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Galvanomagnetic properties of GaMnAs layers obtained by ion implantation: the role of Mn^+ ion energy

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The galvanomagnetic properties of GaMnAs layers obtained by implantation of Mn^+ ions and subsequent pulsed laser annealing were studied. The optimal value of the KrF excimer laser pulse energy density ($\sim 300\,\text{mJ/cm}^2$) for the electrical activation of implanted Mn atoms has been established. It has been shown that layers formed with a dose of $(3-5)\cdot 10^{16}\,\text{cm}^{-2}$ are ferromagnetic after laser annealing, and the implantation energy has virtually no effect on the Curie temperature. It was found that the hysteresis loop width in the anomalous Hall effect strongly depends on the implantation energy: coercive field decreases with decreasing ion energy from 200 to 40 keV.

Keywords: gallium arsenide, Mn ion implantation, laser annealing, anomalous Hall effect, ferromagnetism.

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1. Introduction

It is known [1] that ferromagnetic semiconductors (FMS), i.e. materials combining semiconductor and ferromagnetic properties, can be successfully used in spin electronics devices, for instance, as spin injectors. Conventional semiconductors should be doped with transition element atoms to a level of the order of several atomic percent for ferromagnetic properties to appear, which significantly exceeds the limit of their equilibrium solubility. Consequently, non-equilibrium technological techniques should be used for such doping, among which the use of low-temperature molecular beam epitaxy (LT-MBE) is typical. GaMnAs is a canonical FMS, in which Mn atoms substituting nodes in the gallium sublattice play the role of both localized magnetic moments and acceptors supplying free holes. The typical Curie temperature for GaMnAs grown using the LT-MBE method in the optimized conditions is $T_C \approx 110\,\text{K}$ [1].

The implantation of large doses of Mn^+ ions in GaAs is an alternative method for the formation of GaMnAs. However, the first experiments conducted using rapid thermal annealing (RTA) to restore the crystal structure of GaAs irradiated with manganese ions showed the formation of second phase inclusions (MnAs clusters) [2] in the GaAs matrix, which was associated with the release of excess (above the limit equilibrium solubility) Mn atoms from a GaMnAs solid solution. The use of nanosecond laser pulses for post-implantation annealing turned out to be a solution for the problem [3]. The results of the studies conducted to date (see, for example, the review [4]) basically boil down to the following statements: 1) the obtained GaMnAs layers are ferromagnetic at ion doses of Mn $(1-5)\cdot 10^{16}\,\text{cm}^{-2}$ and energy density of a single pulse (duration 20–30 ns) of an excimer KrF or XeCl laser 0.2–0.4 J/cm^2, which manifests itself in hysteresis magnetic field dependences of both magnetization and anomalous Hall effect, from T_C to 110–120 K; 2) magnetoresistance is negative up to temperatures slightly higher than T_C; 3) the formed layers are single-phase, which is explained by the melting of GaAs to a certain depth in case of absorption of the energy of the laser pulse and the ultrafast (at a speed of the order of several m/s) motion of the recrystallization front from the monocrystalline substrate to the surface, in which the solid-state reaction of the formation of clusters of the MnAs type does not have time to occur. However, it should be pointed out that the Mn^+ ion energies from 50 to 300 keV are used in the articles published so far without any justification for their choice.

In this work, the main attention is paid to the study of the effect of Mn^+ ion energy on the properties of

GaMnAs layers formed by implantation and subsequent laser annealing.

2. Experimental method

Implantation of Mn^+ ions into semi-insulating GaAs(001) plates was performed at room temperature with energies E_i from 40 to 200 keV and with doses D_i from $1 \cdot 10^{13}$ to $5 \cdot 10^{16}\,cm^{-2}$. Annealing with a single pulse of an excimer KrF laser (wavelength 248 nm, pulse duration 30 ns) was used for recrystallization of the amorphized layer and activation of Mn atoms at a radiation energy density of P from 125 to 400 mJ/cm^2. The surface area of the annealed samples was $1-1.5\,cm^2$.

