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The Phase Transformations and Magnetoresistive Properties of Diluted Solid Solutions Based on Fe and Ge Atoms

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In the article, the structure, phase composition and magnetoresistive properties of single- and three-layer films based on Fe and Ge were studied. It is established that in such films eutectic is formed based on diluted solid solutions of Ge atoms in α-Fe layers and of Fe atoms in α-Ge layers at the total concentration of Ge atoms from 3 to 20 at.% in the temperature range of 300-870 K. It is shown that magnetoresistive properties of the films with eutectic composition are not significantly different from the properties of α-Fe films.

Keywords: Film materials based on Fe and Ge, Phase transformations, Concentration of atoms, Solid Solution, Magnetoresistance.

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1. PHASE FORMATION PROCESSES IN FILM SYSTEMS BASED ON Fe AND Ge

Development of spin and sensor electronics stimulates the elaboration of new multilayer functional materials of the ferromagnetic metal/semiconductor type, in which, in contrast to magnetic semiconductor structure formed by the introduction of magnetic impurities into semiconductor, the formation of solid solutions and binary phases is possible [1]. Advanced study of the interconnection between electrophysical, magnetoresistive and magneto-optical properties and phase composition of such systems is connected with the solution of the question about the possibility of their practical application as high-density data recording media, magnetoresistive random access memory, high sensitive elements of multifunctional sensors [2], new types of integrated circuits of special purposes with high integration level [3] and stimulated by the necessity of the solution of some problems of spintronics [4, 5].

A sufficient amount of publications is devoted to the study of the properties of metal/semiconductor film materials. Thus, for example, the authors of the work [6] on the basis of the investigation results of the structure, magnetic and transport properties, Hall effect in Fe/Ge multilayers obtained by the magnetron sputtering method have shown that structure of such samples is a periodic alternation of the layers of polycrystalline Fe and amorphous Ge. It is established that temperature coefficient of resistance has a positive value at room temperature and a negative one – at low temperatures, and value of the Hall coefficient at the multilayer thickness of 5.2 nm is three orders of magnitude larger than in bulk Fe. It is shown that the atomic interdiffusion processes occur near the interfaces and they influence the processes of the exchange antiferromagnetic interaction between layers.

Since Ge crystal lattice is compatible with AlGaAs/GaAs lattice [7], and mobility of electrons and holes in Ge is larger than in GaAs and Si, then Ge combined with metal layers is a more promising material of microelectronics than magnetic semiconductors, whose main disadvantage is a low value of the Curie temperature which does not exceed 116 K.

The investigation results of magnetic and transport properties of Cr/Ge thin films, in which ferromagnetic ordering is observed in a wide temperature range at the concentration of Cr atoms of 4 at. %, are represented in the work [8]. The authors of the work [9] have performed the investigations of the phase formation processes in Ge/Fe/SiO_2 film systems by the X-ray diffraction method in the temperature range of 100-600 K with the thickness of separate layers from 28 to 215 nm. It is established that after thermal treatment during 20 minutes the following equilibrium phases can be formed there: Fe_3Ge, Fe_5Ge_3, Fe_4Ge_3, Fe_6Ge_5, FeGe, and $FeGe_2$.

Phase diagram for a bulk binary Fe-Ge system indicates that formation of a solid solution of Ge atoms in Fe (s.s.(α-Fe)) and six phases of Fe germanides (Fe_3Ge, $Fe_{3.2}Ge_2$, FeGe, $FeGe_2$, $Fe_{13}Ge_8$, and Fe_6Ge_5) is possible in it depending on the concentration of Ge atoms [10]. Since thin films of metal germanides have found a wide application in integrated microelectronic devices, and phase composition of the materials on the metal/semiconductor interface influences the stability of the operating characteristics of these devices, then conditions of their formation are constantly studied. Phases Fe_3Ge (at $T = 670$-1320 K) and $Fe_{3.2}Ge_2$ (at $T = 1420$ K) can be formed in the concentration range of $c_{Ge} = 34$-40 at. %. $Fe_{13}Ge_8$ phase is formed at $T = 1020$ K and then it is peritectoidly decomposed [10]. Iron germanides FeGe and $FeGe_2$ are formed in the films in a wide temperature range, characterized by perfect stoichiometry and almost the absence of homogeneity region [11]. In our previous work [12] we have presented the investigation results of the phase formation processes and magnetoresistive properties of three-layer Fe/Ge/Fe films and shown that at layer-by-layer condensation with further annealing from 300 to 1070 K the formation of iron germanides $FeGe_x$ ($1 \le x < 2$) occurs in the systems over the whole volume of the sample with ferromagnetic properties that leads to the increase in the magnetoresistance (MR) value. It is established that maximum values of MR = 0.35-0.44 % are observed at the total concentration of Ge atoms from 60 to 68 at. %.

