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Solid-state Synthesis of Cobalt Germanides in Epitaxial Ge/α-Co(001) and Ge/β-Co(110) Nanofilms

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The experimental results of a study of solid-state synthesis of cobalt germanides in epitaxial Ge/α-Co(001) and Ge/β-Co(110) nanofilms are presented. For both polymorphic modifications of cobalt, it is demonstrated that the Co_5Ge_7 phase occurs at $\sim 275^\circ C$. When the annealing temperature increases to $\sim 300^\circ C$, the $CoGe_2$ phase forms, which sharply reduces the electric resistance and magnetic characteristics of the samples. The order of the formation of phases and the temperatures at which the phases are formed are not changed based on the polymorphic modification of cobalt.

Keywords: epitaxial growth, nanofilms, solid-state synthesis, Co-Ge system, cobalt germanides.

Studying the chemical interactions between the metals with various semiconductors has shown that the interface acquires new structural and magnetic properties. Chemical reactions on the interface of the films often cause solid-state reactions, which are in the focus of intensive research. The main efforts of this research are focused on studying the formation of silicides on the interface of metallic films with silicon [1]. To a lesser extent, there has been some research of solid-state reactions of metals with germanium. Most studies [2–4] show that as the annealing temperature increases, the Co_5Ge_7 phase on the Co/Ge interface occurs first at a temperature

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of $\sim 300\,^{\circ}$C, and then changes into the $CoGe_2$ phase at a temperature of $\sim 425\,^{\circ}$C. In some works though [5], it is shown that the CoGe phase forms first on the Co/Ge interface, and then as the annealing temperature increases the phases follow the following order: Co/Ge $\rightarrow$ CoGe $\rightarrow$ Co_5Ge_7 $\rightarrow$ $CoGe_2$. A structural analysis of thin films of Co growing on Ge(111) and Ge(001) using photoelectric X-ray diffraction and low-energy electron diffraction, has shown a mixing of Co and Ge at a low temperature ($\sim 100\,^{\circ}$C) and a possible formation of the first $CoGe_2$ phase [6]. The results of photoelectric investigations show a mixing of the layers on the interface between Co and Ge(100) at a very low (~ 170 K) temperature [7]. The $CoGe_2$ and CoGe phases have very low symmetry, and only Co_5Ge_7 has a tetragonal lattice and grows epitaxially between other phases on Ge(111) and Ge(100) surfaces in an ultrahigh vacuum [5, 6]. The chemical reactions and epitaxial growth of Ge on various β-Co and α-Co surfaces have not been investigated.

It is well known that bulk samples of the hexagonal α-Co phase are stable at temperatures below the allotropic $\alpha \leftrightarrow \beta$ transformation. But small samples and thin films of the α-Co phase are often stable at room temperature. This paper reports the findings on solid-phase reactions on the interface between metastable cubic β-Co(001) and hexagonal α-Co(110) films with a polycrystalline Ge layer.

Initial Ge/β-Co(001) and Ge/α-Co(110) film structures were made using thermal evaporation on a monocrystalline MgO(001) substrate in a vacuum of 10^{-5} torr. Samples with an atomic ration close to 3Ge:2Co were used in these experiments. The thickness of the films used was not more than 300 nm. In order to prevent a solid-state reaction between Ge and Co, the Ge film was precipitated at room temperature. The resulting samples were annealed in a vacuum of 10^{-5} torr over 25 °C for 20 minutes at temperatures between 100 °C and 350 °C. X-ray investigations using a DRON-4-07 diffractometer (Cu K_α — radiation) were used to identify the formed phases. Fluorescent X-ray was used to identify the chemical composition and thickness of the films. Measurements of the magnetic crystallographic anisotropy and the saturation of magnetization were made using the method of torsional moment in a maximum magnetic field of 18 kOe. All measurements were made at room temperature.

