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Solid-State Reactions in Ga/Mn Thin Films: Formation and Magnetic Properties of the ϕ-$Ga_{7.7}Mn_{2.3}$ Phase

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Experimental results concerning the solid-state synthesis of the ϕ-$Ga_{7.7}Mn_{2.3}$ phase in Ga/Mn thin films are presented. A ferromagnetic (or ferrimagnetic) state is observed in the samples annealed at temperatures above 250°C. The X-ray diffraction studies demonstrate the formation of the ϕ-$Ga_{7.7}Mn_{2.3}$ phase, which is polycrystalline being grown on glass substrates and exhibits the preferential cube-on-cube orientation on MgO(001) substrates. A strong dependence of the perpendicular anisotropy constant $K_\perp$ and of the effective biaxial anisotropy constant K_1^{eff} on the magnetic field H has been found. Owing to such dependence, the easy axis of magnetization lying in the plane of the film changes its direction approaching the film normal when the increasing magnetic field exceeds 8 kOe. The anomalous behavior of $K_\perp$ and K_1^{eff} constants is explained both by the in-plane stresses arising in the course of the formation of the ϕ-$Ga_{7.7}Mn_{2.3}$ phase and by the direct dependence of magnetostriction constants on the magnetic field. For the ϕ-$Ga_{7.7}Mn_{2.3}$ phase, the saturation magnetization M_S has been determined and the first magnetocrystalline anisotropy constant K_1 has been estimated.

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1. INTRODUCTION

Manganese-based ferromagnetic film materials have unique structural and magnetic properties depending on the conditions of their preparation, composition, planar stresses, density of charge carriers, and temperature [1–4]. Most investigations in this field concern the compounds containing Mn and Ga, with special attention being focused on dilute magnetic semiconductors, which are widely studied owing to their potential applications in spintronic devices. The majority of research projects are studies of epitaxial (Ga, Mn)As thin films, where the ferromagnetic order arises due to the doping of GaAs by Mn^{2+} ions (with a doping level up to 10%) [1, 2]. The studies of Ni–Mn–Ga ferromagnets exhibiting shape memory effect are of special importance for actual applications. These alloys undergo large strains (up to 10%) in the applied magnetic field [3]. The Mn_xGa_{1-x} alloys, which are ferromagnetic at Mn contents exceeding the half doping, have attracted much less attention. The Mn–Ga phase equilibrium in the Ga-rich region of the phase diagram is not known in detail, although the stable, metastable, and even quasicrystalline phases were observed there [5]. For Mn_3Ga, the calculations of the band structure demonstrate that the spin polarization reaches 88% at the Fermi level [6]. The Mn_xGa_{1-x} film samples of different compositions deposited onto the (001)GaAs (001)MgO substrates exhibit the giant perpendicular magnetic anisotropy of about 1.2×10^7 erg/cm^3, exceeding the anisotropy related to the shape memory effect [7, 8]. However, the polycrystalline samples grown under similar conditions have a magnetization vector lying in the film plane [8, 9]. The existence of high perpendicular magnetic anisotropy in the epitaxial films shows that the first magnetocrystalline anisotropy constant in Mn_xGa_{1-x} alloys is rather large. The high spin polarization, giant perpendicular magnetic anisotropy, low saturation magnetization, high Curie temperature, high coercitivity, and good hysteresis characteristics imply that the Mn_xGa_{1-x} thin films are promising for their applications in spintronic devices [10].

The conditions underlying the formation of ferromagnetic phases in the Mn–Ga system are unknown.

