Solid solution formation in Cu/Co ultrathin film systems

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The β–(Co–Cu) fcc solid solution (SS) in multilayer Cu/Co nanocrystalline films (layer number 2 to 8) at ultra-small individual layer thickness (max. 10 nm) has been studied. The electrophysical properties (resistivity and temperature resistance coefficient) of the film alloys,the correlation thereof with the layer number, the total effective thicknessand thecomponent concentrations have been established.

Изучены условия формирования твердого раствора β–(Co–Cu) в многослойных нанокристаллических пленках (число слоев от 2 до 8) на основе Co и Cu с ультрамалой эффективной толщиной отдельных слоев (не более 10 нм). Исследованы электрофизические свойства (удельное сопротивление и ТКС) пленочных сплавов, установлена их корреляция с числом слоев, общей эффективной толщиной и концентрацией компонент.

The interest in the magnetotransport properties of Co/Cu (Ag), Fe/Cr, and other multilayers [1–6] is due to the giant magnetoresistance (GMR) effect observed therein. The particular interest in the modeling samples in the form of $[Co/Cu]_n/S$ multilayers (where S is a substrate) is associated with the fact that elements of granular state are realized therein [7–9], that is, nanocrystallites of hexagonal (hcp) Co are formed in the β–(Co–Cu) solid solution (SS) crystallites containing fcc Cu or in Cu crystallites (in the case of the SS decomposition). The granular state stabilization and the individuality conservation extent of Co and Cu layers effect very considerably the GMR effect magnitude. In this connection, of principal importance associated with the GMR effect are studies on the influence of the phase and structure state, thickness of individual layers, the granular state extent, and heat treatment regimes on the magnetotransport properties of film materials with spin-dependent electron scattering. Although there are numerous works aimed at those problems (see, e.g., [7–15]), this field remains scarcely studied in some aspects. In particular, the phase formation processes in thermally evaporated ultra-thin (about 1 nm thin individual layers) bi- and multilayer Co/Cu films is not studied completely to date. (It is to note that in the works cited above, the samples were obtained by HF magnetron [7] or ionic [8] sputtering, or by electrochemical deposition of granular alloys [13, 14]). Thus, the purpose of this work is to study the structure and phase state of nanodimensional film systems prepared by alternate condensation of Co and Cu layers and to elucidate the conditions of fcc Cu based SS formation therein.

To prepare the samples and to study electrical properties thereof, a high-vacuum setup involving a NMDO-160 magneto-discharge pump was used (for the setup details, see [16]). The residual gas pressure was about 10^{-5} Pa. The Cu films were obtained using resistive technique and the Co ones, by an electron beam gun. The condensation rate was 0.1 nm/s for Cu and 0.01 to

0.02 nm/s for Co. For electron microscopic examinations, a 10 to 20 nm thick carbon film was used as the substrate, while to study the electrical properties, the samples were deposited onto polished glass substrates with melted-in molybdenum bars as cathodes. The film dimensions were as follows: length $l = 11$ mm and width $a = 1$ mm, the Mo electrode diameter being $D = 1.2$ mm. Annealed Al films (about 30 to 40 nm thick) were used as references when interpreting the electron diffraction patterns. The effective thickness of individual layers was determined to within ±0.1 nm from the deposited substance mass using a quartz resonator. The electric resistance was measured using an APPA 109 universal instrument at 0.06 % maximum error, the working voltage being 10 mV. The phase composition and substructure were studied using the following sample groups: Co(5), Cu(5), Co(10) and Cu(10); Co(2)/Cu(5)/S, Co(5)/Cu(5)/S and Co(10)/Cu(10)/S; Co(10)/Cu(5)/Co(10)/S; Co(5)/Cu(10)/Co(10)/Cu(10)/S and Co(10)/Cu(10)/Co(10)/Cu(10)/S; and $[Co(5)/Cu(5)]_4$/S, where S is a substrate and the effective layer thickness values are indicated in brackets.