In order to get epitaxial β-Co(001) layers, cobalt was precipitated at a temperature of $\sim 250\,^{\circ}$C. A strong and singular diffractional reflection of (002) β-Co confirms the formation of an epitaxial β-Co(001) layer (Fig. 1a). Each sample had a biaxial magnetic anisotropy with a constant of $K_2 = -(6.0 - 7.0) \cdot 10^5$ erg/cm^3. The light axis of magnetization of β-Co film coincides with the direction of [110] and [1-10] of the substrate MgO(001), which indicates the presence of orientational correlation [100](001)β-Co $\|$[100](001)MgO during epitaxial growth of cubic cobalt on the surface of MgO(001). These two factors indicate a crystalline perfection of the initial β-Co(001) layers, acquired in the given technological conditions.

The epitaxy of Co on the surface of MgO(001) radically changes when precipitation occurs at temperatures of $\sim$ (370-400) °C. The diffraction patterns of the samples show that α-Co crystalline particles (110) grow on (001) the surface of MgO (Fig. 2a). The analysis performed in the work [8] shows that α-Co(110) crystalline particles grow on MgO(001) following two epitaxial ratios: α-Co(110)[001] $\|$ MgO(001)[110] and α-Co(110)[100] $\|$ MgO(001)[1-10]. The constant K_{eff} of effective biaxial magnetic anisotropy of α-Co(110)/MgO(001) films is $K_{eff} = (1.1\text{-}1.2)\cdot 10^6)$ erg/cm^3. The energy of magnetic anisotropy E_K of a hexagonal crystal (without taking into account the anisotropy in the plane of the film) is $E_K = K_1 \mathrm{Sin}^2\varphi + K_2 \mathrm{Sin}^4\varphi + \ldots$ for α-Co, where $K_1 = 4.3\cdot 10^6$ erg/cm^3, $K_2 = 1.2\cdot 10^6$ erg/cm^3 and φ is the angle between the axis **c** and the direction of magnetization M_S [19]. Assuming that the crystalline particles α-Co(110), growing along the axis **c** in the directions [110] and [1-10] MgO, are interchangeable and all have

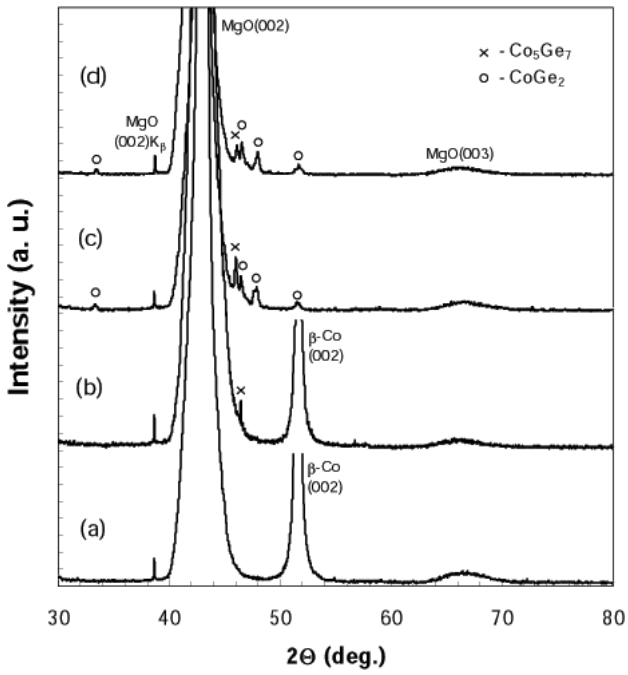

Fig. 1. Diffraction patterns of Ge/β-Co(001) films after annealing: (a) at 20 °C, (b) at 275 °C, (c) at 300 °C, (d) at 350 °C

the same volume, the constant $K_{eff} = K_2$ [9]. The fact that the experimental values of K_{eff} and K_2 are the same confirms the epitaxial growth of α-Co(110) crystalline particles on the surface of MgO(001).

The graphs of the constant of biaxial magnetic anisotropy K_2, the saturation of magnetization M_S and the electric resistance R as a function of the annealing temperature T_S for Ge/β-Co(001) and Ge/α-Co(110) nanofilms all have the same form taking into account experimental uncertainties. Fig. 3 shows graphs of the constant of biaxial magnetic anisotropy K_2, the saturation of magnetization M_S and the electric resistance R as a function of the annealing temperature T_S for the given samples. Up until a temperature of 250 °C the values of K_2 and M_S are not related to T_S, which indicates that no mixing or formation of connections has occurred on the interface between germanium and cobalt. At temperatures around 275 °C the values of K_2 and M_S for the monocrystalline cobalt layer decreased for all samples and at a temperature of 300 °C all samples became completely nonmagnetic. At temperatures $T_S > 300$ °C the values of K_2 and M_S become zero. This suggests a full mixing of the Co and Ge layers and the synthesis of nonferromagnetic cobalt germanides.