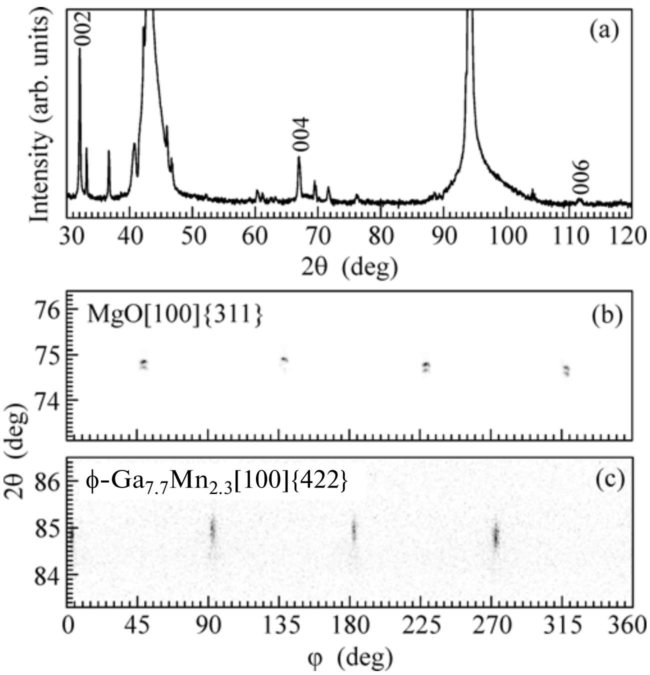

Fig. 1. (a) X-ray diffraction pattern for the Ga/Mn/MgO(001) film samples annealed at 400°C during 0.5 h and the results of the asymmetric φ-scanning of (b) (311) reflections related to the MgO substrate and (c) (422) reflections related to the ϕ-$Ga_{7.7}Mn_{2.3}$ film around the axis perpendicular to the film. These scans reveal the epitaxial orientation of the film.

There are only a few works aimed at the analysis of the chemical interaction between Mn and Ga, where the interphase reactions occurring in the course of the growth of a Mn layer on GaAs [11], GaN [12], and GaSb [13] substrates were studied. However, the solid-state reactions at the interface of the Mn and Ga layers have not yet been studied.

In this work, we study the magnetic properties of the ϕ-$Ga_{7.7}Mn_{2.3}$ phase formed at the Ga/Mn interface at temperatures above 250°C. The ϕ-$Ga_{7.7}Mn_{2.3}$ thin-film samples exhibit the magnetic field dependence of perpendicular and in-plane anisotropy, which is not typical for the layers of 3*d* metals and their alloys.

2. SAMPLES AND EXPERIMENTAL TECHNIQUES

The initial Ga/Mn thin film structures were produced by the successive thermal deposition of Mn and Ga layers onto the glass substrates and onto the MgO(001) surface in vacuum (10^{-6} Torr). In the experiments, we used the 400-nm thick samples with the 3Ga : Mn atomic ratio. The Mn layers were deposited at 220–250°C. To prevent a solid-state reaction between Mn and Ga during the growth, the Ga film was deposited at room temperature. The Ga/Mn samples produced were successively annealed at temperatures ranging from 50 to 400°C, with temperature steps of 50°C. At each step, the sample was kept for 30 min. The saturation magnetization M_S was measured in the film plane and perpendicular to it at the applied magnetic field up to 10 kOe by a Quantum Design MPMS-XL SQUID magnetometer. The perpendicular magnetocrystalline anisotropy constant $K_\perp$ and effective in-plane biaxial anisotropy constant K_1^{eff} were measured by the torque technique at fields up to 18 kOe. The torques perpendicular to the film plane $L_\perp(\varphi)$ and in plane $L_\parallel(\varphi)$ were reduced to the unit volume of the film. To determine the thickness of Ga and Mn layers, we used the X-ray fluorescence analysis. The identification of the formed phases was performed by a DRON-4-07 X-ray diffractometer (CuK_α radiation). The X-ray diffraction studies of the epitaxial orientation of the phases were carried out using a PANalytical X'pert PRO diffractometer with a PIXcel solid-state detector. All measurements were taken at room temperature.