The phase composition of single-layer Co and Cu films in the initial state and after annealing at 630 K followed by cooling down to 300 K corresponds to fcc or hcp phases with lattice parameters close to those in bulk samples, i.e., $a_0 = 0.3615$ nm (Cu), $a_0 = 0.2505$ nm and $c_0 = 0.4089$ nm (Co). In multilayer samples, only the fcc β–(Co–Cu) solid solutions are present, the lattice parameter being dependent on the Co atomic percentage according to the Vegard rule (see Fig. 1). The SS has been concluded to be formed on the base of Cu lattice, because the studied ranges of temperature and the island size of Co films are far enough from the stabilization conditions of fcc Co with $a_0 = 0.354$ nm. However, the extrapolation of $a(c)$ dependence to high Co concentrations points that in this case, the γ–(Co–Cu) SS may likely be formed, that is, on the basis of fcc Co. At the same time, at low Co concentrations, a biphase composition, i.e., β–(Co–Cu) SS and fcc Cu, will take place (see [9] for details). The electron diffraction pattern interpretation is exemplified in Table for the Co(5)/Cu(10)/Co(10)/Cu(10)/S film. Note that the small number of lines in the pattern is due to nanocrystalline sample structure. Calculation of the average island size

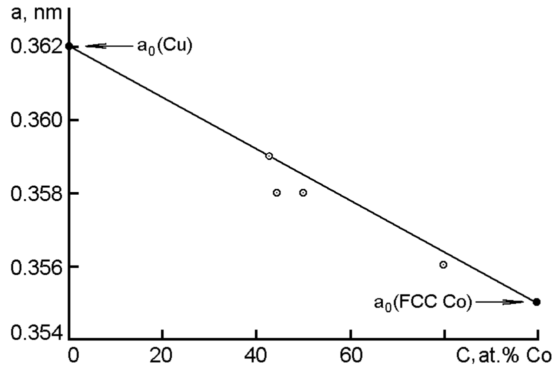

Fig. 1. Dependence of fcc β–(Co–Cu) SS lattice parameter on Co atomic percentage in a multilayer film.

($\bar{L}$) from the electron microscopy data indicates that it is about 3 to 5 times larger in single-layer Cu films than in Co ones. So for the effective film thickness of 5 nm, the island sizes are within limits of 11 to 28 nm for Cu and only 4 to 7 nm for Co. In the β–(Co–Cu) SS samples, the island size is defined by the Cu film although being somewhat smaller than in the single-layer Cu film.

Fig. 2 illustrates the island structure and size distribution for a Co(5)/Cu(5)/C film. When passing to multilayer Co(5)/Cu(10)/Co(10)/Cu(10)/ C and $[Co(5)/Cu(5)]_4$/C film systems, the average island size $\bar{L}$ (calculated by averaging of two measurements in perpendicular directions) is 14 and 11.5 nm, respectively. Such an insignificant $\bar{L}$ variation evidences that Co is dissolved in Cu islands. Otherwise, rings from hcp Co would be observed in electron diffraction patterns. Thus, the β–(Co–Cu) SS is formed directly during the condensation due to dissolution of hcp Co islands in Cu matrix. That scheme agrees well with the energy concept [14, 15] suggesting that the Co/Cu system energy drops sharply if Co atoms are included in the Cu layer as individual atoms or clusters. That viewpoint is confirmed in [18]. A fraction of Co islands

Table. Interpretation of diffraction pattern from β–(Co–Cu) SS

No.	I, rel. units	d_{hkl}, nm	hkl	a, nm	$\bar{a}$, nm
1	Very high	0.2086	111	0.3613	0.3590
2	high	0.1780	200	0.3561	
3	high	0.1267	220	0.3583	
4	medium	0.1085	311	0.3560	

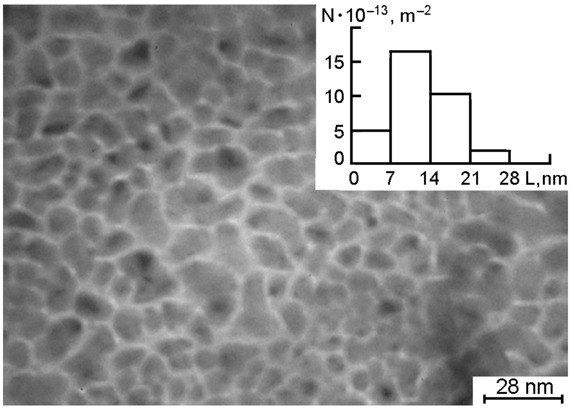

Fig. 2. Microstructure of Co(5)/Cu(5)/C film and the corresponding histogram.

undissolved in the Cu film bulk may become stabilized at its surface as SS islands. This causes the diminution of the island average size in the multilayer system, the phase composition remaining unchanged.

