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# *In situ* Transmission Electron Microscopy and Electron Diffraction Investigation of Solid-State Reactions and Atomic Ordering in Cu/Au Bilayer Nanofilms

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*Solid-state reaction processes and atomic ordering in Cu/Au bilayer nanofilms (with the atomic ratio Cu:Au≈50:50) have been studied in situ by the methods of transmission electron microscopy and electron diffraction in the process of heating from room temperature up to 700 ºC at a heating rate of 4-8 ºC/min. The solid-state reaction between the nanolayers of copper and gold has been established to begin at 180 ºC. The process of atomic ordering has been shown to start simultaneously with the process of the formation of the disordered phase of $Cu_{50}Au_{50}$ at 245 ºC. The formation processes of the ordered phases of: CuAuI ($L1_0$ superstructure) and CuAuII (long period superstructure) have been studied, as well as the phase transition processes: disorder - order (the transition of the disordered structure into the ordered one) and order - disorder (the transition of the ordered structure into the disordered one).*

*Keywords: Cu/Au nanofilm, Intermetallics, Solid state reaction, Phase transition, Atomic ordering, Superstructure.*

## 1. Introduction

Certain interest to the experimental and theoretical investigations of Cu-Au alloys has been caused by the unique character of this system. Cu-Au alloys demonstrate a wide range of interesting phenomena, such as the formation of a number of ordered structures: $Cu_3Au$, CuAuI, $CuAu_3$, the


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formation of a long period modulated structure CuAuII, phase transitions of the type order-disorder etc. [1÷5]. The system Cu-Au is classical for the investigation of the behavior of different properties of metallic alloys and checking the suggested theoretical models.

Of special interest are *in situ* investigations of solid-state reaction processes on the interface between the copper and gold layers, as well as the processes of atomic ordering in Cu-Au alloys. The authors [6] reported the investigation of a solid-state reaction in bilayer thin films of Cu/Au with the gold content of 40÷60 at. %. The initiation temperature of the solid-state synthesis process was shown to be 247-267 ºC, furthermore, the synthesis initiation temperature did not depend on the thickness of the copper and gold layers. In the work by Malis et al. [7] the detailed ordering kinetics in equiatomic CuAu was studied using in situ time-resolved x-ray scattering, a subtle competition between the modulated CuAu II phase and the simple ordered CuAu I phase was found to occur across the CuAu I/ CuAu II phase boundary. In the work by Bonneaux et al. [8] in-situ temperature observations were performed by transmission electron microscopy on a stoichiometric AuCu alloy. This alloy, at heating, undergoes a series of transitions: AuCu I ($L1_0$)→AuCu II (long-period) →AuCu (disordered). However, in spite of numerous experimental and theoretical investigations of Cu-Au alloys the processes of solid-state reaction and atomic ordering in nanosystems still remain not completely understood. Also, the origin of the modulated phase is still under debate [9] and most theoretical models encounter difficulties in predicting the correct CuAuII stability in a narrow temperature range [7].

It is well known that *in situ* transmission electron microscopy (TEM) allows a direct observation of the dynamic process through imaging and selected area electron diffraction (SAED) is an ideal approach for the investigation of microstructure evolution. In this work we report the results of the *in situ* TEM and SAED investigation of the processes of solid-state reactions followed by atomic ordering and order-disorder transition in Cu/Au bilayer nanofilms with the atomic proportion Cu:Au≈50:50.

## 2. Experimental details

Cu/Au bilayer nanofilms were obtained by the method of electron beam deposition in high vacuum with the help of a high vacuum installation MED-020 (Bal-Tec). The base vacuum was $5*10^{-5}$ Pa. The films were obtained by the successive deposition of gold and copper layers onto a substrate [10]. For the evaporation the materials of a high level of purity were used: copper (ADVENT, 99.99 %); gold (ADVENT, 99.99 %) [11]. A fresh cleaved single crystal of NaCl was used as a substrate. The temperature of the substrate during the deposition was equal to room temperature. The deposition rate and the film thickness during the deposition process were controlled with the help of a quartz resonator. The deposition rate was 0.2-0.3 nm/s. The structure and the local element composition of the obtained samples were studied with a transmission electron microscope JEM-2100 (JEOL), equipped with an energy-dispersive spectrometer Oxford Inca x-sight, at the accelerating voltage of 200 kV, also the research was made using a scanning electron microscope JSM-7001F (JEOL), equipped with an energy-dispersive spectrometer Oxford Inca PentaFetx3 and a wave-dispersive spectrometer Oxford Inca Wave 500. The given electron microscopy investigations were carried out by the authors of this work in the Laboratory of electron microscopy of the Siberian Federal University [12, 13]. The films under study were Cu/Au films with the individual layer thickness of: Cu=20±2 nm; Au=28±3 nm. The thickness of the gold and copper layers was selected in such a way that the ratio between these elements amounted to ≈50:50 at. %. The local element composition of the obtained films was controlled by the