3. EXPERIMENTAL RESULTS

In the X-ray diffraction patterns of Ga/Mn/MgO(001) films and Ga/Mn films deposited onto glass substrates at 100°C, we observed weak reflections related to α-Mn and α-Ga phases as well as to the metastable β-, γ-, δ-, and ε-Ga phases. With an increase in the annealing temperature up to 250°C, the reflections given by all phases became more pronounced. This resulted from an increase in the grain sizes and a higher perfection of the crystal structure of these phases. New reflections did not appear. This is a signature of the absence of mixing and formation of new phases at the Ga/Mn interface at temperatures up to 250°C. After annealing at 300°C, the reflections related to Ga and Mn disappear, whereas the reflections corresponding to the cubic ϕ-$Ga_{7.7}Mn_{2.3}$ phase [14] with the lattice constant $a = 0.5594$ nm appear (Fig. 1a). The peaks related to this phase grow somehow with the temperature of annealing, and the (00*l*) reflections are observed. This demonstrates that the orientation of ϕ-$Ga_{7.7}Mn_{2.3}$(001) planes parallel to the Mg(001) plane of the substrate is dominant. To find the basal epitaxial orientation of the phase in the film plane, we performed the asymmetric φ scanning of the characteristic reflections for the film and substrate for the sample inclined by an angle χ, which was equal to the angle between the sample surface and the expected reflection plane. The asymmetric scanning for MgO was performed at $2\theta = 74.77°$ and $\chi = 25.24°$, which corresponds to the (311) reflection. For the ϕ-$Ga_{7.7}Mn_{2.3}$ phase, we have chosen the angles $2\theta = 84.95°$ and $\chi = 14.43°$ corresponding to the (422) reflection. The angular shift between the (311) reflection of MgO and the (422) reflection of ϕ-$Ga_{7.7}Mn_{2.3}$ was equal to 45° (see Fig. 1b). This corresponds to the

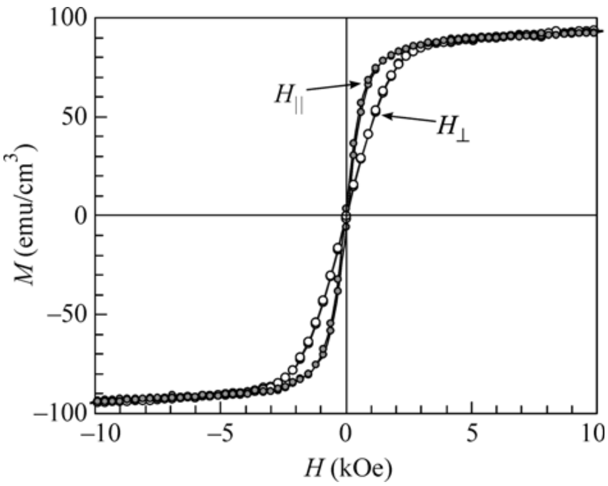

Fig. 2. Magnetization curves M–H for the polycrystalline ϕ-$Ga_{7.7}Mn_{2.3}$ film for the cases of the magnetic field H applied parallel ($H_{||}$) and perpendicular ($H_\perp$) to the film plane.

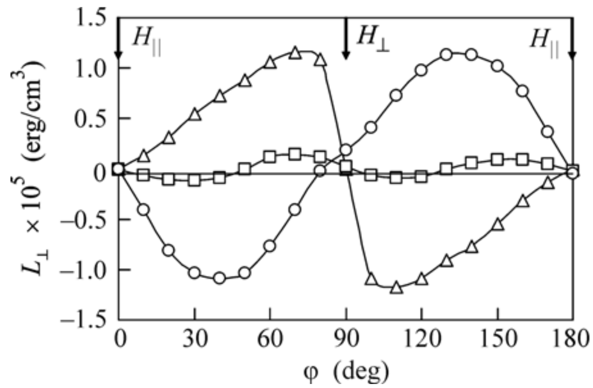

Fig. 3. Evolution of the torque curves $L_\perp(\varphi)$ perpendicular to the plane of the ϕ-$Ga_{7.7}Mn_{2.3}$ sample. The curves were obtained by the rotation of magnetization M_S from the film plane through the normal to it. The measurements were taken at three values of the applied magnetic field H = (△) 4, (□) 8, and (○) 14 kOe. The easy magnetization axis of the film lies in the film plane when fields are below 8 kOe and is aligned parallel to the film normal when fields are above 8 kOe.

