using (3). Due to the relatively small values of the cross-sections for direct excitations of phonons ($\sigma \approx 10^{-22}$ cm^2) and SSE ($\sigma \approx 10^{-23}$ cm^2), the power density for these processes is negligible (~10^{-6} W/cm^2). The probability of the radiative recombination for the K shell of carbon $P_{XR} \approx 0.04$ being small compared to the Auger-recombination ($P_{AR} \approx 0.96$) [11], the processes of XR excitation can be excluded. Therefore, the main role in the film heating is probably played by plasmon, FSE and AE excitations with the subsequent decay to phonons.

Table 1. The values of the characteristic energy losses E_i, the processes cross-sections σ_i and the density of the transmitted power Q_i / S for the inelastic scattering of primary 180 keV electrons in the sample (carbon film) [9].

	Plasmon	Phonon	Carbon C1s core level ionisation followed by			
			Secondary low-energy electrons	Secondary fast electrons	Auger-electron emission	X-ray emision
E_i, eV	~20	~0.1	<50	<2·10^5	~300	~300
σ_i, cm^2	10^{-18}	10^{-22}	10^{-23}	10^{-21}	10^{-20}	10^{-20}
Q_i / S, W/cm^2	~3	~1.5·10^{-6}	<7.5·10^{-6}	<30	0.43	0.02

The mean free path λ of FSE in the energy range $E = 1 \div 10$ keV and AE with $E = 274$ eV (C *KLL* Auger-transition, $\lambda \sim 2$ nm [12]) being less than the film thickness $h = 15$ nm, the electrons' kinetic energy is completely transmitted to the film atomic vibrations via plasmon excitations.

Using equations (2) and (3) on can show that the temperature of the film heated by the electron beam is $T \sim 100$ °C. This value is in agreement with the results of the thermal annealing experiment at T=200°C for 5 min producing the same effect as the bombardment of the sample by 180 keV electrons for 12 min. It can be concluded that the sample heating activates the diffusion of Au atoms inside the carbon film resulting in the nucleation and clusters growth. Note that the local heating of the sample under fast electrons bombardment was reported in [13] for the system of Au nanoclusters initially deposited at the carbon film surface.

The extrapolation of the Au-C phase diagram [14] gives the critical concentration of Au atoms at T~100°C corresponding to the condensation of gold $c_0 \sim 1$ at.%. Therefore in our case at $c_{Au} \sim 10$ at.% $> c_0$ the volume diffusion of Au atoms promoted by the heating of the sample should result in the nucleation and growth of Au clusters. The condensation process according to Volmer-Weber-Zeldovich mechanism starts from the fluctuational formation of subcritical nuclei ($R > R_c$). The estimations show that the temperatures of gold nanoclusters and carbon matrix are equalized in a fraction of a second that is substantially less than a minimal time of the sample bombardment fixed in the experiments (t~1 min). It means that the Au-C system is under isothermal conditions, and the clusters growth at the stage of the coalescence can be described in the frames of Lifshitz-Slyozov model of the diffusive

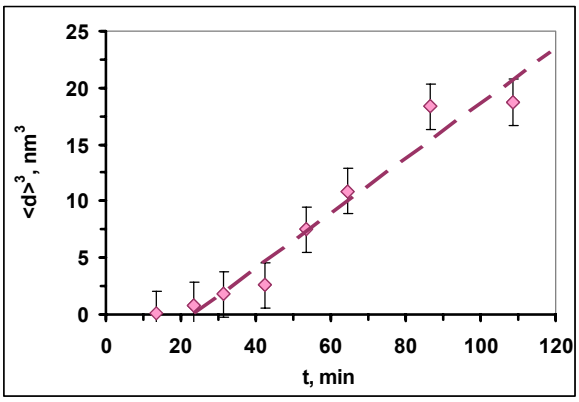

Fig.5. The dependence of the cubic mean clusters size $\langle d \rangle^3$ *on the time t of sample bombardment by fast electrons.*

decomposition of the supersaturated solid solution [15]. According to this model in the asymptotic limit ($t \to \infty$) the number density N of nanoclusters and their critical radius $R_c \sim \langle R \rangle$ [16] ($\langle R \rangle$ is the mean cluster radius) are written as:

$$N(t) = \frac{k_B T c_0(0)}{2\gamma D \nu_0 c_\infty t},$$

$$\frac{R_c(t)}{R_c(0)} = \left(\frac{8}{9} \frac{\gamma \nu_0^2}{k_B T} c_0 D c_\infty t \right)^{1/3} \qquad (5)$$

here γ is the surface tension, $R_c(0)$ is the nucleus' critical radius at the initial time t=0, c_∞ is the equilibrium concentration of Au atoms for the plane interface, c_0 is the initial concentration of Au atoms, $k_B = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann constant, T is the temperature, and D is the diffusion coefficient. As already mentioned, the growth of nanoclusters according to Lifshitz-Slyozov mechanism is characterized by the mean clusters' radius depending on time as $< R(t) > \sim \sqrt[3]{t}$. In order to verify the applicability of this mechanism to our results the experimental data for the mean cluster size are plotted in coordinates $\langle d \rangle^3$ and t in Fig.5. It is seen that the value $\langle d \rangle^3$ monotonically increases with time and within the experimental error shows a linear dependence for $t > 30$ min, that corroborates the possibility of the description of Au clusters growth in the frames of Lifshitz-Slyozov mechanism. On the other hand, the product of the mean cluster volume and the clusters' number density giving the overall number of gold atoms in nanoclusters, according to the mass conservation law, should not change with time. The experimental dependence of $n_{cl}(t)$ representing the overall number of Au atoms in nanoclusters per unite volume, reaches its saturation limit corresponding to the number of all deposited Au atoms at $t \approx 100$ min. (see Fig.3,b). It indicates that at this time scale there are no free atoms between clusters and the following clusters growth should be described by another mechanism. It should be also noted that the shape of the clusters size distributions obtained from the TEM images does not correspond to the classic size distributions in the Lifshitz-Slyozov model. The reason for the observed discrepancy can be in the change of the clusters growth conditions due to the influence of the electron beam on the carbon film (its damage), and the change of the heat transfer mechanism due to the clusters growth and their increased impact into the sample heating. Therefore, the growth of nanoclusters in the system under investigation can be qualitatively described in the frames of Lifshitz-Slyozov mechanism only at the time scale between 30 and 100 min of sample bombardment by fast electrons.

5. Conclusions

The bombardment of the amorphous film formed by pulsed laser co-deposition of Au and C atoms, by fast electrons in the TEM is experimentally demonstrated to result in the nucleation and growth of Au nanoclusters embedded in carbon film, with the mean cluster size (1-4 nm) depending on the bombardment time. The effect of the electron bombardment is proved to be equal to the thermal annealing of the initial two-component Au-C system. The proposed mechanism of sample heating by fast electrons due to plasmon excitations followed by their decay to phonons allows the estimation of the local film temperature T~100°C. The observed features of Au clusters growth in carbon film can be caused by the activation of clusters coalescence under the electron beam.

The focused electron beam and the character time scale of clusters nucleation and growth (10-100 min) provide the opportunity to control clusters mean size and location within the area limited by the electron beam size. It opens the possible application of the technique in nanolithography for the formation of planar nanoclustered structures with the given topology.

Acknowledgments

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