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REGULAR ARTICLE

Electrophysical Properties of Nanoscale Functional Materials Based on Fe and Ge for Sensor Electronic

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The results of studies of the electrophysical properties of nanoscale functional materials based on Fe and Ge under phase formation conditions was presented. It was established that during annealing of two- and three-layer films based on Fe and Ge with a total thickness of up to 100 nm, iron germanides are formed in the form of FeGe, $FeGe_2$ or Fe_2Ge phases, which are thermally stable in a wide temperature range. Based on the experimental temperature dependences of resistance, the phase transition temperature from amorphous to crystalline state was determined: $T_{a\to c}$ = 580-600 K. At the annealing of film samples based on Fe and Ge with a fixed thickness of the Fe layer, an increase in the resistivity is observed in the first heating cycle in the temperature range of 300-700 K, which indicates intensive healing of defects and its sharp decrease in the range of 700-900 K. This feature of the temperature dependence of resistance is explained by the phase formation processes and is confirmed by electron microscopic studies. The TCR is (3-9)$\cdot 10^{-4}$ K^{-1}, which indicates the high thermal stability of iron germanide films. It is shown that films Fe_2Ge, FeGe and $FeGe_2$ films are promising materials for use in multifunctional sensors for engineering and medical applications for continuous monitoring systems of physical parameters.

Keywords: Metal germanide films, FeGe, $FeGe_2$ and Fe_2Ge phases, Electrophysical properties, Temperature coefficient of resistance, Transition from amorphous state to crystalline state, Sensor elements for affordable and clean energy systems.

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1. INTRODUCTION

The development of sensor electronics requires the implementation of new functional materials based on metals and semiconductors, in which, unlike magnetic semiconductor structures formed by introducing magnetic impurities into a semiconductor, it is possible to implement the mechanism of spin-dependent electron scattering, the formation of granular solid solutions (s.s.) and binary phases [1-3].

The relevance of studying the properties of multicomponent film systems based on metals and semiconductors after homogenization is becoming increasingly widespread, since such materials can provide high temperature stability of elements and their compatibility with electronic elements of integrated circuits, which is ensured by close values of crystal lattice parameters and makes it possible to form heterostructures – epitaxial layers with a low dislocation density.

The study of the temperature dependences of the resistance for two-component films based on Fe and Ge remains relevant, since their application mainly involves the possibility of obtaining temperature stability of the operating characteristics of sensor elements for affordable and clean energy systems.

In-depth study of the electrophysical properties of such materials is stimulated by the possibility of obtaining important information necessary for solving certain important problems of solid-state physics.

The study of the relationship between the electrophysical properties and phase composition of such systems is also related to the question of the possibility of their practical application as media for recording information with increased density and highly sensitive elements of multifunctional sensors for engineering and medical systems [4-7].

Today, the properties of multilayer film systems based on metals have been studied in sufficient detail. However, the electrophysical (resistivity, temperature coefficient of resistance – β) properties of two-component film alloys based on metals and semiconductors as promising functional materials remain poorly studied.

The aim of the work was to study the electrophysical properties of film iron germanides from the point of view of their practical application as sensor electronics elements.

2. RESULTS AND DISCUSSION

2.1 Phase Formation Processes

When studying the phase state and microstructure of single-layer Ge films as a component of two-component systems based on Fe and Ge, we found that Ge films at

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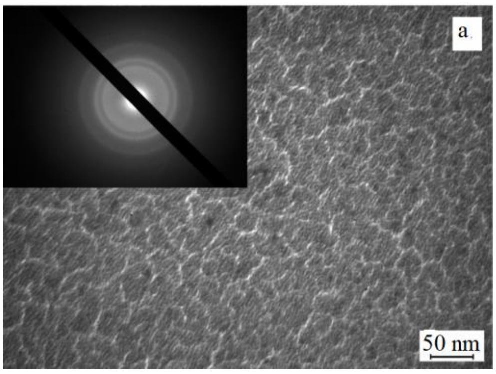
relatively low temperatures have an amorphous structure and crystallize at a certain temperature.