Beside the structure and phase state features specified above, we have found that the β–(Co–Cu) lattice parameter depends somewhat on the Co condensation rate. So, as the rate is increased from 0.15 to 0.20 nm/s, the parameter a decreases from 0.3605 to 0.3580 nm. This can be explained by accumulation of vacancies in the SS islands. In the same manner, as the Co condensation rate increases thrice, $\bar{L}$ value for Co island becomes approximately halved. The diffraction and electron-microscopic studies and conclusions concerning the β–(Co–Cu) formation kinetics supplement the electric resistance measurements during the multilayer system condensation. An example of such dependence is presented in Fig. 3. The distinctions in the $R(\tau)$ dependences in the cases of Cu and Co deposition (cf. insets a and b in Fig. 3) are associated with the layer-by-layer or island-like growth of Cu and Co films. This is confirmed by [17, 18]. The increase of the film system resistance followed by its decrease during the further condensation of Co(5) is associated with formation of Co islands at the film surface and the subsequent dissolution thereof in the Cu matrix. This statement is confirmed indirectly by the value of thermal resistance factor (β) of multilayer film systems (at T = 300 K, $\beta = (1.2 \text{ to } 1.4)\cdot10^{-3}$ K^{-1} being intermediate between those for Cu and fcc Co).

Thus, the structure and phase state of ultra-thin nanocrystalline Co/Cu film systems has been studied. It has been found that in bilayer and multilayer samples, the

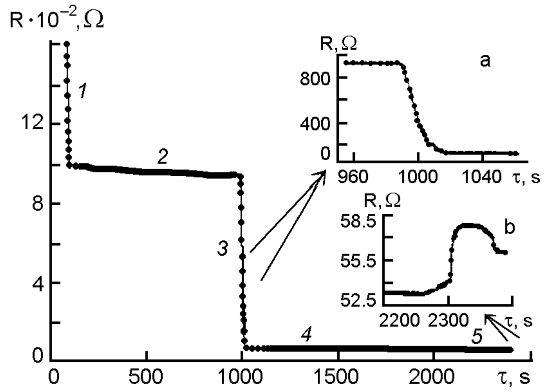

Fig. 3. Resistance changes during the Co(5)/Cu(10)/Co(10)/Cu(10)/S film condensation: condensation of Co(10) layer onto Cu(10)/S (*1*); holding of the Co(10)/Cu(10)/S system (*2*); condensation of Cu(10) layer onto Co(10)/Cu(10)/S (*3*); holding of the Cu(10)Co(10)/Cu(10)/S system (*4*); condensation of Co(5) layer onto the Cu(10)Co(10)/Cu(10)/S (*5*).

β–(Co–Cu) SS based on Cu fcc lattice is formed already in the course of condensation. The SS lattice parameter dependence on Co atomic concentration answers to the Vegard rule. The average island size in the multilayer systems is smaller than that in single-layer Cu films, thus evidencing an incomplete solubility of Co islands in the Cu matrix and the presence thereof as β–(Co–Cu) SS particles at the surface of the Cu underlayer or within the channels therein. It is possible to continue the investigation by studying electrophysical properties of film alloys in the form of β–(Co–Cu) or γ–(Co–Cu) SS.

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Утворення твердого розчину в ультратонких плівкових системах на основі Cu та Co

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Вивчено умови формування твердого розчину β–(Co–Cu) у багатошарових нанокристалічних плівках (кількість шарів від 2 до 8) на основі Co та Cu з ультрамалою товщиною окремих шарів (не більше 10 нм). Досліджено електрофізичні властивості (питомий опір та ТКО) плівкових сплавів, встановлено їх кореляцію з кількістю шарів, загальною ефективною товщиною та концентрацією компонент.