Electrical measurements at room temperature using Nanometrics HL5500 system were performed in Van der Pauw geometry using indium ohmic contacts to the surface of the samples. Galvanomagnetic properties at temperatures 10−300 K were studied by scanning a magnetic field applied perpendicular to the surface of structures in the range ±3600 Oe. In this case, the samples were placed in a closed-cycle helium cryostat JanisCCS-300S/202, and measurements were performed using source measure unit Keithley 2400. A comparative study of the magnetofield dependences of the Hall effect was performed using samples obtained by implantation of ions at relatively low (40 and 50 keV) and at relatively high energy (180 and 200 keV).

The method of X-ray photoelectron spectroscopy (XPS) was used to study the distribution of implanted Mn in GaAs. The measurements were performed using ultra-high vacuum system Omicron Multiprobe RM. AlKα-radiation with an energy of 1486.7 eV was used to excite the photoemission. The profiles of the distribution of element concentrations across the depth in GaAs were obtained by etching the surface with argon ions with an energy of 1 keV and an angle of incidence of 45°. The atomic concentration of elements in the layers was determined using the method of relative sensitivity factors.

3. Experimental results and their discussion

Measurement of the dose dependence of the concentration of current carriers after pulsed laser annealing (PLA) demonstrated that there is a threshold dose (in particular, for energy 200 keV is $1 \cdot 10^{15}\,cm^{-2}$), starting from which the acceptor effect of implanted manganese manifests itself. The layer concentration of holes increases monotonously with a further increase of the Mn^+ ion dose, reaching for doses $D_i = (3-5) \cdot 10^{16}\,cm^{-2}$ values $p_s \approx (5-7) \cdot 10^{15}\,cm^{-2}$ (at measurement temperature $T_m = 300\,K$). Therefore, the implantation doses of $3 \cdot 10^{16}$ and $5 \cdot 10^{16}\,cm^{-2}$ providing a high layered concentration of free holes were selected for further studies.

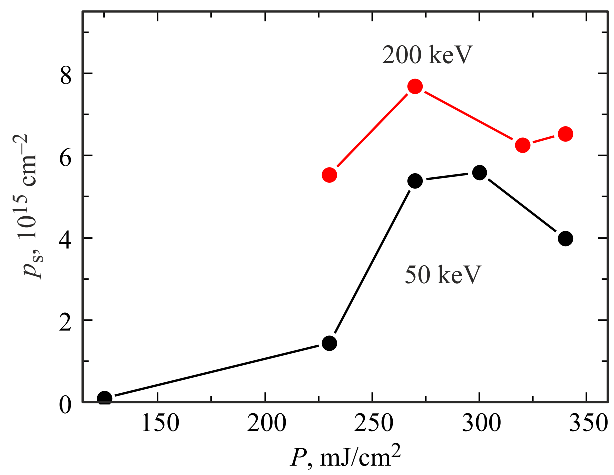

Figure 1. The dependence of the layer concentration of holes in GaAs irradiated with Mn^+ ions with an energy of 50 and 200 keV and a dose of $5 \cdot 10^{16}\,cm^{-2}$ on the energy density of the laser pulse.

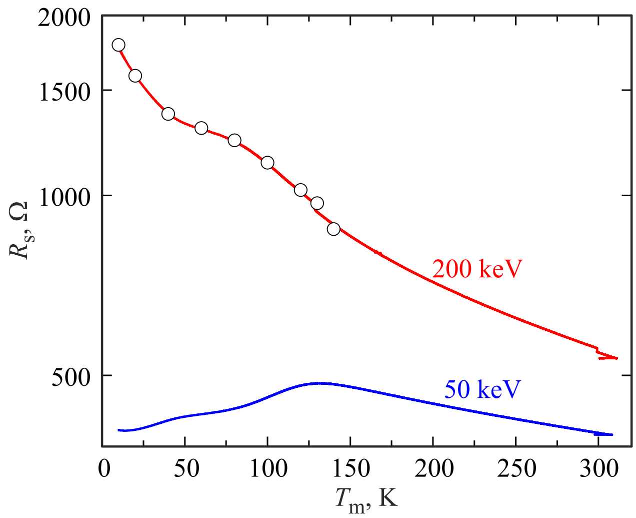

Figure 2. The dependence of surface resistance on measurement temperature for GaAs samples irradiated with Mn^+ ions with energies of 50 and 200 keV, dose $5 \cdot 10^{16}\,cm^{-2}$ and annealed by a laser pulse with $P = 300$ mJ/cm^2.