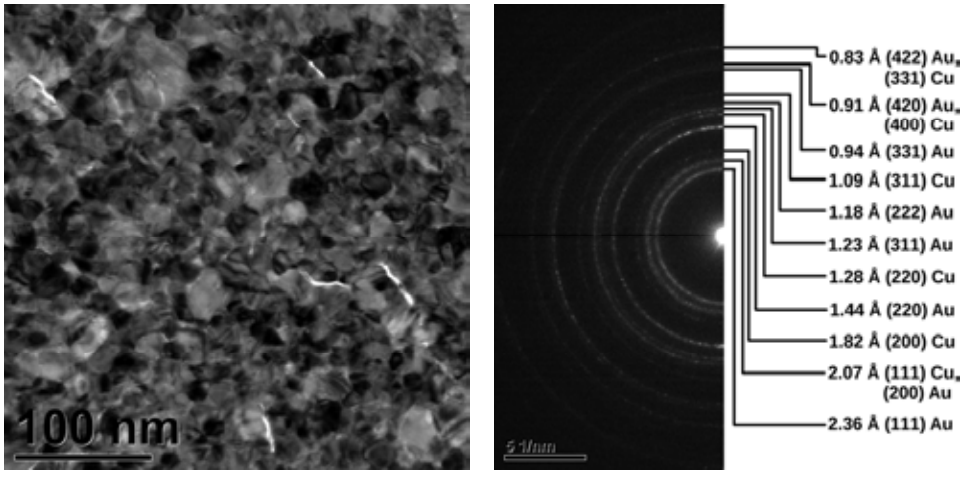
method of energy dispersion spectroscopy. In the thin film samples under study the deviation from the atomic ratio Cu:Au=50:50 did not exceed ±2 at. %.

The obtained samples were *in situ* investigated by the method of transmission electron microscopy and electron diffraction with the aim of obtaining the phase composition change in the Cu/Au films in the process of thermal heating. The heating of the film samples was carried out directly in the column of the transmission electron microscope JEM-2100 (the vacuum was $1*10^{-6}$ Pa) with the help of a special sample holder (Gatan Model 652 Double Tilt Heating Holder), which allows controlled sample heating from room temperature up to as high as +1000 ºC. Cu/Au bilayer nanofilms were separated from the substrate in room temperature distilled water, then the films were put on a molybdenum TEM grid and heated up to 700 ºC. The heating rate was from 4 to 8 ºC/min. Also, the sample annealing was carried out at a fixed temperature. Simultaneously with the heating SAED patterns were registered and synchronous sample temperature measurements were carried out. The registration of the SAED patterns was performed at a rate of 4 frames per minute, thus the heating rate of (4 ºC/min) 1 frame corresponded to the sample temperature change of 1 ºC. The interpretation of the electron diffraction patterns was made using the software DigitalMicrograph (Gatan), and crystal structure databases: ICDD PDF 4+ [14], Pearson's Crystal Data [15].

