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Effect of substrate temperature on crystalline structure and galvanomagnetic characteristics of Ni–Cu alloy thin films

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The phase composition, crystalline structure and magnetoresistance of the Ni–Cu alloy thin films of various thickness and concentrations have been studied. Influence of substrate temperature on the crystalline structure formation processes and phase composition of the films has been considered. Dependences of magnetoresistance $\Delta R/R_0$ and coercive force H_c on the substrate temperature have been established.

Исследованы фазовый состав, кристаллическая структура и магнитосопротивление тонких пленок сплава Ni–Cu с различными толщинами и концентрациями компонент. Рассмотрено влияние температуры подложки на процессы формирования кристаллической структуры и фазовый состав пленок сплавов. Установлены зависимости величины магнитосопротивления $\Delta R/R_0$ и коэрцитивной силы H_c от температуры подложки.

The condensation in vacuum is one of the widely used techniques to obtain thin films and has a number of advantages as compared with other techniques (electric deposition, chemical deposition from solutions, cathode sputtering, etc.). The films obtained by this technique are characterized by high purity due to use of high vacuum. Moreover, this technique provides obtaining homogeneous films of preset thickness having a defined structure and physical properties by varying the crystallization parameters within a wide range. One of the basic parameters that influence the film crystallization process on a substrate is the substrate temperature T_s, any change of that causes changes in series of simultaneous processes. Thus, the T_s elevation results in increased mobility of the condensed atoms which migrate along the substrate surface, intensified desorption of adsorbed atoms of the substance being deposited (as well as foreign particles and impurities), decreased concentration of surface defects, thus favoring the formation of coarse-grained films with more perfect structure, which have improved grain-oriented pattern. The purpose of this work is to characterize the substrate temperature dependence of crystalline structure, phase composition, as well as magnetoresistance (MR) of Ni–Cu alloy thin films.

The samples of Ni–Cu alloy films of 35 to 100 nm thickness with copper concentration (C_{Cu}) 10 to 40 at.% were obtained in VUP-5M vacuum unit (residual pressure 10^{-3} to 10^{-4} Pa) using separated evaporation of components according to the procedure [1]. The samples for electron-microscopic examinations were condensed on (001) KBr chips. The samples for magnetoresistance measurements were condensed on polished glass plates with preset copper contacts. The required fixed substrate temperatures T_s (293 K, 373 K, 473 K and 573 K) were provided by a copper block of substrate holders connected with the heater and was measured using a differential copper-constantan thermocouple at an accuracy of ±10 K. The film thickness d was measured using MII-4 microinterferometer equipped with interference pattern computer registration system [2] (the measurement accuracy amounts 10 to 20 %, depending on the film thickness). The concentrations of components in the obtained alloys were evaluated both by calculations (according to [1]), and using an EDS X-ray micro-analyzer installed in a REM-103-01 scanning electron microscope. The crystalline structure of Ni–Cu film alloys was stabilized by 2 or 3 annealing cycles up to 673 K in VUP-5M vacuum installation. The electron-microscopic and electron diffraction investigations of samples were carried out using EM-125 electron microscope. The magnetoresistance [3] of Ni–Cu alloy films $\Delta R/R_0$=$(R_H$-$R_0)/R_0$ was measured as described in [2]. The longitudinal MR $(\Delta R/R_0)_{||}$ and transversal MR $(\Delta R/R_0)_{\perp}$ values were determined depending on the mutual arrangement of the field and the current direction in the sample.