We have to note that in spite of a large amount of the experimental data concerning the phase formation processes in the films based on Fe and Ge at different concentrations of the non-magnetic component atoms,

physical properties of the diluted solid solutions (s.s.) of Ge atoms (total concentration of Ge atoms from 1 to 27 at. %) in Fe films remain little-studied.

In connection with this, the aim of the present work consisted in the investigation of the magnetoresistive properties of (α-Fe) s.s. or (α-Ge) s.s. It is clear that in this case one should not expect some new properties, but, nevertheless, it is important to know, to what extent different concentration of the non-magnetic component atoms in the film of magnetic metal influences the magnetoresistive properties of the whole system.

2. EXPERIMENTAL TECHNIQUE

Formation of three-layer Fe/Ge/Fe samples was performed in the working chamber of the vacuum plant VUP-5M (vacuum of ~ 10^{-3}-10^{-4} Pa) by the thermal evaporation method with the layer-by-layer condensation of separate layers on glass ceramic substrates (S) through the mask with geometric sizes of (1 × 10) mm². The electrical resistance (accuracy of ± 0.05 %) and temperature (accuracy of ± 1 K) of the films were controlled using digital multimeters of UT70D and UT70B types and chromel-alumel thermocouple, respectively. Thermal treatment of the samples was carried out during three cycles heating ↔ cooling in the temperature range of 300-1070 K.

Magnetoresistive properties were investigated in the automated mode [13] at the temperature of $T = 300$ K using the four-point scheme in three measurement geometries, namely, the longitudinal, transverse, and perpendicular (see Fig. 1). Constant magnetic field was generated by electromagnets, whose maximum magnetic induction (B) was equal to 450 mT.

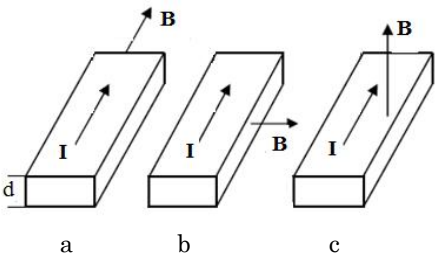

Fig. 1 – Measurement geometries of MR: a – longitudinal (| |); b – transverse (┼); c – perpendicular (⊥) geometries

We have used the following relation for MR:

$$MO = \frac{R(B) - R(450)}{R(450)} = \frac{\Delta R}{R(450)},$$

where R_B is the resistance of the film sample in the external magnetic field, $R(450)$ is the sample resistance at $B = 450$ mT.

Investigation of the structure and phase composition of the film samples was performed by the transmission electron microscopy and electronography methods (microscope PEM-125 K). Diffraction patterns were interpreted according to the standard technique described in the work [14].

The total concentration of atoms of separate components was calculated by the formula

$$c_i = \frac{D_i d_i \mu_i^{-1}}{D_{Fe} d_{Fe} \mu_{Fe}^{-1} + D_{Ge} d_{Ge} \mu_{Ge}^{-1}},$$

where D and μ are the density and molar mass of Fe and Ge atoms.

Thickness of separate layers was controlled by the method of quartz resonator that provided high measurement accuracy (± 1 nm).

3. EXPERIMENTAL RESULTS

Investigation of the phase transformation processes in three-layer based on Fe and Ge and single-layer Ge films has been performed. It is established that single-layer Ge films of the thickness to $d \cong 20$ nm are in the amorphous state (Fig. 2a), and with the decrease in the thickness the transition temperature $T_{a\to\kappa}$ from the amorphous state into the β-Ge or α-Ge slightly increases, but it does not exceed 550 K that satisfactorily agrees with the results of the work [15], according to which $T_{a\to\kappa} = 520$-620 K for Ge films of the thickness of 10-25 nm. We note that the phase size effect [16] becomes apparent in single-layer Ge films, and, as a result, the high-temperature Ge β-phase at temperatures less than 600 K is observed in crystallized films of the thickness to 10 nm.

At thicknesses larger than 10 nm only the low-temperature α-phase is formed. Its lattice parameter varies in the range of 0.563-0.565 nm (diamond type lattice) that agrees well with the literature data for bulk Ge $a_0 = 0.5657$ nm [17]. Slight decrease in the lattice parameter in thin samples, as it is known, has a typical character and is also connected with the phase size effect. The high-temperature β-phase (β-Sn type lattice) has the following lattice parameters: $a = 0.592$ and $c = 0.697$ nm.

