

# Solid-State Synthesis and Atomic Ordering in Thin Cu/Au Films (Atomic Ratio, Cu : Au = 3 : 1)

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**Abstract**—In situ transmission electron microscopy investigations of the processes of solid-state synthesis and atomic ordering in bilayer Cu/Au nanofilms (atomic ratio, Cu : Au = 3 : 1) are conducted. It is found that solid-state synthesis starts at 170°C. A Cu<sub>3</sub>Au atomic-disordered structure (Fm3m space group; lattice constant,  $a = 3.76 \pm 0.01$  Å) forms at 280°C. Annealing the film for 1 hour at 380°C produced a Cu<sub>3</sub>AuI (*L*<sub>1</sub> type) atomic-ordered superstructure, a Pm-3m space group, and lattice constant,  $a = 3.76 \pm 0.01$  Å in the bulk of the film.

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## INTRODUCTION

Cu and Au films are now widely used in microelectronics. Studies of solid-state synthesis and atomic ordering in Cu–Au systems are therefore of considerable scientific and practical interest, as changes in the phase composition and ordering of Cu–Au systems lead to variations of physical properties. Even though studies of Cu–Au systems have been performed for quite some time, the mechanisms of solid-state synthesis and atomic ordering in such systems are still not completely clear. Most experiments use either powders with particles ~10–100 μm in size [1] or films ~1–10 μm thick [2]; only in a relatively few works have Cu–Au films ~10–100 nm thick been studied [3]. Ordering in Cu–Au systems is achieved in most works by means of prolonged annealing. The duration of annealing ranges from one hour [3] to several hundreds of hours [1].

The aim of this work was to study solid-state synthesis and atomic ordering processes in thin bilayer Cu/Au nanofilms (thickness, ~50 nm).

## EXPERIMENTAL

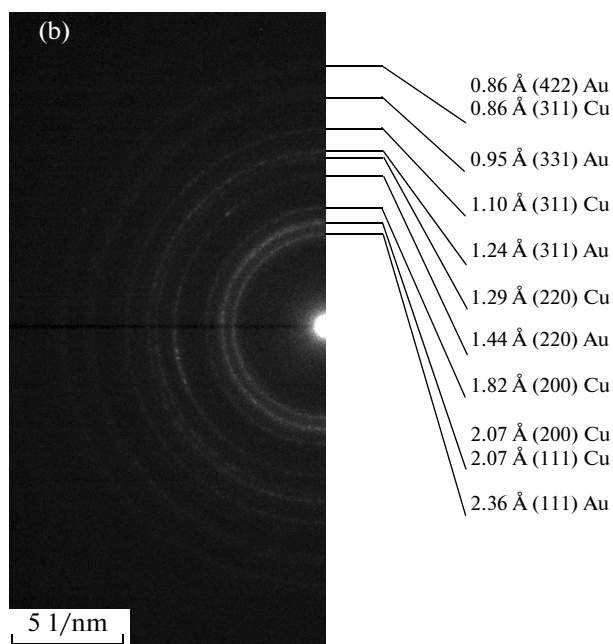
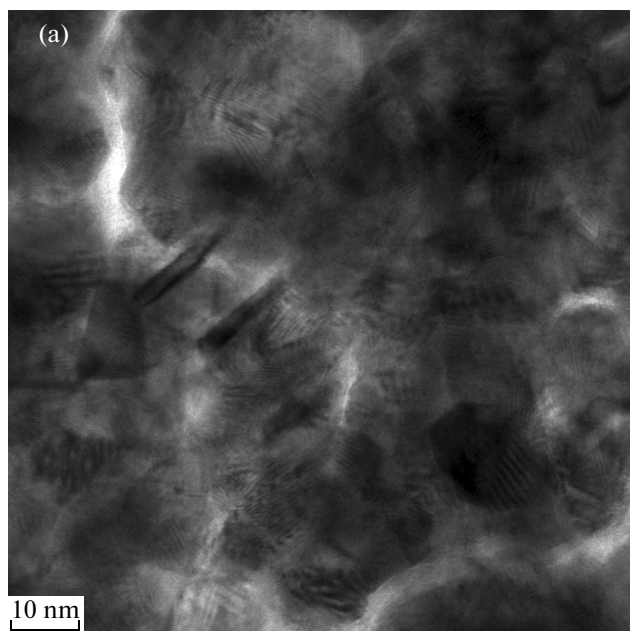
Thin film samples of Cu/Au were produced by electron-beam evaporation using the MED-020 high vacuum coating system (Bal-tec). The base pressure was  $5 \times 10^{-5}$  Pa. The films were produced by the alternating evaporation of gold and copper layers onto a base. A freshly split single crystal of NaCl at room temperature was used as the substrate. The thickness of the films during evaporation was controlled using a quartz resonator. The mean rate of evaporation was 0.3 nm/s. In the investigated films, the thickness of the copper layer was 32 nm, while that of the gold layer was 16 nm. The thicknesses of the gold and copper layers