preferential epitaxial growth of the phase at the MgO(001) surface according to the orientation relationship

$$\phi\text{-}Ga_{7.7}Mn_{2.3}(001)[110] \parallel MgO(001)[100]. \quad (1)$$

Relationship (1) ensures a good matching of the lattices and the absence of epitaxial stresses at the ϕ-$Ga_{7.7}Mn_{2.3}$/MgO(001) interface. The initial Ga/Mn film samples are nonmagnetic up to 250°C. A magnetization arising after annealing the samples at 300°C proves the initiation of the solid-state reaction between the Ga and Mn layers and the formation of the ferromagnetic (or ferrimagnetic) ϕ-$Ga_{7.7}Mn_{2.3}$ phase. Figure 2 shows the magnetization curves for the Ga/Mn film in the plane perpendicular to the plane of the sample. These curves have a similar shape and do not exhibit any hysteresis. The saturation magnetization and saturation field are $M_S = 95 \pm 10$ emu/cm³ and about 3 kOe, respectively. The measurements of the torque $L_\perp(\varphi)$ perpendicular to the sample plane demonstrate an unusual behavior of the easy axis in the applied magnetic field H. At low H values (up to 8 kOe), the magnetization lies in the film plane, whereas at magnetic fields exceeding 8 kOe, the magnetization becomes aligned parallel to the film normal (see Fig. 3). It is seen in Fig. 3 that $L_\perp(\varphi)$ contains not only the component related to the perpendicular anisotropy $K_\perp \sin 2\varphi$ but also the component $K_{4\perp}\sin 4\varphi$ related to the biaxial anisotropy. The Fourier-series expansion for $L_\perp(\varphi)$ curves shows that $K_\perp$ is linearly dependent on H up to 16 kOe and obeys the relationship

$$K_\perp = (1.4\text{–}1.8H \pm 0.4) \times 10^5 \text{ erg/cm}^3, \quad (2)$$

where the magnetic field H is taken in kilooersteds.

Within the experimental error, all magnetic features in Ga/Mn/MgO(001) films are reproducible. The biaxial magnetic anisotropy $K_{4\perp}$ in the plane perpendicular to the film surface implies the existence of some thin layer with the magnetization lying in the film plane (both in polycrystalline Ga/Mn films and in textured Ga/Mn/MgO(001) films). This layer alongside, with the layer with the perpendicular magnetic anisotropy, creates the effect of biaxial anisotropy. Similar effective biaxial anisotropy is exhibited by the mutually transverse uniaxial particles precipitating in Fe_2NiAl single crystals. The analysis of such situation has demonstrated that this type of anisotropy can be modeled by two noninteracting magnetic wires crossing each other at an angle of 90° [15]. In contrast to polycrystalline Ga/Mn films deposited onto glass substrates, the Ga/Mn/MgO(001) samples are not isotropic in the film plane. The torque curves $L_{||}(\varphi)$ measured in the sample plane demonstrate the existence of biaxial anisotropy with the easy axes coinciding with the [100] and [010] directions of the MgO(001) substrate. The biaxial anisotropy is due to the preferential orientation of the ϕ-$Ga_{7.7}Mn_{2.3}$ phase at the MgO(001) substrate, following from the orientation relationship (1). Therefore, the maximum value $L_{||}^{max}$ of the torque $L_{||}(\varphi)$ should meet the relationship $K_1^{eff}\eta = 2L_{||}^{max}$, where K_1^{eff} is the effective first magnetocrystalline anisotropy constant for the ϕ-$Ga_{7.7}Mn_{2.3}$ phase and η is the relative volume fraction of (001) crystallites in the sample. Experimental $L_{||}(\varphi)$ curves also demonstrate the anomalous dependence of K_1^{eff} on the magnetic field H given by the expression

$$K_1^{\text{eff}} = (0.4 + 0.5H \pm 0.2) \times 10^5 \text{ erg/cm}^3. \qquad (3)$$

4. DISCUSSION OF THE RESULTS

The formation of the ϕ-$Ga_{7.7}Mn_{2.3}$ phase was recently discovered in the course of the epitaxial growth of $MnGa_3$ films on the GaSb(001) substrate at 300°C. However, the Hall effect measurements show that this phase does not have any magnetic order [13]. This contradicts with the results of this work, where we demonstrate that the ϕ-$Ga_{7.7}Mn_{2.3}$ phase is ferromagnetic (or ferrimagnetic) at room temperature. This phase is characterized by low values of M_S, K_1, and $K_\perp$, in contrast to the highly anisotropic Ga–Mn phases with the high Mn content. The origin of the perpendicular magnetic anisotropy in Ga_xMn_{1-x} films is related to the epitaxial growth of such phases as tetragonal $Mn_{3-\delta}$–Ga ($0 < \delta < 1$) with the DO_{22} structure, δ-Mn_xGa_{1-x} ($0.55 < x < 0.60$), and Mn_2Ga_5 [7, 8] with the c axis perpendicular to the sample plane. However, the samples under study are polycrystalline and contain the ϕ-$Ga_{7.7}Mn_{2.3}$ phase. This result, as well as the observed strong magnetic field of $K_\perp$ and K_1, can be explained by the effect of isotropic stress σ acting in the film plane and arising in the course of the synthesis of the ϕ-$Ga_{7.7}Mn_{2.3}$ phase. For polycrystalline films, the perpendicular anisotropy $K_\perp$, in addition to the shape anisotropy $2\pi M_S^2$, includes also a contribution $3\lambda_S\sigma/2$ resulting from the magnetoelastic energy related to the stress