Figure 1 shows the dependences of the layer concentration of holes on the energy density of the annealing laser pulse for two implantation energies of 50 and 200 keV. The figure shows that the maximum activation of implanted manganese atoms is achieved at a laser annealing energy density of about 300 mJ/cm^2. Therefore, the energy density of $P = 300$ mJ/cm^2 was used for the formation of GaAs layers irradiated with Mn^+ ions in studies of galvanomagnetic properties described below.

Figure 2 shows the temperature dependence of the surface resistance (R_S) for GaAs samples irradiated with Mn^+ ions with a dose of $5 \cdot 10^{16}\,cm^{-2}$ and two energies of 50 and 200 keV, after PLA with $P = 300$ mJ/cm^2. Solid

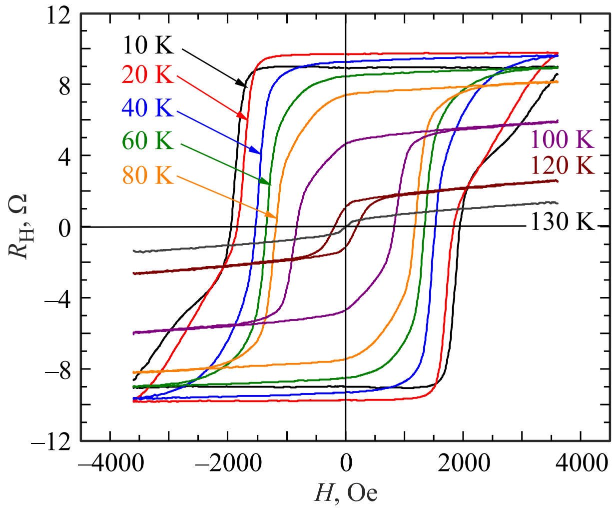

Figure 3. Magnetic field dependences of the Hall resistance (R_H) for GaAs irradiated with Mn^+ ions with an energy of 200 keV and a dose of $5 \cdot 10^{16}$ cm^{-2}, after PLA with $P = 300$ mJ/cm^2 for different measurement temperatures. The magnetic field is applied perpendicular to the sample plane.

lines are used to record the values of the surface resistance when the samples are cooled to 7 K, and individual points on the dependence $R_S(T_m)$ show the values when the sample is heated (in zero magnetic field) with $E_i = 200$ keV. It is obvious that the dependencies in case cooling of the samples and in case of heating practically coincide.

The peak at 131 K on the dependence $R_S(T_m)$ for $E_i = 50$ keV and the absence of a clear extremum for $E_i = 200$ keV calls attention to itself. Usually, the peak on the dependence $R_S(T_m)$ corresponds to the Curie temperature for FMS. However, we previously [5] noted discrepancies in the determination of the Curie temperature for samples with an implantation energy of 180 keV according to measurement data $R_S(T_m)$ and temperature dependences of the magnetic field dependences of the Hall effect. Therefore, the Hall effect was studied in the temperature range of 7−300 K for a reliable determination of the magnetic characteristics of the obtained samples.

Figure 3 shows the results of measurement of the magneto-field dependences of the Hall effect for a GaMnAs sample after implantation of Mn^+ ions with an energy of 200 keV ($D_i = 5 \cdot 10^{16}$ cm^{-2}, $P = 300$ mJ/cm^2).

It can be seen that the Hall effect is anomalous with a hysteresis loop up to 120 K, although the nonlinearity of the dependence $R_H(H)$ is clearly visible at 130 K. It should be noted that the magnetic field required for saturation exceeds the field of 3600 Oe used by us in case of the lowest measurement temperatures, i. e. at 10 and 20 K the hysteresis loops are partial. The coercive field H_c decreases monotonously with an increase of T_m at higher temperatures. The type of dependence $R_H(H)$ shown in Figure 3 is typical for ferromagnetic layers of GaMnAs [4].

Noticeable differences are observed with respect to magneto-field dependences of the Hall effect for layers obtained by implantation of Mn^+ ions with an energy of 50 keV (ion dose and energy density at PLA are the same as for samples with an implantation energy of 200 keV). Figure 4 shows the dependences of R_H on the magnetic field strength for a sample with $E_i = 50$ keV. It can be seen that, the hysteresis loop noticeably narrowed compared with the sample obtained at $E_i = 200$ keV. At the same time, an anomaly (non-linearity in the magnetic field) in the Hall effect is observed up to $T_m = 120$ K.