In single-layer Ge films, a phase size effect is observed [8-10], as a result of which in crystallized films with a thickness of up to 10 nm, a high-temperature β-phase of Ge is observed at temperatures below 600 K. At thicknesses greater than 10 nm, only a low-temperature α-phase is formed. Its lattice parameter varies within 0.563-0.565 nm (diamond-type lattice), which is in good agreement with the literature data $a_0 = 0.5657$ nm for bulk Ge [11].

Some decrease in the lattice parameter in thin samples is typical and is also associated with the phase size effect. The high-temperature β-phase (lattice type β-Sn) has lattice parameters $a = 0.592$ and $c = 0.697$ nm. The lattice parameter of the Fe and Ge films is very close to the a_0 for bulk samples. This is a qualitative confirmation of the fact that impurity atoms are almost absent in the sample volume.

Additional confirmation of the oxidation processes is the observation of moire patterns, since GeO_2 is not formed in the form of separate crystallites, but on the surface of already formed ones. The formation of moire patterns occurs due to the close values of some interplanar distances of α-Ge and GeO_2 (for example, d_{220} (α-Ge) ≅ 0.2096 nm and d_{200} (GeO_2) ≅ 0.2102 nm).

On the diffraction patterns of the three-layer systems Fe(10)/Ge(x)/Fe(10)/S (S – substrate) (Fig. 1), annealed to a temperature $T_a = 870$ K, in case of $c_{Fe} < c_{Ge}$ solid solution lines of Fe atoms in Ge are fixed (s.s.(Ge, Fe)) with traces GeO_2, such films have a finely dispersed structure (crystallite sizes 25-30 nm). In three-layer systems, which annealed to 1070 K, based on s.s. (Ge, Fe) iron germanides $FeGe_x$, де $1 \leq x < 2$ are formed.



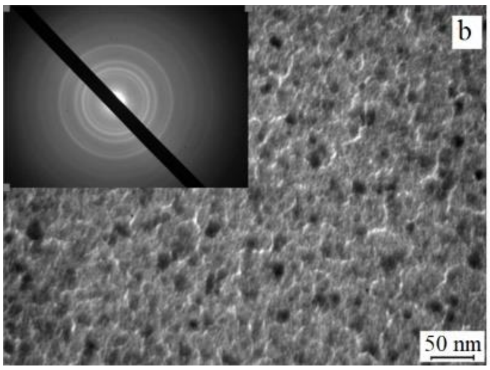


Fig. 1 – Microstructure and diffraction patterns on insets from the Fe(10)/Ge(20)/Fe(10)/P (phase FeGe) film in the initial state: unannealed (a) and annealing to 800 K (b)

We have established that if the FeGe phase is formed on the basis α-Fe, an increase in the lattice parameter of the bcc-Fe by 0.009 nm and a decrease in the parameter of the fcc-Ge by 0.0001 nm is observed. In the process of annealing to 600K, the so-called Fe(Ge) decays with the formation of the $FeGe_2$ phase and the release of α-Fe, which leads to a sharp drop in resistance. Also, in the process of annealing, the healing of the crystalline structure of the film and the formation of the so-called labyrinth structure, which is visible in microscopic images of the structure. Further annealing to 800 K leads to the further formation of the $FeGe_2$ phase in the mass of free α-Fe.

Iron germanide films FeGe and $FeGe_2$, which are widely used as diode and contact structures of integrated microelectronic devices, are formed in a wide temperature range at a total concentration of Ge atoms from 50 to 70 at. % and are characterized by close to ideal stoichiometry and practically no homogeneity region. In a binary system based on Fe and Ge, during annealing [12], both magnetic ($FeGe_2$, FeGe and $FeGe_2$) and non-magnetic (Fe_3Ge, Fe_5Ge_3, Fe_4Ge_3 and Fe_6Ge_5) equilibrium phases are formed.