## 3. Results and discussion

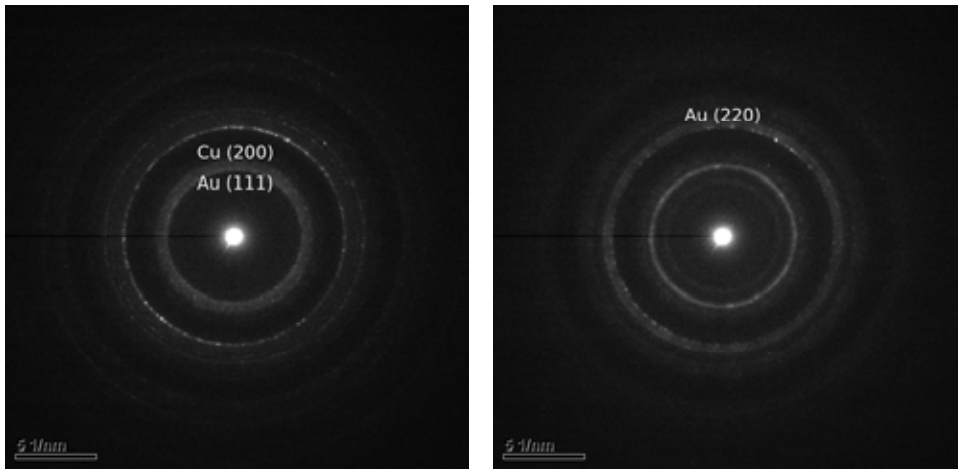
In the initial state Cu/Au bilayer nanofilms consisted of crystallites with the size of ≈10-20 nm (Fig. 1a). The diffraction reflections in the electron diffraction pattern (Fig. 1b), obtained by the method of selected area electron diffraction from the area with a diameter of ≈1 μm, have a polycrystalline view. The interpretation of the diffraction reflections showed the presence of 2 phases with face-centered cubic (FCC) lattices: Cu (the space group Fm-3m, the lattice parameter a=3.62 Å) [16], and, Au (the space group Fm-3m, the lattice parameter a=4.08 Å) [17].

The *in situ* electron diffraction investigations of the phase composition change of the Cu/Au films of in the process of thermal heating carried out at a rate of 4-8 ºC/min, showed that at 180 ºC the first




(*a*) (*b*)

Fig. 1. TEM image (a) and SAED pattern (b), of a Cu/Au film in the initial state



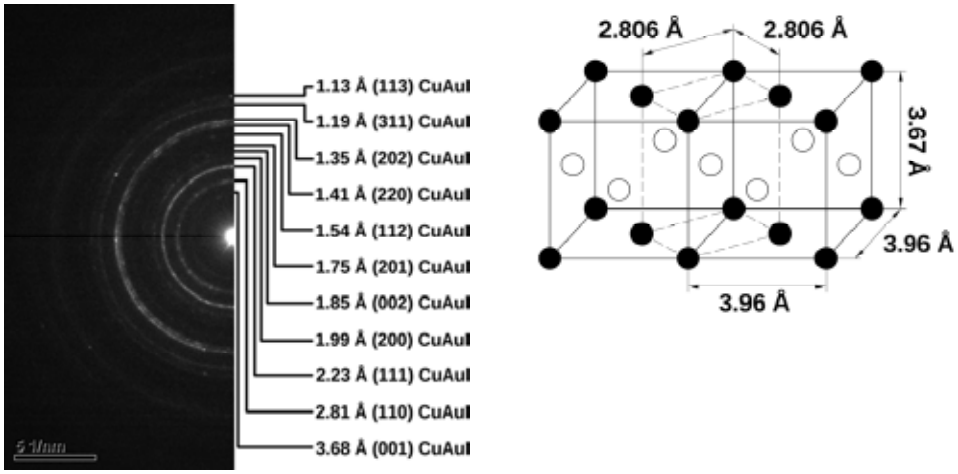

(*a*) (*b*)

Fig. 2. SAED patterns of a Cu-Au film at 225 ºC (a) and 285 ºC (b

features of a solid-state reaction were marked in the SAED pattern. The diffraction ring blurring began which indicated the beginning of the reaction at the interface of the Cu and Au nanolayers and upon reaching the temperature of 225 ºC (Fig. 2a) the diffraction reflections were blurred, namely the ones which were closer to the center of the SAED pattern: Au(111), Au(200), Cu(111), Cu(200). The maximum reflection blurring in the SAED pattern was observed upon reaching the temperature of 240 ºC. It is worth noting that at 240°C not all the diffraction reflections of the phases Cu [16] Au [17] were blurred. So, the diffraction reflection of Au(220) was blurred only upon reaching the temperature of 285 ºC (Fig. 2b). At present there is no explanation of the observed phenomenon.