In our opinion, the dependences of the coercive field H_c and the spontaneous Hall resistance (R_H^S) on temperature are more reliable data for determining the Curie temperature compared to the graphs $R_S(T)$. At the same time, the value H_c was determined directly from the dependencies shown in Figures 3 and 4, and the spontaneous Hall resistance, which is proportional to the spontaneous magnetization of the FMS, was determined by plotting the Arrott dependencies (the technique is described in detail in [5]). Figure 5 shows the dependences of these values H_c and R_H^S on the measurement temperature for samples obtained by implantation of Mn^+ ions with a dose of $5 \cdot 10^{16}$ cm^{-2} after PLA with $P = 300$ mJ/cm^2 for two irradiation energies 50 (Figure 5, *a*) and 200 keV (Figure 5, *b*).

It can be seen that the Curie temperature values determined by the temperature dependences H_c and R_H^S coincide well with each other and are equal to 120 K for $E_i = 50$ keV and 130 K for $E_i = 200$ keV. We previously showed [5] that the Curie temperature significantly depends on the implantation dose with the ion implantation energy Mn^+ 180 keV and is 120 K for the dose of $5 \cdot 10^{16}$ cm^{-2}

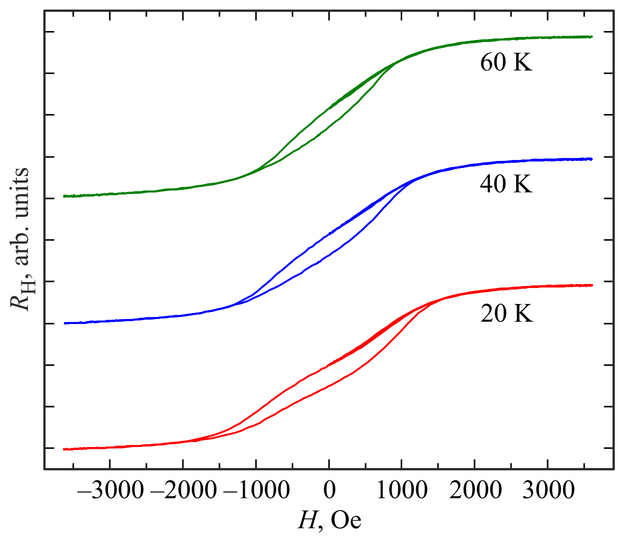

Figure 4. The magnetic field dependences of the Hall resistance for a sample obtained by implantation of Mn^+ ions with an energy of 50 keV and a dose of $5 \cdot 10^{16}$ cm^{-2}, after PLA with $P = 300$ mJ/cm^2 at measurement temperatures of 20−60 K. The magnetic field is applied perpendicular to the sample plane. The curves are shifted vertically for clarity.