were chosen so that the atomic ratio was 3 : 1. The structure and elemental composition of the Cu/Au films were studied on a JEM-2100 (JEOL) transmission electron microscope equipped with an Inca X-sight energy-dispersive spectrometer (Oxford). The amount of copper in the studied film samples was  $74 \pm 0.5$  at %, while that of gold was  $26 \pm 0.5$  at %.

In situ electron-microscopy studies of the change in phase composition of the Cu/Au films due to heating were performed using the produced samples. The film samples were heated directly in the column of the JEM-2100 transmission electron microscope using a special sample holder (Model 652 Double Tilt Heating Holder, Gatan). This allowed the controlled annealing of a sample from room temperature to +1000°C. The Cu/Au films were heated at the rate of 4 to 300°C/min from room temperature up to 600°C; annealing was also performed at a fixed temperature of 380°C. During heating, the electron diffraction patterns and the temperature of the sample were recorded synchronously. The electron diffraction patterns were analyzed using the DigitalMicrograph program (Gatan) together with the ICDD PDF 4+ [4] and Pearson databases on crystal structure [5].

## RESULTS AND DISCUSSION

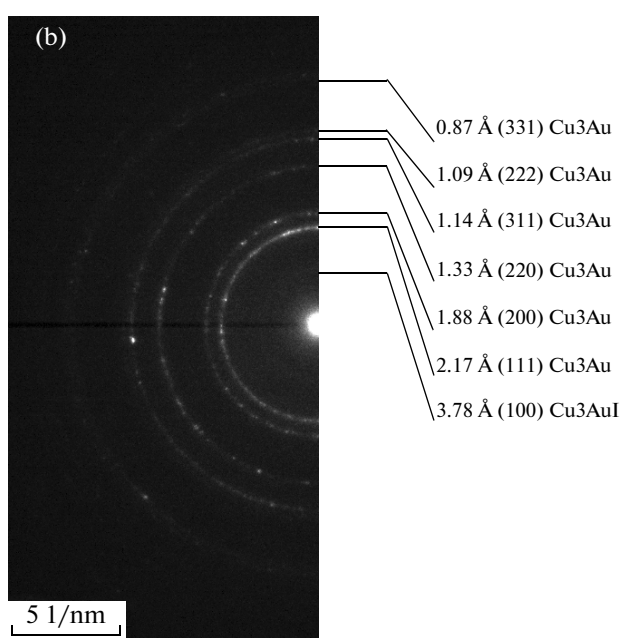
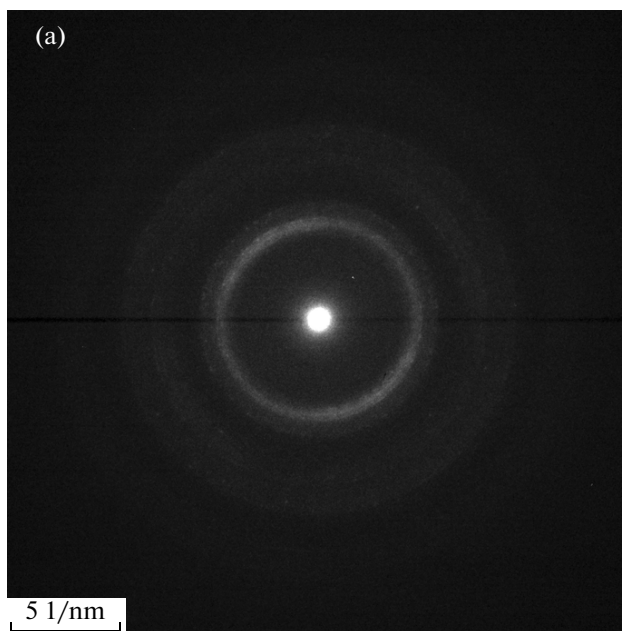
In their initial state, the films consisted of crystallites 10–20 nm in size (Fig. 1a). Diffraction reflexes in the electron diffraction pattern (Fig. 1b), obtained by means of microdiffraction from a region of about 1 μm, were of a polycrystalline character similar to cubic face-centered lattices (FCC) : Cu (space group, *Fm-3m*; lattice constant,  $a = 3.62$  Å) [6] and Au (space group, *Fm-3m*; lattice constant,  $a = 4.08$  Å) [7].