The Fe_3Ge (ε) phase is formed in the temperature range ~ 1050–400 °C; the $Fe_{3,2}Ge_2$ (β) phase is formed with an open maximum at 1170 °C in the concentration range 34–40 at. %. With a further decrease in temperature, the region of its homogeneity slightly narrows to a temperature of 800 °C, after which it remains practically constant.

Depending on the annealing temperature and the concentration of iron atoms in film systems equilibrium phases are formed: Fe_3Ge, Fe_5Ge_3, Fe_4Ge_3, Fe_6Ge_5, FeGe and $FeGe_2$.

2.2 Electrophysical Properties: Resistivity and Temperature Coefficient of Resistance

A characteristic feature of the temperature dependences of the resistivity $\rho(T)$ and the temperature coefficient of resistance $\beta(T)$ for Ge and Fe-based systems is the large ρ and, accordingly, the relatively small β. This can be explained by the formation of confined solid solutions of Ge atoms in the Fe layer.

The dependence of the resistivity (Fig. 2 and 3) on the first annealing cycle is characterized by a constant decrease in the resistivity, which indicates the processes of defect healing, recrystallization and phase formation. The subsequent heating-cooling cycles are the same, which indicates the stabilization of the electrophysical properties.

The results studies have shown that the finely dispersed structure, the formation of impurities due to interaction with atoms of the residual atmosphere, and the processes of phase formation under conditions of mutual diffusion of component atoms affect the nature of the temperature dependences of the resistivity and TCR.

In general, the results of the studies indicate that during the thermal annealing of samples with a fixed thickness of the Fe layer, an increase in the resistivity is observed in the first heating cycle in the temperature range $\Delta T_1 = 300\text{-}700$ K, which indicates intensive healing of defects and its sharp decrease at $\Delta T_2 = 700\text{-}900$ K, which we explain by phase formation processes.

The results of the studies indicate that the transition of the film from the amorphous state to the crystalline state occurs at temperatures $T_{a \to c} = 580\text{-}600$ K, depending on the thickness of the sample.

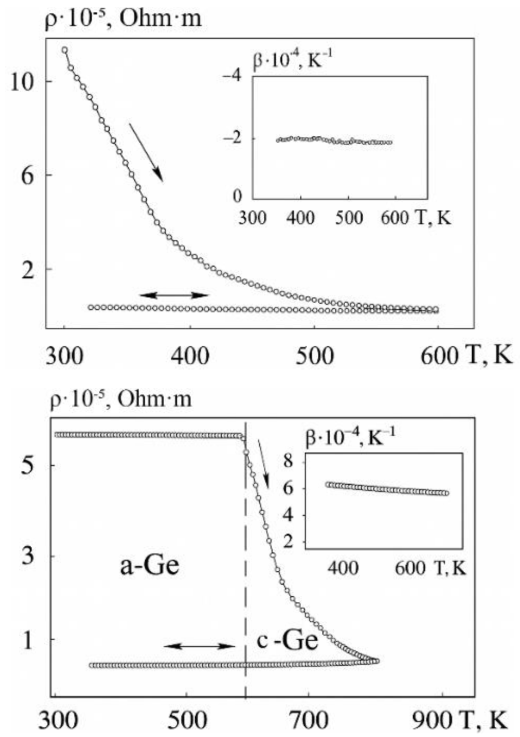
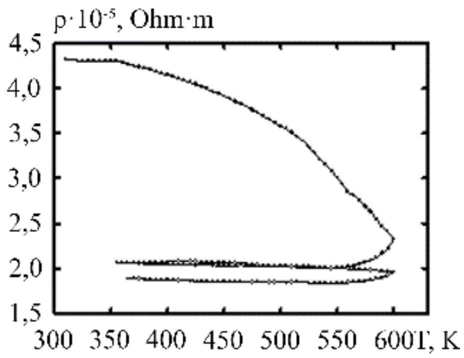
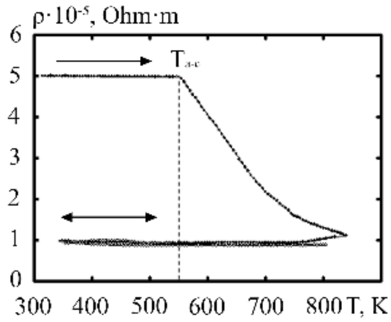