At the sample heating up to 245 ºC one observed the appearance of the diffraction reflections corresponding to a new phase, FCC lattice (the space group Fm3m), with the lattice parameter a=3.87±0.02 Å, which corresponds to the disordered phase $Cu_{50}Au_{50}$ [18]. In the SAED pattern, along with the reflections corresponding to the FCC lattice with the parameter a=3.87±0.02 Å one observed a weak superstructure reflection (the relative reflection intensity being $I_{rel.}$≈5 %), corresponding to the atomic interplanar spacing of d=2.8±0.1 Å. Upon reaching 280 ºC in the SAED pattern it was possible to see one more weak superstructure reflection, corresponding to d=3.7±0.1 Å. In the process of further heating up to as high as 350 ºC (Fig. 3a), the intensity increase of the superstructure reflections (d=2.8 Å, 3.7 Å) was observed with respect to the intensity of the FCC lattice reflections.

The atom ordering in the alloys which have the composition close to that of $Cu_{50}Au_{50}$ is known to lead to the formation of CuAuI phase [19], which is an ordered $L1_0$ superstructure. The interpretation of the diffraction reflections (Fig. 3a) showed that the reflections corresponding to the interplanar spacings 2.8±0.1 Å and 3.7±0.1 Å, could be identified as the ones corresponding to the interplanar spacings of the ordered CuAuI phase: $d_{110}$=2.804 Å and $d_{001}$=3.670 Å [20]. Given in Fig. 3b is a scheme of the atom location in the ordered structure CuAuI. It is worth noting that there exist two descriptions of the unit cell of the phase CuAuI (Fig. 3b): a classical description, with the space group being P4/mmm and the following lattice parameters: a=b=3.966 Å, c=3.670 Å [20]; a modern description, with the space group being P4/mmm, and the lattice parameters, such as a=b=2.806 Å, c=3.67 Å [21] in

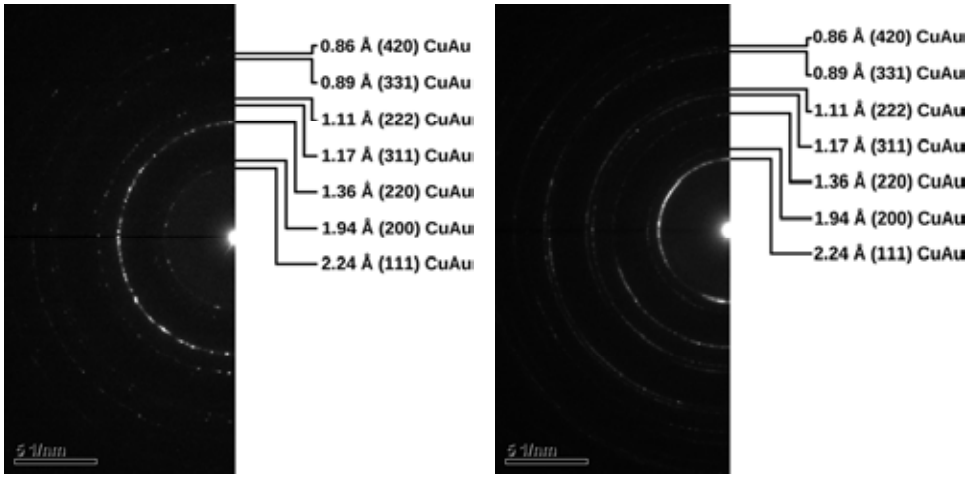



(*a*) (*b*)

Fig. 3. SAED pattern of the Cu-Au film at 350 ºC (a) and the atom location model in the ordered superstructure CuAuI (b). The black circles indicate the copper atoms, the hollow ones are used to indicate the gold atoms. The solid lines show two unit cells of the phase CuAuI in the classical description [20], the dash-and-dot lines show one unit cell of CuAuI in the modern description [21]