In all the obtained film samples, the fcc Ni–Cu alloy with crystal lattice parameter a_{fa} = 0.352 to 0.357 nm is formed, that conforms well with the parameter value a_0 = 0.3542 to 0.3615 nm for bulk Ni–Cu alloys [4] (at C_{Cu} varying from 0 to 100 at.%). The electron-microscopic images and respective electron diffraction patterns of Ni–Cu alloy films deposited on KBr substrates at various temperatures T_s (deposition rate about 0.5 nm/s) and then heat-treated up to 673 K are presented in Fig. 1. In all investigated cases, formation of alloy takes place already at the condensation stage, and electronography data confirm this phenomenon. The films crystallized at room temperature are characterized by a fine-grain structure with crystallite sizes about 5 to 10 nm (Fig. 1a), and the diffraction pattern in the form of slightly diffused rings (insertion in Fig. 1a) corresponds to this structure that evidences the small size and random orientation of the crystal grains. The substrate temperature elevation up to 373 K does not result in any noticeable increase of grain size, as is seen in Fig. 1c; however, very weakly expressed texture maxima are observed in the diffraction pattern (insertion in Fig. 1c) and this is an evidence of the starting oriented growth of some grains with respect to the substrate. The further substrate temperature rise to T_s = 473 K during the condensation process results in formation of crystalline structure with crystallite sizes of 50 to 70 nm (Fig. 1e). At the same time, increased number of oriented grains evidenced by contraction of small arcs at the rings of electron-diffraction patterns (insertion in Fig. 1e).

In the films deposited at T_s = 573 K, a coarse-grain structure with grain size L of about 70–100 nm (Fig. 1g) is observed, and the diffraction pattern in the form of thin rings with spot reflexes of corresponding orientation (001) arranged thereon (inset in Fig. 1g) answers to this structure. Moreover, supplementary reflexes are observed in electron diffraction patterns (designated by D in the inset in Fig. 1g), which can be explained by the presence of twins, and this is a characteristic feature of thin films of many metals with fcc lattice crystallized on alkaline halides at thermal evaporation in vacuum (twins being present on every {111} plane). The strips connecting the (200) and (111) reflexes in the electron diffraction pattern (inset in Fig. 1g) evidence small size of the twins. Some weak supplementary reflexes (designated as T in the inset in Fig. 1g) can be explained by double diffraction (an electron beam diffracted from (001) oriented matrix hits a twin and is diffracted once more, or vice versa), and occur at a deflection from accurate orientation [100], i.e. when the film is somewhat inclined. Similar crystallographic investigations were carried out for a series of pure metals, in particular, for Ni and Cu [5]. The results obtained by us conform well to these data taking into consideration the concentration influence of components on the formation of crystalline structure of alloy films. The oriented growth of the investigated Ni–Cu alloy thin films starts at $T_s \approx$ 373 K (for Ni/NaCl and Cu/NaCl, these temperatures are T_s = 423 K and T_s = 293 K, respectively [5]).

The films of Ni–Cu alloy obtained by deposition on (001) KBr chip at various substrate temperatures were annealed in vacuum together with the substrate up to 673 K (annealing of films on the substrate at higher temperatures is inexpedient due to intense sublimation of KBr that results in damage of the film sample). Annealing of the alloy films obtained at room temperature and at T_s = 373 K results in a considerable increase of the crystallite size up to 100 nm and more (Fig. 1c,d). Formation of twins (D in Fig. 1d) is also observed as well as increase in number of grains are oriented in parallel with the substrate plane (inset in Fig. 1d). In films obtained at substrate temperatures of 473 K and 573 K, when being annealed up to 673 K, in addition to the growth of grain size up to 200 nm, new