Phase composition of the formed at room temperature and annealed in the range of 300-870 K three-layer Fe(10)/Ge(x)/Fe(20)/S film systems at $x = 2$, 4, 6, 8, 10, 15 nm undergoes changes, since diluted (α-Fe) s.s. of Ge atoms in Fe film with the bcc-lattice and the lattice parameter $a = 0.284$ nm ($c_{Ge} = 0$) and $a = 0.286$ nm ($c_{Ge} = 12$ at. %) is formed there. Here, some crystallites with the sizes and habitus similar to the single-layer Ge films are electron-microscopically fixed. It is not inconceivable that formation of the s.s. based on Ge α-phase occurs along with the s.s based on the α-Fe, i.e. one is talking about the eutectic state of the film system.

The electron-microscopic investigations of the crystallization kinetics of Ge films indicate the two-stage process. For example, in relatively thin films (to 10 nm) at the annealing to 570 K two sub-systems of crystallites are formed: the first one with the average size of $L_1 \cong 5$ nm and concentration of $n_1 \cong 10^{15}$ m^{-2} and the second subsystem – $L_2 \cong 60$-70 nm and $n_2 \cong 3 \cdot 10^{14}$ m^{-2}. In the films of the thickness more than 20 nm and annealed in the temperature range of 570-800 K two subsystems of crystallites also take place: $L_1 \cong 60$-80 nm and $L_2 \cong 115$-160 nm and the total concentration of $N \cong 2.5 \cdot 10^{14}$ m^{-2} (Fig. 2b). At the temperature of 800 K formation of GeO_2 oxide occurs in a rather small amount, but it is fixed by the electron-diffraction method. Observation of the moiré fringes serves the additional

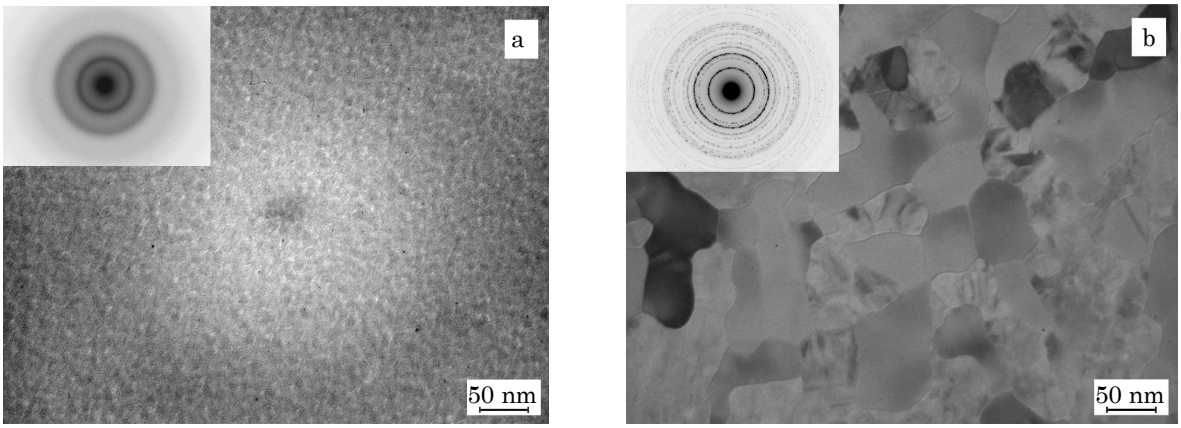

Fig. 2 – Microstructure and the corresponding electron diffraction patterns from single-layer Ge(20) films obtained at T_s = 420 K (a) and T_s = 800 K (b). Film thickness in nm is given in the brackets

Table 1 – Dependence of the MR value on the annealing temperature at different measurement geometries

Film (thickness, nm)	c_{Ge}, at. %	T_a = 300 K			T_a = 870 K		
		MR, %			MR, %		
		∥	+	⊥	∥	+	⊥
Fe(30)/S	0	– 0.20	0.06	0.03	– 0.03	0.05	–
Fe(10)/Ge(4)/Fe(15)/S	8	0.08	0.04	0.03	0.03	0.03	0.02
Fe(10)/Ge(6)/Fe(20)/S	9	0.09	0.03	0.02	–	–	–
Fe(10)/Ge(6)/Fe(15)/S	11	0.09	0.04	0.03	0.03	0.01	0.1
Fe(10)/Ge(8)/Fe(20)/S	12	0.08	0.03	0.04	0.03	0.02	0.01
Fe(10)/Ge(10)/Fe(20)/S	15	0.08	0.03	0.05	0.03	0.02	0.02