**Fig. 1.** (a) Electron microscopy image and (b) electron diffraction pattern obtained from a Cu/Au film in the initial state.

During heating, the first weak changes in the diffraction patterns obtained from the samples were observed at a temperature of 170°C. Smearing of the diffraction rings began, indicating the start of a reaction at the border between Cu and Au. Complete smearing of the diffraction reflexes in the diffraction image was observed at a temperature of 250–260°C (Fig. 2a).

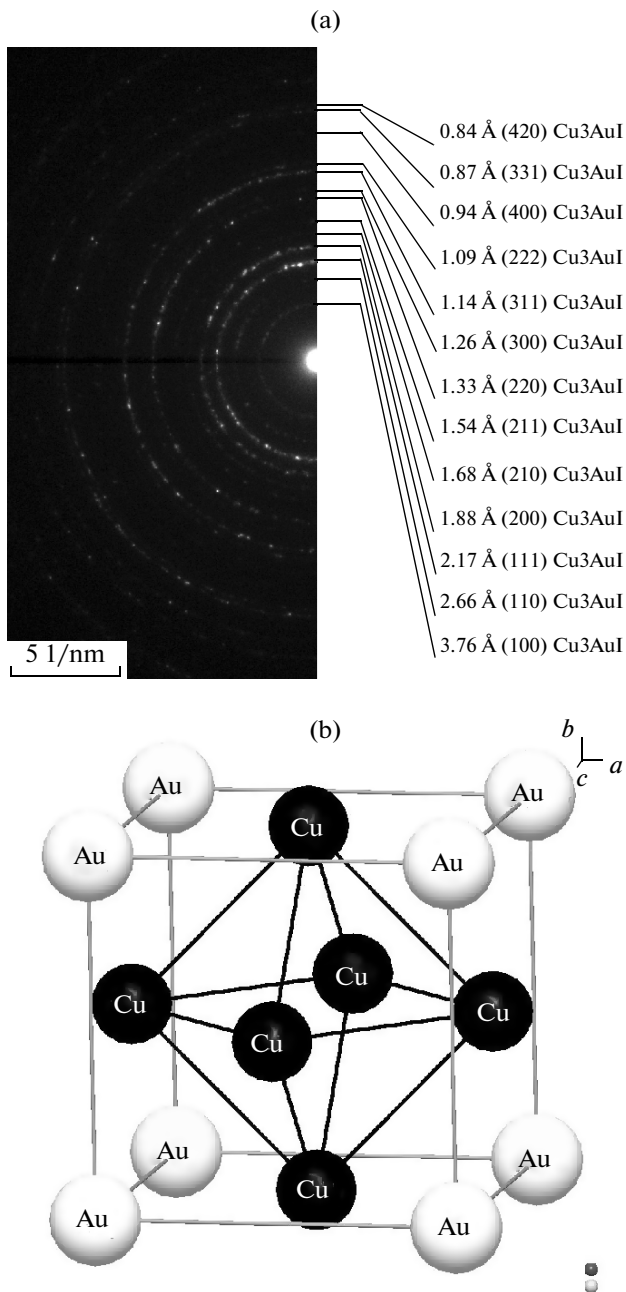
The emergence of diffraction reflexes corresponding to a new phase different from those of pure Cu and Au [6, 7] was observed at a temperature of 280°C during subsequent heating of the samples. When the sam-