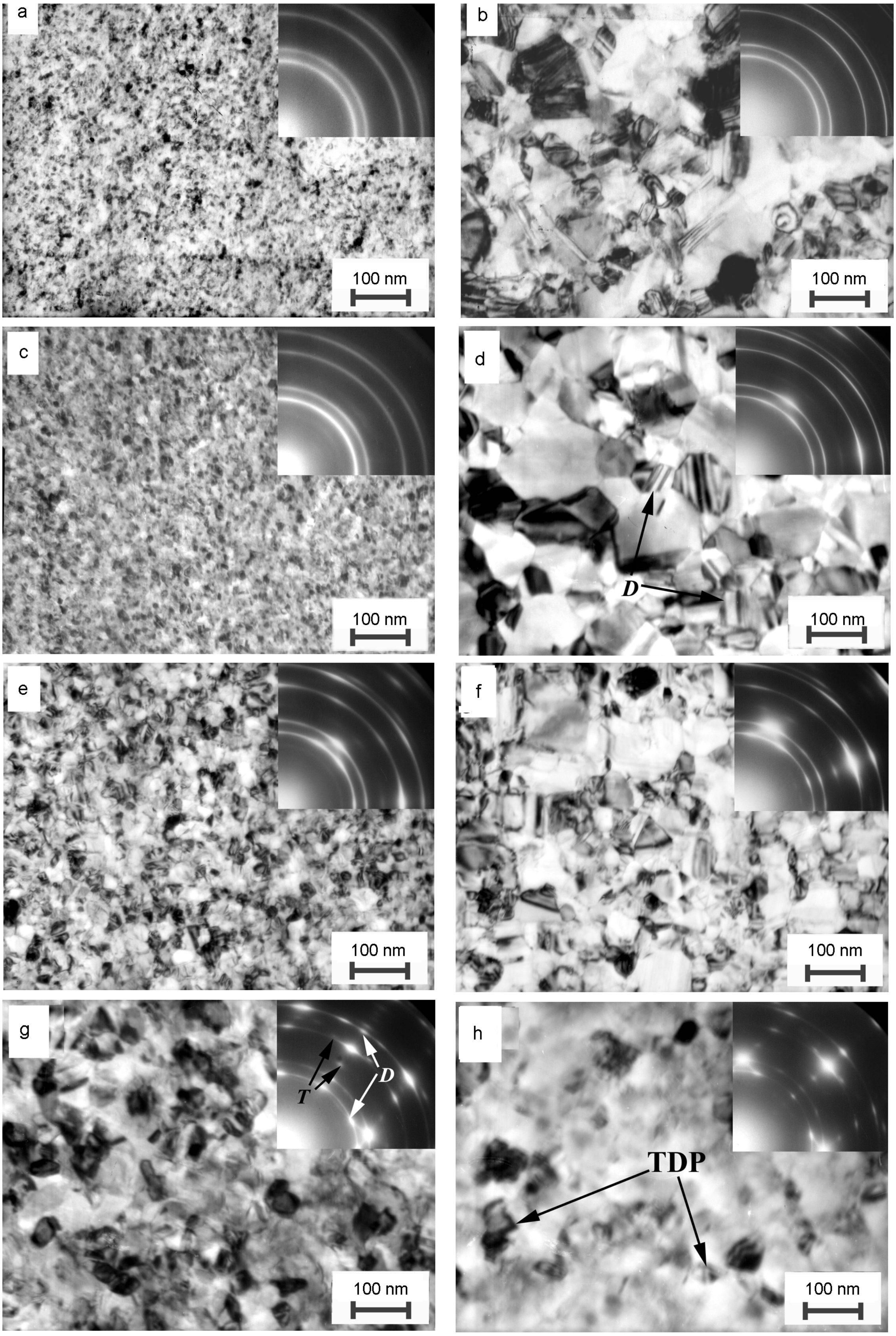

Fig. 1. Microstructure and electron diffraction patterns of Ni–Cu alloy films (d = 40 to 59 nm, C_{Cu} = 24 to 29 at. %) deposited on (001) KBr chips at T_s (K): 293 (a, b); 373 (c, d); 473 (e, f); 573 (g, h) for freshly-deposited (left column) and annealed up to 673 K (right column) samples.

Table. Dependence of galvanomagnetic characteristics of Ni–Cu alloy films on the deposition conditions and crystalline structure of samples

d, nm	C_{Cu}, at.%	T_s, K	L, nm		$(\Delta R/R_0)_{\parallel}$, %		$(\Delta R/R_0)_{\perp}$, %		H_c, kA/m	
			Before annealing	After annealing	Before annealing	After annealing	Before annealing	After annealing	Before annealing	After annealing
42	24	293	5–10	up to 100	0.08	0.18	−0.04	−0.09	6.5	1.1
59	27	373	5–10	up to 150	0.17	0.40	−0.07	−0.40	0.8	3.8
39	24	473	50–70	up to 200 formation of grains with L ~ 5–10 nm	0.12	0.23	−0.18	−0.18	1.7	1.8
41	29	573	70–100	up to 200 formation of grains with L ~ 5–10 nm	0.07	0.07	−0.06	−0.06	1.5	1.5

crystallites are also observed to appear of L ~ 5 to 10 nm (Fig. 1f,h) supplementary reflexes shown in the corresponding electron diffraction patterns (insets in Fig. 1f,h) are caused by both twinning and presence of tetrahedrons consisting of stacking faults (TDP in Fig. 1h).