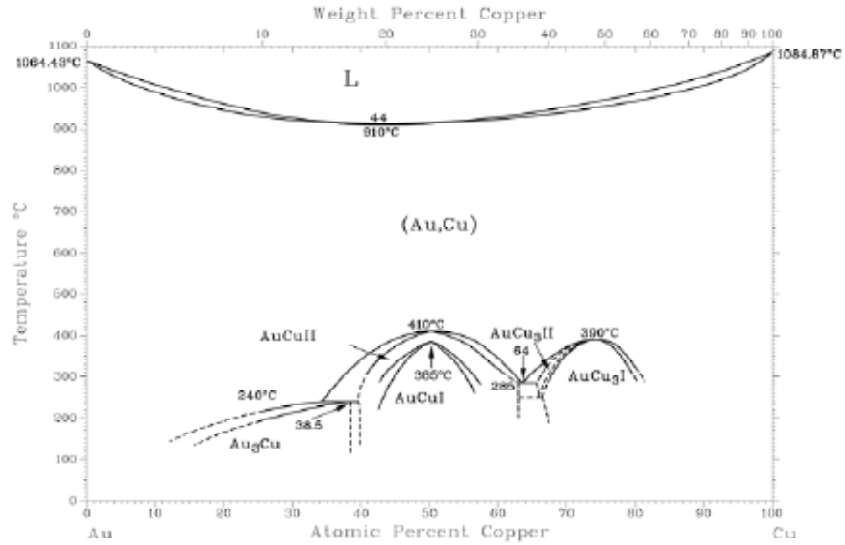
Fig. 3b this cell is shown by the dash-and-dot line. In the present work the classical description [20] of the unit cell of CuAuI is used to identify the reflections of the phase CuAuI. In the SAED pattern (Fig. 3a) one observes a complete set of reflections corresponding to the CuAuI phase, besides the reflection intensity corresponds to the tabular values. In the process of further heating up to 390 ºC, no phase composition changes occurred.

Upon reaching the temperature of 390 ºC the phase transition order-disorder began, i.e. the ordered CuAuI phase began to transfer into the disordered phase $Cu_{50}Au_{50}$. Beginning from 390 ºC the SAED pattern showed the intensity decrease of the diffraction reflection of CuAuI $d_{001}$=3.70 Å, and at 396 ºC there appeared the intensity decrease of the reflection of CuAuI $d_{110}$=2.81 Å. At 420 ºC all the superstructure reflections completely disappeared and in the electron diffraction pattern (Fig. 4a) only the diffraction reflections characteristic of the disordered phase $Cu_{50}Au_{50}$ are present [18]. Consequently, at 420 ºC, in the film under study, the ordered CuAuI phase completely transferred into the disordered phase $Cu_{50}Au_{50}$. However, it is worth noting that the diffraction reflection intensities in the SAED patterns of the Cu-Au films upon heating up to 420 ºC and higher (one carried out experiments with the sample heating up to as high as 700 ºC) showed the "abnormal" intensity distribution, which is not characteristic of the FCC lattice. Thus, the reflection corresponding to $d_{111}$=2.24 Å had an extraordinarily weak intensity, this reflection should have the relative intensity $I_{rel.}$=100 %. In this connection, a relatively weak reflection $d_{220}$=1.36 Å ($I_{rel.}$=22 %) [18], had the intensity $I_{rel.}$=100 % in the SAED pattern (Fig. 4a). When the sample was rapidly cooled (the cooling rate was ~300 ºC/min) down to the temperature which was almost equal to room temperature, the ratio of the reflection intensities in the SAED pattern did not qualitatively change. In the SAED pattern (Fig. 4b), obtained when the sample was tilted by 20º with the help of a goniometer, the intensities of the main reflections become characteristic of the standard FCC structure. Based on this fact it is possible to make a conclusion about the preferred crystallite orientation at the formation of the disordered phase $Cu_{50}Au_{50}$ in the process of




(*a*) (*b*)

Fig. 4. SAED patterns of the Cu-Au films at 420 ºC: without the sample tilt (a), with the sample tilt by 20º (b)




(*a*) (*b*)

Fig. 5. Phase diagram of Cu-Au [19]

heating the Cu-Au films up to 420 ºC and higher. The crystallites $Cu_{50}Au_{50}$ were formed in such a way that the {220} atomic planes were oriented normally to the film plane.