**Fig. 2.** Electron microdiffraction patterns obtained from a Cu/Au film after heating to (a)  $T = 260^\circ\text{C}$  and (b)  $T = 330^\circ\text{C}$ .

ples were heated to a temperature of 330°C, the diffraction reflexes of the new phase became clearer (Fig. 2b). The diffraction pattern did not change when the samples were heated to 360°C. Analysis of the diffraction image (Fig. 2b) revealed a disordered FCC lattice (space group,  $Fm-3m$ ) with the lattice constant  $a = 3.76 \pm 0.01 \text{ \AA}$  corresponding to the  $\text{Cu}_3\text{Au}$  phase [8].

It should be noted that along with reflexes corresponding to an FCC lattice with  $a = 3.76 \text{ \AA}$ , a superstructure reflex with a low intensity corresponding to an interplane distance of  $3.7 \pm 0.1 \text{ \AA}$  was observed in the diffrac-



**Fig. 3.** (a) Electron microdiffraction pattern obtained from a Cu/Au film after annealing at  $T = 380^\circ\text{C}$ ; (b) model of atomic positions in the atomic-ordered Cu<sub>3</sub>AuI (type  $L1_2$ ) superstructure.

tion image at a temperature as low as  $280^\circ\text{C}$ . Up to a temperature of  $360^\circ\text{C}$ , the intensity of this reflex did not change appreciably. At a temperature of  $380^\circ\text{C}$ , the superstructure reflex was clearly distinguishable and weak traces of another superstructure reflex corresponding to  $2.6 \pm 0.1 \text{ \AA}$  appeared. It is well known that atomic ordering in Cu–Au alloys with compositions close to Cu<sub>75</sub>Au<sub>25</sub> leads to the formation of the Cu<sub>3</sub>AuI phase, which is an atomic-ordered superstructure of the  $L1_2$  type (space group,  $Pm\text{-}3m$ ; lattice constant,  $a = 3.747 \text{ \AA}$ ) [9]. Assum-

ing that the formation of an atomic-ordered superstructure of the  $L1_2$  type began in the investigated samples as a result of heating, the observed reflexes can be identified as superstructural relative to the Cu<sub>3</sub>Au atomic-disordered phase [8]. The observed reflexes corresponding to the interplane distances  $3.7 \pm 0.1 \text{ \AA}$  and  $2.6 \pm 0.1 \text{ \AA}$  can then be identified with the interplane distances of the atomic-ordered Cu<sub>3</sub>AuI phase:  $d_{100} = 3.747 \text{ \AA}$  and  $d_{110} = 2.649 \text{ \AA}$  [9].

To form an atomic-ordered Cu<sub>3</sub>AuI (type  $L1_2$ ) superstructure in the bulk of the Cu–Au film samples heated to  $380^\circ\text{C}$ , the films were annealed at a temperature of  $380^\circ\text{C}$  for one hour. During annealing the intensity of the superstructure reflexes increased. Analysis of the diffraction image after annealing (Fig. 3a) showed that a full set of diffraction reflexes corresponding to the atomic-ordered Cu<sub>3</sub>AuI (type  $L1_2$ ) superstructure with the  $Pm\text{-}3m$  space group and lattice constant  $a = 3.76 \pm 0.01 \text{ \AA}$  was observed. The obtained value coincides within the limits of error group with the data obtained by X-ray diffraction: space group,  $Pm\text{-}3m$ ; lattice constant,  $a = 3.747 \text{ \AA}$  [9]. A three-dimensional model of the atomic-ordered Cu<sub>3</sub>AuI (type  $L1_2$ ) superstructure is shown in Fig. 3b [9].

To determine the temperature stability of the atomic-ordered Cu<sub>3</sub>AuI superstructure, the sample was heated from room temperature to  $600^\circ\text{C}$  at a rate of  $4^\circ\text{C}/\text{min}$ . At a temperature of  $395^\circ\text{C}$ , the intensity of the superstructure reflexes began to diminish. When a temperature of  $420^\circ\text{C}$  was reached, the superstructure reflexes became virtually indistinguishable in the diffraction image, suggesting the transition of the atomic-ordered Cu<sub>3</sub>AuI phase to the atomic-disordered Cu<sub>3</sub>Au phase.

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