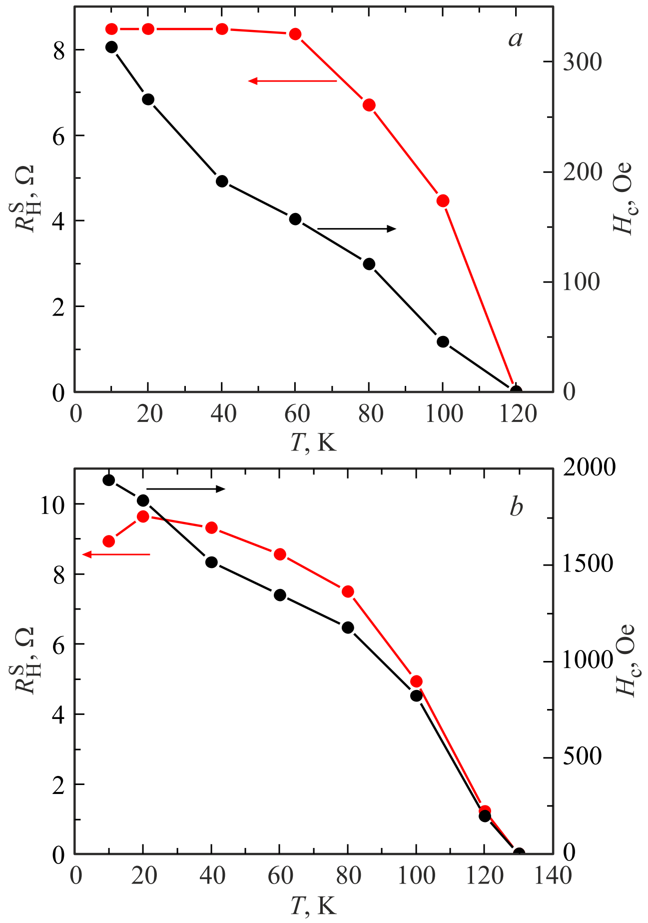

Figure 5. Dependences of the spontaneous Hall coefficient R_H^S(left scales) and the coercive field H_c (right scales) for GaAs samples irradiated with Mn^+ ions ($D_i = 5 \cdot 10^{16}\,cm^{-2}$, $P = 300\,mJ/cm^2$) with energy *a*) 50 and *b*) 200 keV.

($P = 300\,mJ/cm^2$). Taking into account this fact and the data in Figure 5, we can assert that the Curie temperature in the range of $E_i = 50-200$ keV practically does not depend on the ion energy Mn^+, but is determined by the implantation dose.

The type of magnetic field dependences of the Hall effect strongly depends on the Mn^+ ion energy; this applies primarily to the coercive field. For instance, the value H_c is 1830 Oe for $E_i = 200$ keV, 1020 Oe for 180 keV [5] and 270 Oe for 50 keV at a measurement temperature of 20 K ($D_i = 5 \cdot 10^{16}\,cm^{-2}$ and $P = 300\,mJ/cm^2$ in all these samples). It should be noted that the coercive field is weakly dependent on the ion dose. For instance, Ref. [[5], Figure 9] showed that the value H_c is 1100, 910 and 1020 Oe for implantation doses of $1 \cdot 10^{16}$, $3 \cdot 10^{16}$ and $5 \cdot 10^{16}\,cm^{-2}$ respectively (for $E_i = 180$ keV and $P = 300\,mJ/cm^2$).

The trend of „narrowing“ of hysteresis loops with a decrease of implantation energy persists in case of $E_i = 40$ keV, as well. Figure 6 shows the magnetic field dependence of the Hall effect for implantation of Mn^+ ions with an energy of 40 keV and a dose of $3 \cdot 10^{16}\,cm^{-2}$ ($P = 300\,mJ/cm^2$).

The coercive field for this sample is ~ 95 Oe at 20 K. The temperature dependence of the surface resistance (upper inset in Figure 6) shows a distinct peak at 94 K, which can be taken as an estimate of the Curie temperature for this sample.

The measurements of the planar Hall effect were performed due to the small value of H_c. Figure 6 (bottom insert) shows the magnetic field dependence of the resistance of the planar Hall effect (R_{PH}) at low temperature. Areas of almost symmetrical significant change (more than 10 Ω) of the values of R_{PH} are visible. It was previously noted [6] that GaMnAs layers obtained by the LT-MBE method on plates with an orientation of (100) have two axes of light magnetization [100] and [010] located in the plane of the samples. The transition of the magnetization vector under the action of an external magnetic field from one axis of light magnetization to another results in a sharp change of the magnitude of R_{PH}. It should be noted that a similar dependence $R_{PH}(H)$ is observed up to 80 K, although the amplitude of the resistance change of the planar Hall effect decreases with the increase of measurement temperature (for example, to 3 Ω at 60 K). The distance between the minima (from 330 Oe at 7 K to 200 Oe at 40 K) also monotonously decreases with the growth of T_m (on the magnetic field strength scale). The presented dependence $R_{PH}(H)$ shows that the studied GaMnAs obtained by implantation of Mn^+ ions with an energy of 40 keV has a significant magnetization component in the plane of the layer. This component moves from one