According to the phase diagram of the system Cu-Au (Fig. 5) the stability area of the ordered CuAuI phase is spread from room temperature up to as high as 385 ºC, in the temperature range from 385 ºC to 410 ºC there is an area of stability of the ordered structure CuAuII, and, above 410 ºC the disordered phase $Cu_{50}Au_{50}$ with the FCC lattice is stable [19]. In this connection it becomes clear why at 390 ºC the destruction of the phase CuAuI began and at 420 ºC the phase transition into the structurally-disordered FCC lattice occurred. However, in this work, in the process of heating in the

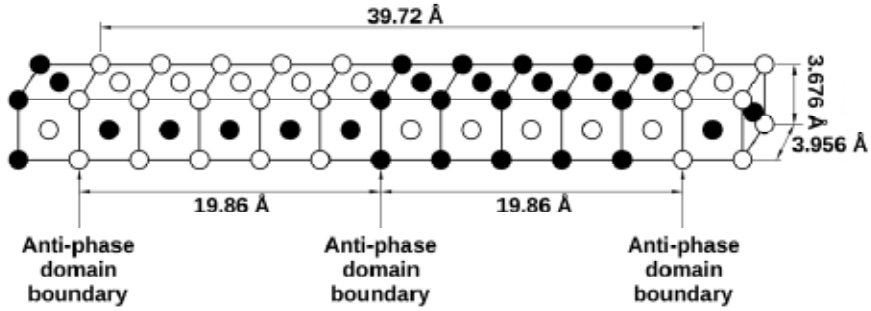



Fig. 6. Model of the atom location in the ordered superstructure CuAuII [24]. The black circles indicate the copper atoms, the hollow ones show the gold atoms

temperature range of 385-410 ºC no formation of the CuAuII phase was observed. It is quite clear that it occurred due to the lack of time for the formation of the phase CuAuII. At a heating rate of 4-8 ºC/min, the sample heating from 385 to 410 ºC goes within only 3-6 min. According to paper [22] for the formation of the phase CuAuII, heating for, at least, 30-45 min at 390 ºC is necessary.

The phase CuAuII, is a long period ordered structure, the space group being Imcm, the lattice parameters are: a=3.96 Å, b=39.72 Å, c=3.68 Å [23]. Fig. 6 shows the scheme of the atom location in the ordered structure CuAuII. The unit cell of the structure CuAuII (see Fig. 6) can be presented as a sequence of ten tetragonal CuAuI cells [20] along the direction b, moreover, within one half of the unit cell all the planes (001) are filled with gold atoms and in the other half- with copper atoms. Thus, an anti-phase boundary is formed on a half of the long unit cell translation [24].

