Ferromagnetism and transport in Mn and Mg co-implanted GaAs

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Abstract. We investigated the influence of Mn and Mg co-implantation accompanied by rapid thermal annealing on magnetic and galvanomagnetic properties of p-GaAs. We characterized the samples with SQUID magnetometry and magnetotransport measurements in the temperature interval 4.2 K<T<400 K. Magnetization measurements reveal ferromagnetism up to 400 K (limited by the experimental setup) in all implanted samples. Temperature dependences of resistance, magnetoresistance and Hall effect have been measured in the temperature range 4.2<T<300 K. The anomalous Hall effect is visible up to 195 K and shows influence of ferromagnetism of Ga1-xMnxAs solid solution on galvanomagnetic properties of holes. Above this temperature, ferromagnetism survives due to the MnAs and Ga1-xMnx clusters. The magnetoresistance changes from colossal negative to enhanced positive with increasing temperature near T=35 K.

1. Introduction
Mn-doped GaAs is an attractive diluted magnetic semiconductor (DMS) for a new spin-based electronics. It has been shown that the Curie temperature (Tc) in Ga1-xMnxAs can be raised by increasing the hole concentration as well as Mn concentration [1]. Although Mn acts as an acceptor in GaAs, the hole activation ratio is much less than unity and the hole concentration tends to saturate due to the compensation of Mn acceptors by the defects [2,3]. Therefore, some additional doping of acceptor impurity is needed to achieve a high hole concentration. It has been theoretically shown that the formation of Mn interstitials and Mn-related clusters are enhanced with increasing the hole concentration due to the Fermi energy effect [4]. A significant reduction of Mn interstitials is achieved by the molecular beam epitaxy (MBE) growth of the GaAs based heterostructures followed by low-temperature annealing. Such procedure leads to the value of Tc=250 K [5]. Ion implantation of Mn is also one of methods to fabricate samples with carrier-mediated ferromagnetism. This method was used to produce ferromagnetic hole-doped (Ga,Mn)As [6-8].

In the present study we investigated the influence of Mn and Mg ion co-implantation accompanied by rapid thermal annealing on magnetic and galvanomagnetic properties of p-GaAs.
2. Samples and experimental

Investigated structures were fabricated on semi-insulating GaAs (100) substrate by ion implantation of Mn+ with the energy of 100 keV and dose of $10^{16}$ cm$^{-2}$. To stimulate an enhancement of hole concentration in implanted layers, additional acceptor doping by Mg+ ion implantation was performed. The energy of Mg+ ions (45 keV) was selected for coincidence of peaks for Mg+ and Mn+ ion distributions. Dose of Mg+ ion implantation was varied from $10^{14}$ to $10^{15}$ cm$^{-2}$. After implantation and cleaning of the surface rapid thermal annealing (RTA - 10 seconds) was performed in a flow of argon at temperature range from 700 to 800 °C. Thus $p$-type conductivity layer in GaAs was formed by double implantation. All implantations were performed in conditions to avoid a canalization of incident ions. Some parameters of samples are listed in table 1. We found that annealing of our samples at $T\geq 750$ °C forms in the samples solid solution $Ga_{1-x}Mn_xAs$ and clusters of MnAs and $Mn_xGa_{1-x}$ due to decay of supersaturated solid solution of Mn in GaAs [6]. According to our measurements the buried nanoclusters are formed at a depth of about 150 nm below the sample surface. This agrees with the local Mn concentration observed by SIMS. Additional implantation of Mg increases hole concentration.

| №  | Mg ion dose, $10^{14}$/cm$^2$ | $T_{a}$ °C | $R_s$, kOhm/$\mu$m | $T=300K$ | $T=77K$ | $T=4.2K$ |
|----|-----------------------------|-------------|---------------------|----------|----------|----------|
| 1  | 0                           | 700         | 3.93                | 2360     | -        | -        |
| 2  | 0                           | 800         | 1.30                | 12       | -        | -        |
| 3  | 3                           | 800         | 1.27                | 9.1      | -        | -        |
| 4  | 10                          | 700         | 5.07                | 29.5     | -        | -        |
| 5  | 10                          | 725         | 2.90                | 8.7      | -        | -        |
| 6  | 10                          | 750         | 2.38                | 20.5     | 29500    | -        |

Surface morphology (AFM) and magnetic imaging (MFM) of implanted and annealed samples were investigated at room temperature by microscope "Solver Pro", provided by NT-MDT company (Zelenograd, Russia). According to AFM, clusters with height up to 50 nm and diameter up to 300 nm are visible on the surface (fig. 1a). Some of them reveal magnetic contrast (fig. 1b). Structural properties of samples we investigated in [6].