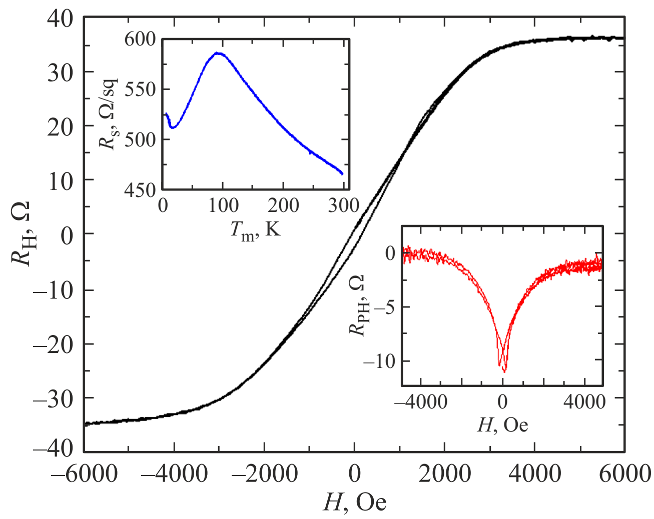

Figure 6. Magnetic field dependence of the Hall effect (field perpendicular to the surface, $T_m = 20$ K) for a GaAs sample obtained by implantation of Mn^+ ions with an energy of 40 keV and a dose of $3 \cdot 10^{16}\,cm^{-2}$after PLA with $P = 300\,mJ/cm^2$. The upper insert shows the temperature dependence of the surface resistance, and the lower insert corresponds to the magneto-field dependence of the planar Hall effect (the field is applied along the surface of the sample) at 7 K.

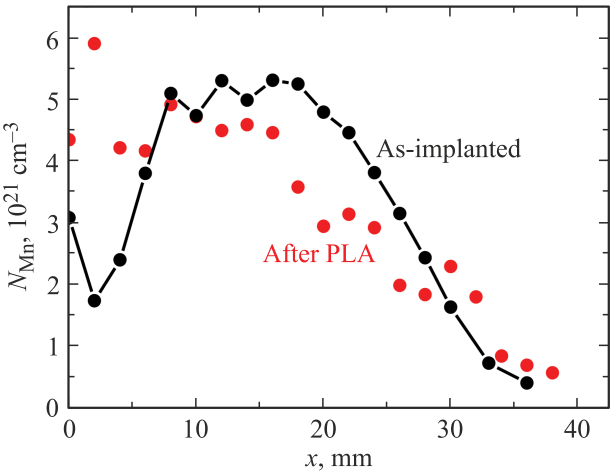

Figure 7. Profiles of the distribution of Mn atoms across the depth (x) obtained by the XPS method for GaAs irradiated with ion energy of 40 keV, dose of $3 \cdot 10^{16}\,\mathrm{cm}^{-2}$, before and after PLA with $P = 300\,\mathrm{mJ/cm}^2$.

axis of light magnetization to another when the intensity of the external magnetic field changes, like a GaAs structure with a delta-doped layer of Mn [7].

In this regard, it makes sense to compare the thicknesses of the doped layers obtained by implantation with different energies. The Mn doping profiles obtained by secondary ion mass spectrometry with an energy of 180 keV are provided in [5]; it is shown that the thickness of the Mn-doped layer is approximately 220 nm for a dose of $3 \cdot 10^{16}\,\mathrm{cm}^{-2}$ and PLA with $P = 300\,\mathrm{mJ/cm}^2$. The doping profiles obtained in this study for a GaAs sample doped with Mn^+ ions with an energy of 40 keV are shown in Figure 7.

It can be seen that the manganese atoms in the implanted non-annealed GaAs are mainly concentrated in a layer with a thickness of 35 nm. XPS profiling shows a peak concentration of N_{Mn}, located at a depth of about 12–16 nm. It should be noted that according to calculations performed using the SRIM program [8], the maximum distribution should have a depth of 26.9 nm for ion energy of Mn^+ $E_i = 40$ keV. Obviously, the difference between the calculated and experimental distributions is attributable to ion sputtering, which is large for sufficiently heavy ions of the type Mn^+ and at relatively low energies (the sputtering coefficient $S = 9.66$ at./ion for Mn^+ ions with $E_i = 40$ keV according to SRIM calculations). The distribution of Mn atoms is modified in the result of PLA: the concentration of N_{Mn} slightly decreases compared to the non-annealed sample at depths from 12 to 28 nm, and an increase of the concentration of manganese to $\sim 6 \cdot 10^{21}\,\mathrm{cm}^{-3}$ is observed near the surface (in the layer up to 6 nm). The latter is a characteristic feature of GaMnAs annealed by pulsed laser method (this was observed, for example, for $E_i = 180$ keV in [5]) and is usually explained by the segregation of Mn atoms to the surface during the movement of the recrystallization front during cooling after pulsed laser annealing.