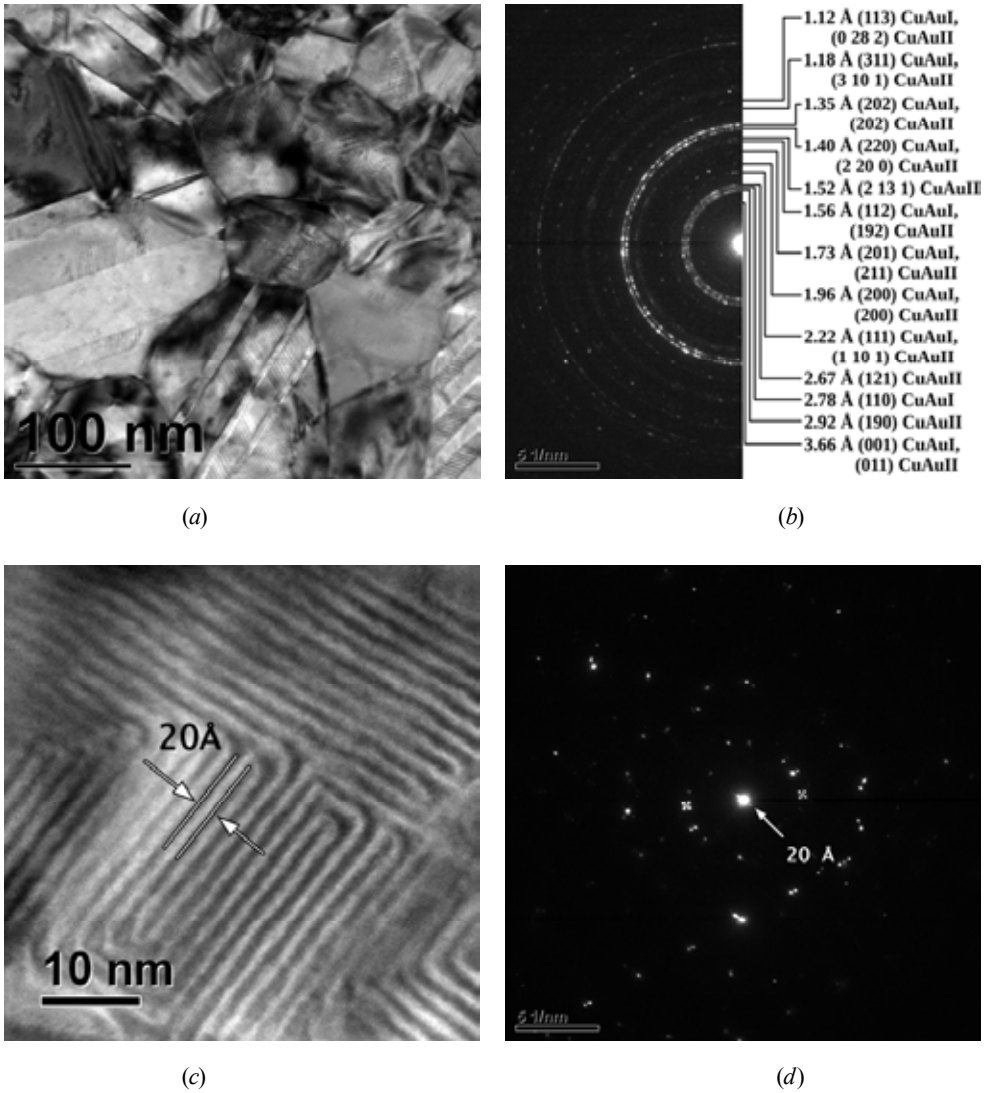
For the purpose of the formation of the ordered structure CuAuII from the structurally disordered state a Cu/Au bilayer nanofilm was heated to 500 ºC, and then, successive annealing in the temperature range from 420 to 370 ºC with a step of 10 ºC was carried out followed by cooling down to a temperature which was close to room temperature at a rate of ~300 ºC/min. The annealing time at each fixed temperature was 20 min. During the annealing process continuous registration of SAED patterns was carried out at a rate of 4 frames per min.

After the annealing at 400 ºC first changes of the SAED patterns were observed – there appeared slightly broadened low intensity reflections which were superstructural for the disordered phase $Cu_{50}Au_{50}$. The appearance of these reflections indicates the beginning of the formation of an ordered structure, i.e. the beginning of the phase transition disorder-order. After the annealing at 380 ºC the intensity of the superstructural reflections in the SAED patterns increased and they became more distinct. After the annealing at 370 ºC, as well as at the sample cooling to room temperature no distinct changes of the diffraction reflections occurred in the SAED patterns.

Fig. 7a demonstrates a TEM image of a Cu-Au film after a series of annealings in the temperature range of 420-370 ºC. One observed the increase of the size of Cu-Au crystallites from 10-20 nm in the initial state to 70-100 nm after this series of annealing procedures. The interpretation of the reflections in the SAED pattern (Fig. 7b), obtained after a series of annealings allows one to make a conclusion that both the phase CuAuII, and the phase CuAuI are present in the film. The phase composition interpretation is complicated by the fact that most of the atomic interplanar spacings of the ordered phases CuAuI and CuAuII practically coincide. Consequently, the major part of rather

intensive reflections will overlap in the electron diffraction pattern. The reflection corresponding to big interplanar spacings which are characteristic of the long period ordered phase CuAuII, and are not present in the structure CuAuI, such as: $d_{020}$=19.86 Å; $d_{040}$=9.93 Å; $d_{060}$=6.62 Å; $d_{080}$=4.965 Å; but they have the relative intensity of the order or considerably lower than 1 %, thus they are not observed in the SAED pattern (Fig. 7b).