Fig. 1 (a) AFM and (b) MFM–images of the same area of GaAs surface co-implanted by Mn+ and Mg+ ions and annealed at $T_a=750$ °C (sample 6)

For measurements of the magnetization in the temperature interval 4.2–400K in magnetic fields up to 7T, a SQUID magnetometer Quantum Design Co. Ltd. MPMS-7 was used. The measurements were performed by applying the magnetic field parallel to the surface of samples. Temperature dependences of resistance have been measured in the temperature range 4.2≤T≤300 K. Magnetoresistance and Hall effect have been measured by a conventional four probe technique in the temperature range 4.2≤T≤200 K in magnetic field $B$ up to 6 T applied perpendicular to the sample surface.
3. Results and discussion

3.1. Transport properties. All samples had $p$-type conductivity. In Mn implanted sample resistance increases very rapidly when temperature decreases and becomes more than $10^6 \, \Omega$ at $T<100 \, K$ (fig. 2a). Increasing of RTA temperature from $700 \, ^\circ C$ to $800 \, ^\circ C$ essentially decreases resistance of sample and introduces a kink in $R_s(T)$ dependence (fig. 2b). For $T_s \geq 750 \, ^\circ C$ Ga$_{1-x}$Mn$_x$As and MnAs, Mn$_x$Ga$_{1-x}$ clusters are formed in GaAs due to decay of supersaturated solid solution of Mn in GaAs [6]. At $T<T_c$ the spin flip scattering disappears because of ferromagnetism [9], mobility increases and resistance decreases. This effect looks like a kink in the experimental dependence of $R_s(T)$ (see fig. 2b).

![Fig. 2 Temperature dependence of sheet resistance of Mn only implanted samples with RTA temperature (a) 700 °C and (b) 800 °C](image)

When temperature decreased sheet resistance $R_s$ of Mn and Mg co-implanted samples increased as shown in fig. 3a. The increasing of Mg concentration (samples 4,5,6) increases high temperature resistivity, but decreases resistivity in low temperature region. In the temperature range between 50 and 110 K a kink is visible in $R_s(T)$, which is a characteristic of the ferromagnetic transition [10]. According to the Hall effect data (after subtracting anomalous part, see later) hole concentration decreased when temperature decreased (fig. 3b).

3.2. Magnetic properties. All samples showed ferromagnetism up to 400 K (limitation of SQUID), as indicated by hysteresis loop in the magnetization (all samples studied showed qualitatively similar...
magnetic behaviour). The hysteresis loops show clear temperature dependence over the entire range of temperatures studied, as can be seen in fig. 4a. The saturate value of magnetization at T=400 K is nearly identical to that at T=40 K. In fig. 4b we plot ZFC and FC data for one of the sample. Due to diamagnetic matrix the value of M is negative. As it is seen in fig. 4a and fig. 4b there are different magnetic phases in the samples, one with $T_c$ about 50 K and second with $T_c$ above room temperature. The first value of $T_c$ is very typical for hole mediated ferromagnetism in Ga$_{1-x}$Mn$_x$As solid solutions and the second one is due to formation of MnAs clusters. The Curie temperature for bulk MnAs is about 315 K. In the temperature interval 50-315 K magnetization is due to MnAs clusters, partly by solid solutions Ga$_{1-x}$Mn$_x$As (in which $T_c$ increases with temperature as hole concentration increases [11]) and clusters of Mn$_x$Ga$_{1-x}$. The Curie temperature in Mn$_x$Ga$_{1-x}$ depends on Mn content and increases as $x$ increases. At $x=56\%$ $T_c$ is equal to 600 K [12]. In the investigated samples hole mediated long range magnetic order of magnetic ions of Mn coexists with ferromagnetic clusters MnAs and Mn$_x$Ga$_{1-x}$. Long range order is suppressed at T=50–100K, that is at T=$T_c$ typical for uniform magnetic films of Ga$_{1-x}$Mn$_x$As, fabricated by laser ablation or sputtering. Measurements indicate the presence of buried MnAs nanoclusters with a structural phase transition around 315 K, in accord with the first order magneto-structural phase transition of bulk MnAs. Mn$_x$Ga$_{1-x}$ and MnAs clusters were observed in our samples [6].