The diffraction patterns change based on the relationships of $K_2(T_S)$ and $M_S(T_S)$. Fig. 1 shows the X-ray spectrum for Ge/β-Co(001) nanofilms at their initial temperatures and after annealing at temperatures of 275 °C, 300 °C and 350 °C. After annealing at a temperature of 275 °C, the diffractional reflection for (002)β-Co decreased and new weaker peaks formed, which indicates a formation of polycrystalline phases as a product of the reactions (Fig. 1b). The diffractional reflections for many of the phases of the Co-Ge films are the same, but the reflection when $2\Theta = 45.8°$ can only come from a peak of the (222)Co_5Ge_7 phase. This suggests that the Co_5Ge_7 phase forms first on the Ge/β-Co(001) interface at a temperature of 275°C. At a

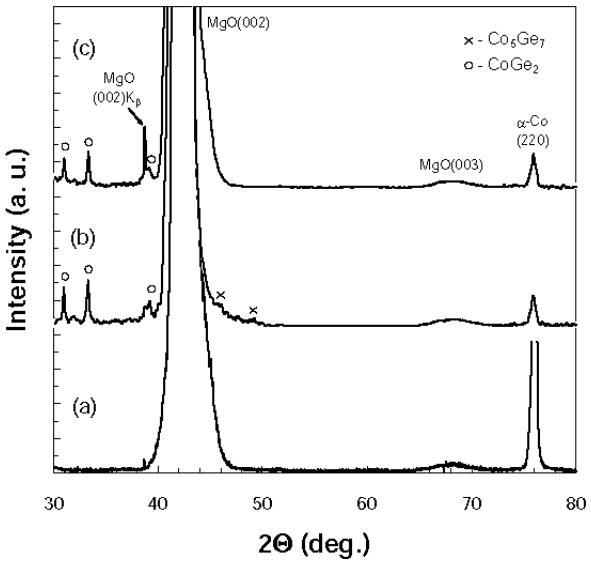

Fig. 2. Diffraction patterns of Ge/α-Co(110) films after annealing: (a) at 20 °C, (b) at 300 °C, (c) at 350 °C

temperature of 300°C the reflection from (002)β-Co disappears, but the peak from (222)Co_5Ge_7 grows, which indicates a further increase in volume for this phase (Fig. 1c). The reflection from the $CoGe_2$ orthorhombic phase also appears at this temperature. At a temperature of 350°C the peak from (222)Co_5Ge_7 decreases and the Co_5Ge_7 phase turns into the $CoGe_2$ phase, which becomes the dominant product in the reactions (Fig. 1d).

As shown by the decrease of the constant of biaxial magnetic anisotropy $K_2(T_S)$ and by the decrease of the saturation of magnetization $M_S(T_S)$, the solid-state reaction in Ge/α-Co(110) nanofilms, just like in the Ge/β-Co(001) nanofilms, starts at a temperature of 275 °C. But there are no new reflections on the diffraction patterns, which might indicate the formation of a new phase that has a disordered finely-dispersed structure. The diffraction patterns after annealing at a temperature of 300 °C show reflections that belong to the $CoGe_2$ and Co_5Ge_7 phases (Fig. 2b). The weak peak from (222)Co_5Ge_7 disappears from the diffraction pattern after annealing at a temperature of 350 °C, which suggests a decrease of the Co_5Ge_7 phase in the products of the reaction (Fig. 2c). Only the reflections from the $CoGe_2$ phase remain after annealing at a temperature of 350 °C, so the transformation of the (222)Co_5Ge_7 peak is the same for both the Ge/α-Co(110) and the Ge/β-Co(001) nanofilms. This suggests that the disordered finely-dispersed Co_5Ge_7 phase in the Ge/α-Co(110) nanofilms also forms at a temperature of 275 °C and precedes the formation of the $CoGe_2$ phase. An analysis of the above mentioned facts suggest that the order of the formation of phases in the Ge/α-Co(110) and Ge/β-Co(001) nanofilms is the same.