It is worth noting that since the unit cell of CuAuII consists of repeated unit cells of CuAuI (Fig. 6), then, in the case of any structure defects occurring in the process of the formation of the phase CuAuII, the reflections characteristic of the phase CuAuI will be observed in an electron diffraction pattern. The most intensive reflection which allows one to determine the presence of the phase CuAuI in the sample is the reflection $d_{110}$=2.800 Å with the relative intensity of 24 % [20], and the reflection




(*a*) (*b*)

(*c*) (*d*)

Fig. 7. TEM images (a, c), obtained at different magnifications; and the corresponding SAED patterns (b, d), of the Cu-Au film after a series of annealings in the temperature range of 420-370 ºC (the sample temperature during the imaging was equal to room temperature)

with a closer interplanar spacing in the CuAuII phase – $d_{091}$=2.824 Å has the relative intensity of only 0.1 % [23].

Fig. 7c shows a TEM image of a single crystallite, in the image the structure characteristic of the phase CuAuII [25] is observed. The period of the location of the domain walls is ≈20 Å, which coincides with the period shown in Fig. 6. The interpretation of the reflection spots observed in the SAED pattern (Fig. 7d) of a single crystallite unambiguously confirms that this crystallite has the long period ordered structure CuAuII. In the SAED pattern one observes the reflections corresponding to $d_{020}$=19.86 Å [23], as well a satellite reflections which is characteristic of the electron diffraction patterns observed from the phase CuAuII [24, 25].

## 4. Conclusion

Cu/Au bilayer nanofilms were obtained by the method of electron beam deposition in high vacuum. The thickness of the individual layers was: Cu=20±2 nm; Au=28±3 nm (the atomic ratio Cu:Au≈50:50 at. %). *In situ* transmission electron microscopy and electron diffraction investigations of the processes of solid-state reactions and atomic ordering in Cu/Au bilayer nanofilms were carried out. The processes were initiated by controlled sample heating in the column of a transmission electron microscope. The samples were heated from room temperature up to 700 ºC. The solid-state reaction between the copper and gold nanolayers was established to begin at 180 ºC. The temperature of the reaction beginning did not depend on the sample heating rate (the heating rate was from 4 to 8 ºC/min). The process of the atomic ordering was shown to begin simultaneously with the formation of the disordered $Cu_{50}Au_{50}$ FCC structure at 245 ºC. The investigations of various phase transitions were carried out, such as order-disorder and disorder-order. The transition of the ordered CuAuI phase ($L1_0$ superstructure) into the disordered phase $Cu_{50}Au_{50}$ was observed during the sample heating, the transition process began at 390 ºC and finished at 420 ºC. During the formation of the disordered phase $Cu_{50}Au_{50}$ in the process of heating of the Cu-Au films up to 420 ºC and higher the crystallites of $Cu_{50}Au_{50}$ were shown to have the preferred orientation. The crystallites $Cu_{50}Au_{50}$ were formed in such a way that the {220} atomic planes were oriented normally to the film plane. The transition of the disordered $Cu_{50}Au_{50}$ phase into the ordered phases CuAuII and CuAuI was observed in the processes of several annealings carried out at the temperature decrease in the range from 420 to 370 ºC. At 400 ºC the process of the ordered structure formation began and after annealing at 380 ºC crystallites of the ordered CuAuII and CuAuI phases were formed in the film.

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# *In situ*-исследования твердофазных реакций и атомного упорядочения в двухслойных нанопленках Cu/Au методами просвечивающей электронной микроскопии и дифракции электронов

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*Методами просвечивающей электронной микроскопии и дифракции электронов проведены in situ-исследования процессов твердофазных реакций и атомного упорядочения в двухслойных нанопленках Cu/Au (с атомным соотношением Cu:Au≈50:50) при нагреве от комнатной температуры до 700 ºС при скорости нагрева 4-8 ºС/мин. Установлено, что твердофазная реакция между нанослоями меди и золота начинается при 180 ºС. Показано, что процесс атомного упорядочения начинается одновременно с процессом формирования неупорядоченной фазы $Cu_{50}Au_{50}$ при 245 ºС. Исследованы процессы формирования атомно-упорядоченных фаз: CuAuI ($L1_0$ сверхструктура) и CuAuII (длинно-периодическая сверхструктура), а также процессы фазовых переходов беспорядок-порядок (переход неупорядоченной структуры в атомно-упорядоченную) и порядок-беспорядок (переход атомно-упорядоченной структуры в неупорядоченную).*

*Ключевые слова: нанопленка Cu/Au, интерметаллиды, твердофазная реакция, фазовый переход, атомное упорядочение, сверхструктура.*