Fig. 4 (a) Magnetization loops at different temperatures (diamagnetic background was subtracted) and (b) zero field cooling (ZFC) and field cooling (FC) data for sample 6

3.3. Anomalous Hall effect and magnetoresistance. One of the methods to detect the spin-polarized carriers is the anomalous Hall effect. The anomalous Hall effect is measurable up to about 195 K and shows the hole-mediated ferromagnetism of Ga$_{1-x}$Mn$_x$As solid solution formed after Mn implantation and rapid thermal annealing (fig. 5a). Above this temperature, ferromagnetism survives due to the MnAs and Ga$_{1-x}$Mn$_x$ clusters. The interaction between these clusters and holes in the semiconducting matrix should be very small because of the Schottky barriers at the boundaries. That is why anomalous Hall effect disappears at T=50–100K, that is at T=$T_c$ typical for uniform magnetic films of Ga$_{1-x}$Mn$_x$As, fabricated by laser ablation or sputtering. Measurements indicate the presence of buried MnAs nanoclusters with a structural phase transition around 315 K, in accord with the first order magneto-structural phase transition of bulk MnAs. Mn$_x$Ga$_{1-x}$ and MnAs clusters were observed in our samples [6].

In our opinion, the observed experimental facts testify that the presence of the fluctuation potential in the conducting channel of the structures, caused by nonuniform distribution of the Mn ions, plays a significant role in the transport and magnetotransport phenomena in the investigated structures. As Mn is an acceptor, and carriers in the conducting channel are holes, maximal local concentration of Mn corresponds to the minimum of a potential relief. In this case carriers in the channel move in the areas of a maximal hole concentration corresponding to the maximal concentration of Mn in which a maximal concentration of the magnetic moment (ions of Mn) is realized. Thus, the increase in concentration of Mn leads to strengthening of the magnetic properties and in the formation of the areas with a higher hole concentration. The disorder and the amplitude of fluctuation potential are increased. As a result, the anomalous Hall effect is observed. There are two main reasons for this: (i) increase of
the concentration of magnetic ions (Mn) in general; (ii) increase in local concentration of Mn is the most preferable for current areas.

Contribution of the anomalous Hall effect to the Hall voltage has been observed in samples with high Mn concentration. We shall note, however, that in all samples an activation dependence of conductivity was observed at temperature below 50 K. Anomalous Hall effect is observed simultaneously with an activation type of the temperature dependence of conductivity. Let us also note that signs of the normal Hall effect and the anomalous Hall effect coincide (positive), as well as in the case of samples Ga1-xMnxAs with much higher concentration of Mn [13].

Fig. 5 (a) Hall resistivity $R_{\text{Hall}}$ (inset shows the anomalous part of Hall resistivity) and (b) relative magnetoresistance of sample 3 at different temperatures

The magnetoresistance shown in fig. 5b for one of the samples changes from negative to positive with increasing temperature near $T=35$ K. The high value of positive magnetoresistance can be explained by the enhanced geometric magnetoresistance effect in inhomogeneous semiconductors [14]. Colossal negative magnetoresistance as in manganites [15] was observed in investigated samples (see fig. 5) but in high magnetic fields magnetoresistance saturates. A similar magnetoresistance recently was observed for spin-dependent tunneling in granular ferromagnetic (Ba0.8Sr0.2)2FeMoO6 [16]. The structure of our samples and the behavior of negative magnetoresistance in our case are very similar and may explain the effect. The work was supported by RFBR, grants 05.02.17029a and 05-02-16624a.

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