The average size of the Co_5Ge_7 and $CoGe_2$ crystalline particles was determined from the diffraction pattern peaks using Sherrer's formula. For the Ge/β-Co(001) and Ge/α-Co(110) samples, the average size of the crystalline particles was 17–30 nm.

One of the stages of a solid-state reaction is the breaking of chemical bonds in the reactants. The energy of the bonds in α-Co is almost the same as the energy of the bonds in β-Co, since the enthalpy of the $\Delta H^{\beta\to\alpha} = -220$ cal/mole transition β-Co $\to$ α-Co is small. This shows

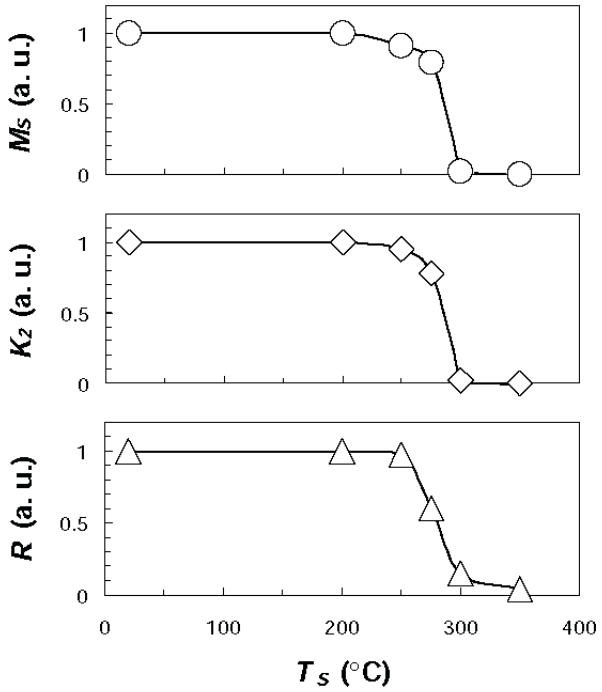

Fig. 3. Saturation of magnetization M_S, magnetic anisotropy constant K_2 , electric resistance R of the epitaxial Ge/β-Co(001) and Ge/α-Co(110) nanofilms as a function of the annealing temperature T_S

that small differences in the energies of the polymorphous reactants does not have an effect on the behavior of solid-state synthesis. In most cases, the enthalpy of the transition from the amorphous phase to the crystalline phase is ~ 1000 cal/mole. Because of this, regardless of whether amorphous, polycrystalline or monocrystalline reactants are used, the order of formation of phases and the temperatures at which each phase forms are the same.

This study shows that annealing polycrystalline Ge nanofilms, precipitated on epitaxial β-Co(001) and α-Co(110) surfaces, leads to the formation of finely-dispersed polycrystalline Co_5Ge_7 and $CoGe_2$ phases at temperatures of $T_0^1 \sim 275\,^\circ$C and $T_0^2 \sim 300\,^\circ$C, respectively. Small differences in the energies of the polymorphous β-Co and α-Co modifications of cobalt do not have an effect on the order of formation of phases and the temperatures at which each phase forms.

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Твердофазный синтез германидов кобальта в эпитаксиальных Ge/α-Co(001) и Ge/β-Co(110) нанопленках

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Представлены экспериментальные результаты исследования твёрдофазного синтеза германидов кобальта в эпитаксиальных Ge/α-Co(001) и Ge/β-Co(110) нанопленках. Показано, что для обеих полиморфных модификаций кобальта фаза Co_5Ge_7 формируется первой при температуре ∼ 275° C. С увеличением температуры отжига при температуре ∼ 300° C образуется фаза $CoGe_2$, которая резко уменьшает электрическое сопротивление и намагниченность образцов. Различные полиморфные модификации кобальта не изменяют последовательность формирования фаз и их температур инициирования.

Ключевые слова: эпитаксиальный рост, нанопленки, твердофазный синтез, Co-Ge система, германиды кобальта.