Typical dependences of the longitudinal and transversal MR obtained for the freshly-condensed films and those annealed up to 673 K are similar to the data reported in [3, 6] for Ni films in weak magnetic fields. The transversal effect of magnetoresistance has negative sing, and this is characteristic feature for the component of Ni alloy [3, 6, 8]. A hysteresis of $\Delta R/R_0(H)$ dependence is observed for all investigated samples of Ni–Cu alloys with copper concentration $C_{Cu} < 35$ at.%; this is due to the presence of domain structure [3, 7] and thereby of various mechanisms of conductivity electron scattering depending on the value of external magnetic field induction. As is seen in Table, the values of MR and coercive force H_c depend on both the Cu concentration and the substrate temperature at which the films were obtained. The magnetoresistance of alloy films condensed at room temperature has been investigated and stated in detail by us in [2, 9]. The resulting values of the longitudinal and transversal MR obtained by us conform quite well to the values of the respective quantities obtained in [10] for the $Ni_{81}Cu_{19}$ films of various thickness electrodeposited at room temperature in magnetic fields with induction up to 0.7 T.

The value of the coercive force H_c considerably lower as compared to the films obtained on the substrate at room temperature [2] is a peculiarity of the alloy films obtained at temperature $T_s = 373$ K. Moreover, the coercive force H_c at $T_s = 373$ K is less than that for the films obtained at room temperature and then annealed up to 673 K. After annealing of these films, the MR value increases by a factor of 2 to 3; the coercive force becomes equal to the H_c for the films condensed at room temperature and annealed up to 673 K. A similar situation is also observed for the films obtained at $T_s = 473$ K. It should be noted that after annealing of these samples, the H_c remains essentially unchanged while the MR value increases by a factor of 1.5 to 2 as compared to the freshly-condensed films. For the Ni–Cu alloy films obtained at $T_s = 573$ K, neither $\Delta R/R_0$ nor H_c values are changed after annealing up to 673 K. Such peculiarities in of magnetoresistance and coercive force behavior of Ni–Cu alloy films condensed on substrate at various temperatures can be explained by specific properties of the crystal structure (increased grain size, decrease of imperfection) and magnetic structure. Increase of the film MR after annealing, in our opinion, is also connected with the modification of magnetic anisotropy.

To conclude, it is proved that in Ni–Cu alloy thin films obtained at various substrate temperatures, the fcc phase with the crystal lattice parameter $a_{fa} = 0.352$–0.357 nm is observed to be formed within the whole investigated interval of thickness ($d = 35 \div 100$ nm) and concentrations

(C_{Cu} = 10–40 at.%). The samples obtained at T_s = 293 K and T_s = 373 K are characterized by the fine-grain structure with crystallite sizes of about 5 to 10 nm. The substrate temperature rise at condensation up to T_s = 473 K and T_s = 573 K results in formation of crystalline structure with grains of 50 to 70 nm and of 70 to 100 nm, respectively. At the same time, the number of grains grown at preset orientation increases. The annealing of the alloy films results in increase of crystallite size up to 100–200 nm, depending on the substrate temperature. A hysteresis of $\Delta R/R_0(H)$ dependence is observed for all investigated samples of Ni–Cu alloys at copper concentration of $C_{Cu} < 35$ at.%, and this is due to the presence of domain structure. The MR and coercive force H_c values depend both on the alloy composition and on the substrate temperature at the film deposition.

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Вплив температури підкладки на кристалічну структуру та гальваномагнітні властивості тонких плівок сплаву Ni–Cu

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Досліджено фазовий склад, кристалічну структуру та магнітоопір тонких плівок сплаву Ni–Cu з різними товщинами та концентраціями компонентів. Розглянуто вплив температури підкладки на процеси формування кристалічної структури та фазовий склад плівкових сплавів. Встановлено залежності величини магнітоопору $\Delta R/R_0$ та коерцитивної сили H_c від температури підкладки.