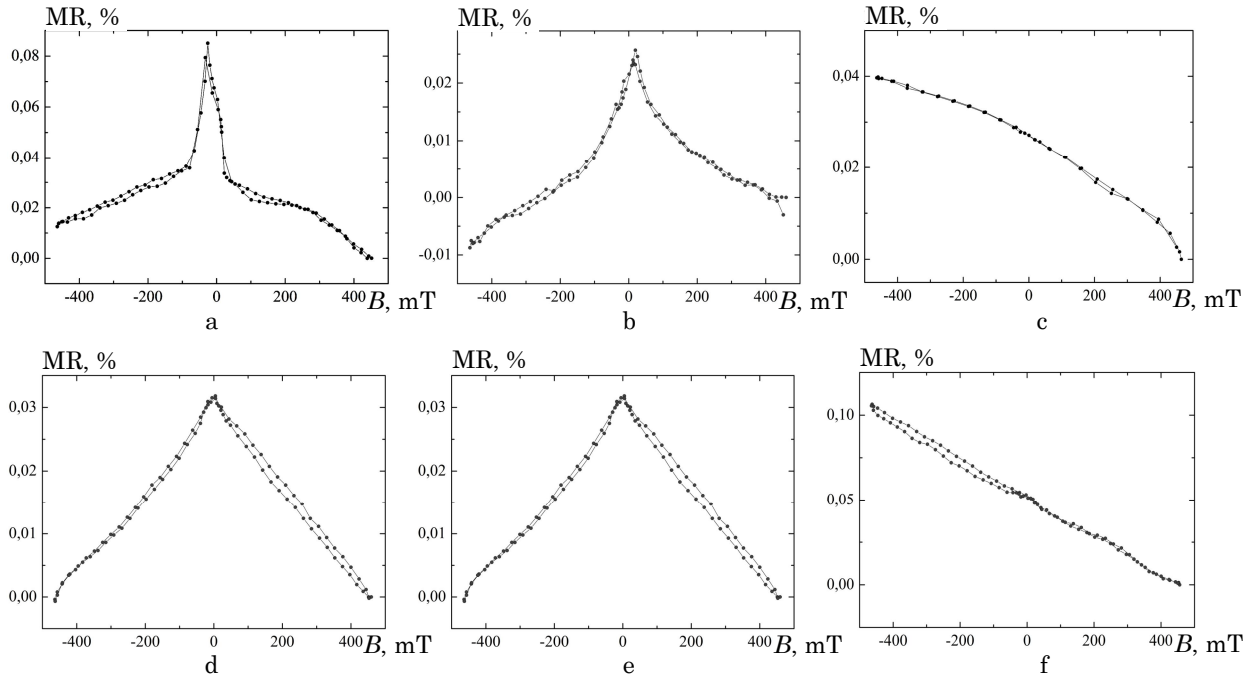

Fig. 3 – Dependence of the MR value on the magnetic induction for the unannealed (a-c) and annealed to 870 K (d-f) system Fe(10)/Ge(8)/Fe(20)/S for the longitudinal (a, d), transverse (b, e) and perpendicular (c, f) measurement geometries

confirmation of the oxidation processes, since GeO_2 is formed not in the form of separate crystallites, but on the surface of the already formed crystallites. Formation of the moiré fringes occurs in connection with close values of some interplanar spacings of the α-Ge and GeO_2 (for example, d_{220} (α-Ge) ≅ 0.2096 nm and d_{200} (GeO_2) ≅ 0.2102 nm).

Crystallites of the size of 12-20 nm and additional lines are observed on the electron diffraction patterns of three-layer Fe(10)/Ge(*x*)/Fe(20)/S films except of the oxide, that is, most probably, connected with the formation of the phase of unknown composition of the Fe_xGe_y type.

The following features and distinctions of the field dependences of the MR value for Fe/Ge(*x*)/Fe/S films

were established. Firstly, difference in the MR value and sign takes place only in the longitudinal measurement geometry (Fig. 3a, d; Table 1) in both unannealed and annealed films. In Fe films the MR value in absolute magnitude is about two times larger and has a negative sign that can be explained by the ordering of the film domain structure, which is accompanied by the increase in the resistance in the external magnetic field. Secondly, the MR value in the transverse and perpendicular measurement geometries has the same sign as in Fe films, but its slight decrease is observed (Fig. 3b-f), and in the case of the perpendicular geometry in the unannealed three-layer films a certain increase in the MR value with the increase in the effective thickness of Ge layer takes place. Obtained results concerning the MR value of three-layer systems can be explained by the diffusion of Ge atoms into the α-Fe lattice, resulting in the formation of the diluted s.s. and, as a consequence, efficiency of the exchange interaction of Fe atoms decreases and domain structure is disordered. If formation of Fe germanide takes place, this will give an additional negative contribution to the MR value.

As a result of the analysis of the obtained data, one can conclude that formation of the diluted s.s. does not considerably influence the magnetoresistive properties in comparison with single-layer Fe films.

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