Fig. 2 – Temperature dependence of resistivity for the film system Fe(10)/Ge(20)/Fe(10)/S (FeGe phase) upon annealing to 600 K (a) and 800 K (b).



a



b

Fig. 3 – Temperature dependences of resistivity for film systems in the initial state Fe(10)/Ge(6)/Fe(10)/P (a) and Fe(10)/Ge(30)/Fe(10)/P (b). After annealing – Fe_2Ge (a) and $FeGe_2$ (b) phases.

3. CONCLUSIONS

1. It has been established that during heat treatment of two- and three-layer films based on Fe and Ge with a total thickness of up to 100 nm, iron germanides are formed in the form of FeGe, $FeGe_2$ or Fe_2Ge phases.

2. Based on the experimental temperature dependences of resistance, the temperature of the phase transition from the amorphous to the crystalline state was determined: $T_{a \to c}$ = 580-600 K.

3. In the process of annealing of film samples with a fixed thickness of the Fe layer, an increase in the resistivity is observed in the first heating cycle in the temperature range ΔT_1 = 300-700 K, which indicates intensive healing of defects and its sharp decrease at ΔT_2 = 700-900 K, which we explain by the processes of phase formation and is confirmed by electron microscopic studies. It was obtained that the $\beta = (3\text{-}9) \cdot 10^{-4}$ K^{-1}.

4. At the metal-semiconductor junction, an electric field is created, the vector of which is directed from the semiconductor to the metal. The electric field almost does not penetrate the metal, but is localized in the near-surface layer of the semiconductor.

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Електрофізичні властивості нанорозмірних функціональних матеріалів на основі Fe і Ge для сенсорної електроніки

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У роботі наведені результати досліджень електрофізичних властивостей нанорозмірних функціональних матеріалів на основі Fe і Ge в умовах фазоутворення. Установлено, що під час термообробки дво- тришарових плівок на основі Fe і Ge загальною товщиною до 100 нм відбувається формування германідів заліза у вигляді фаз FeGe, $FeGe_2$ або Fe_2Ge, які термостабільні в широкому інтервалі температур. На основі експериментальних температурних залежностей опору визначена температура фазового переходу із аморфного до кристалічного стану: $T_{a \to к}$ = 580-600 К. У процесі термовідпалювання плівкових зразків на основі Fe і Ge з фіксованою товщиною шару Fe спостерігається зростання питомого опору на першому циклі нагрівання в інтервалі температур 300-700 К, що вказує на інтенсивне заліковування дефектів та його різке спадання в інтервалі 700-900 К. Така особливість температурної залежності опору пояснюється нами процесами фазоутворення і підтверджується електронно-мікроскопічними дослідженнями. Величина ТКО складає $(3\text{-}9)\cdot 10^{-4}$ К$^{-1}$, що вказує на високу термічну стабільність плівок германідів заліза. Показано, що плівки германідів заліза Fe_2Ge, FeGe and $FeGe_2$ є перспективними матеріалами для використання в багатофункціональних сенсорах інженерного та медичного застосування для систем безперервного моніторингу фізичних параметрів.

Ключові слова: Плівки германідів металів, Фази FeGe, $FeGe_2$ та Fe_2Ge, Електрофізичні властивості, Температурний коефіцієнт опору, Перехід аморфний стан – кристалічний стан, Сенсорні елементи для доступних та чистих енергетичних систем.