$$K_\perp = 2\pi M_S^2 \pm 3\lambda_S\sigma/2, \qquad (4)$$

where λ_S is the saturation magnetostriction, and plus and minus signs correspond to the compression and tensile stress, respectively. Comparing expressions (4) and (2), we find that $\lambda_S \sim H$ and $2\pi M_S^2 = (1.4 \pm 0.4) \times 10^5$ erg/cm^3 and, hence, we get a rough estimate M_S = 120–170 emu/cm^3 for the saturation magnetization for the ϕ-$Ga_{7.7}Mn_{2.3}$ phase. A slight difference between this estimate and the measured value M_S = (95 ± 10) emu/cm^3 is caused by a thin layer with the magnetization lying in the sample plane, which was not taken into account in expression (4).

Similar expressions for K_1 were found for the (001) epitaxial films [16]

$$K_1^{\text{eff}} = K_1 \pm \sigma(2h_4/3 + 2h_3), \qquad (5)$$

where h_3 and h_4 are the magnetostriction constants. Assuming that the relative volume fraction of the (001) crystallites is $\eta = 1/4$–$3/4$, and comparing expressions (3) and (5), we get an estimate $K_1 = -(0.8 \pm 0.4) \times 10^5$ erg/cm^3 for the first magnetic anisotropy constant of the ϕ-$Ga_{7.7}Mn_{2.3}$ phase. The negative value of K_1 is due to the coincidence of the easy axes with the $\langle 110 \rangle$-type directions, which are the projections of the $\langle 111 \rangle$-type directions onto the film plane.

It is important to note that (Ga, Mn)As dilute magnetic semiconductors, Ni_2MnGa alloys with the ferromagnetic shape memory, and ϕ-$Ga_{7.7}Mn_{2.3}$ phases are close to one another in their crystal structure and lattice constants. This implies a similarity in their physical and chemical properties. In particular, all these materials exhibit a strong effect of stresses on their magnetic properties. For example, the Ni_2MnGa alloys are characterized by giant magnetostriction [3], whereas in (Ga, Mn)As, the variation of the ratio of compression to tensile stresses leads to the rotation of the easy axis from the film plane to its normal [2]. This shows that the characteristic features of the chemical interaction between Ga and Mn atoms underlie the unique magnetic properties of the compounds based on these elements.

5. CONCLUSIONS

It has been shown that the solid-state reaction in the Ga/Mn thin-film structures is initiated at the annealing temperatures of about 250°C and is accompanied by the formation of the ferromagnetic (or ferrimagnetic) ϕ-$Ga_{7.7}Mn_{2.3}$ phase. This phase grows in a polycrystalline form on glass substrates and as partially oriented on the MgO(001) substrate. The saturation magnetization, M_S = (95 ± 10) emu/cm^3, has been determined and the first magnetocrystalline anisotropy constant has been estimated as $K_1 = -(0.8 \pm 0.4) \times 10^5$ erg/cm^3. The experimental data demonstrate a pronounced linear magnetic field dependence of the biaxial in-plane anisotropy, and the perpendicular anisotropy constants. When the applied magnetic field is increased above 8 kOe, the easy axis changes its direction from the film plane to the normal to it. This effect is related to the dominant role of the magnetoelastic contribution to the total anisotropy energy. The possibility of controlling the direction of the easy axis by the applied magnetic field makes the ϕ-$Ga_{7.7}Mn_{2.3}$ samples promising for applications related to spintronic devices.

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