The integral concentration of Mn atoms in the annealed layer is equal to $1.24 \cdot 10^{16}\,\mathrm{cm}^{-2}$, which is $\sim 41\%$ of the implanted dose. The loss of manganese is also associated with intensive sputtering of the sample during ion implantation. The layer concentration of holes (i.e. electrically active manganese) at $E_{\mathrm{i}} = 40$ keV, $D_{\mathrm{i}} = 3 \cdot 10^{16}\,\mathrm{cm}^{-2}$ and $P = 300\,\mathrm{mJ/cm}^2$ according to measurements of the Hall effect at 300 K (at a temperature when the Hall effect is normal) was $3.19 \cdot 10^{15}\,\mathrm{cm}^{-2}$. Hence, the average volume concentration of free carriers over a layer with a thickness of 35 nm is equal to $\sim 9 \cdot 10^{20}\,\mathrm{cm}^{-3}$, which, when compared with the average values of N_{Mn} in the layer, means good activation (about 26%) as a result of in the selected mode.

Attention should be paid to the significant difference in the form of hysteresis loops in the anomalous Hall effect for layers obtained by implantation of manganese ions at relatively high (200 keV) and low (40 keV) energies. The appearance of hysteresis loops at low temperatures for a sample doped with an energy of 200 keV (Figure 3) suggests the position of the easy axis in this layer perpendicular to the surface (along the direction of the magnetic field when measuring the Hall effect). This is not typical, for example, for GaMnAs samples grown on GaAs(001) substrates using the usual molecular beam epitaxy procedure; the easy axis in these layers is located in the sample plane (see, for example, [9]). The location of the easy axis perpendicular to the plane of the GaMnAs layer was observed earlier if a buffer relaxed InGaAs layer was grown between the GaAs substrate (001) and the GaMnAs layer with a lattice parameter greater than the lattice parameter of GaAs and GaMnAs, and creating tensile stresses in the GaMnAs layer [10]. We can assume that the front of laser high-temperature exposure (melting) with a pulse energy of $300\,\mathrm{mJ/cm}^2$ did not reach the layers of the substrate undisturbed by irradiation in the layer obtained by implantation of Mn^+ ions with an energy of 200 keV, therefore, there is an intermediate layer between the annealed GaMnAs layer and the initial GaAs that contains residual radiation defects and has an increased lattice parameter because of this (the presence of such a deformed layer was noted by us in GaAs samples irradiated with Mn^+ ions with an energy of 180 keV [5]). This problem does not exist in case of thinner implanted layers (with ion energy 40–50 keV) and the annealed layer recrystallizes, starting with undisturbed GaAs. A magnetization component appears parallel to the surface of the sample as a result of this, as well as due to the impact of the shape factor in thin layers (on the order of 35 nm for 40 keV). This, in the limit of a very thin layer, can result in a hysteresis-free magnetic field dependence of the magnetization when a magnetic field is applied perpendicular to the sample plane (i.e., to a hysteresis-free dependence of the resistance of the anomalous Hall effect).

4. Conclusion

It has been experimentally shown that GaMnAs formed by implantation of Mn^+ ions with a dose of $(3-5) \cdot 10^{16}\,cm^{-2}$ and subsequent pulsed laser annealing is a ferromagnetic semiconductor for ion irradiation energies 40−200 keV. The maximum layer concentration of holes in the formed layers is achieved after laser annealing with a pulse energy density of $\sim 300\,mJ/cm^2$. The Curie temperature of GaMnAs turned out to be practically independent of the implantation energy and was equal to 120−130 K for the dose of manganese ions $5 \cdot 10^{16}\,cm^{-2}$. The width of the hysteresis loop in the abnormal Hall effect decreases with a decrease of the implantation energy. The axis of light magnetization is directed perpendicular to the sample plane for layers formed at 200 keV. The main magnetization component is located along the sample plane for layers formed at 40 keV, which is explained both by the sufficient depth of the thermal effect of the annealing laser pulse and by the influence of the shape factor due to a decrease of the thickness of the doped layer.

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Conflict of interest

The authors declare that they have no conflict of interest.

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