Physics of the Solid State, 2024, Vol. 66, No. 9

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Ferromagnetism in GaAs structures delta-doped with Fe

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Received June 7, 2024
Revised July 8, 2024
Accepted July 9, 2024

The work examines the formation of GaAs structures with a Fe delta-doping layer using the method of pulsed laser deposition in vacuum. The structures with the Fe delta-doping layer deposited within 25 and 35 s can be characterized as the intrinsic ferromagnetic semiconductor with the Curie temperature of 70−80 K. In structures with the Fe delta-doping layer deposited within 45 s, the formation of some second ferromagnetic intermetallic phase with the Curie temperature of 100−120 K is observed.

Keywords: magnetic semiconductors, A^3B^5 semiconductors, GaAs, pulsed laser deposition, spintronics.

DOI: 10.61011/PSS.2024.09.59217.152

1. Introduction

New stage of production and study of magnetic semiconductors and semiconductor structures based on them is associated with epitaxial layers of semiconductors A^3B^5, heavily doped by Fe atoms. Unlike relatively well studied class of magnetic semiconductors A^3B^5 : Mn, where the reproducible results for different semiconductor matrices state Curie temperature (T_C) below room temperature (in particular, up to 200 K for most studied material (Ga,Mn)As), for magnetic semiconductors of class A^3B^5 : Fe single phase layers with T_C over 300 K and intrinsic ferromagnetism were obtained. So, by method of molecular beam epitaxy (MBE) we obtained the epitaxial layers (Ga,Fe)Sb with $T_C \approx 340$ K [1] and layers (In,Fe)As with $T_C \approx 305$ K [2] (at Fe concentration about 10 at.%). In our laboratory of Scientific Research Physical Technical Institute NNSU by method of pulsed laser deposition (PLD) the epitaxial layers (In,Fe)Sb [3] and GaAs:Fe [4] 20−60 nm thick with iron concentration up to 20 at.% and Curie temperature above 300 K were first obtained. PLD method provides the epitaxial layers A^3B^5 : Fe and multilayer heterostructures with layers A^3B^5 : Fe based on different matrices A^3B^5 with concentration of Fe admixture up to 23 at.% [5]. Obtaining of the high temperature magnetic semiconductor based on common GaAs is an important stage for the discipline of magnetic semiconductors. Our studies showed that for occurrence of high-temperature intrinsic ferromagnetism in the epitaxial layers GaAs : Fe the embedding of significant (10−20 at.%) amount of Fe is necessary. GaAs : Fe, layers obtained by us using PLD method demonstrated ferromagnetism in transport and magnetooptical properties. The intrinsic ferromagnetism in GaAs : Fe layers is unambiguous confirmed by spectral studies of the magnetic circular dichroism (MCD) [4]. Features of PLD layers GaAs : Fe is that Fe atoms equiprobably substitute Ga and As. Unlike the high-temperature ferromagnetic semiconductor (Ga,Fe)Sb and (In,Fe)Sb, in GaAs : Fe the Fermi levels is at allowed states of Fe impurity level in band gap, not in any allowed band. The exchange ferromagnetic interaction in GaAs : Fe, probably, is associated with the Zener double exchange mechanism.

In present paper we submit results in creation of GaAs-structures delta-doped with Fe. Admixture embedding as delta-layer potentially allows its local concentration increasing (and, hence, probability of exchange interaction between atoms of 3d admixture) and to reduce effect on the crystalline perfection of semiconductor structure.

2. Experimental procedure

GaAs structures delta-doped with Fe were obtained in the following way: on substrate i-GaAs (001) with 2-degree miscut angle a undoped buffer GaAs 20−30 nm thick was formed by laser sputtering of GaAs target; further Fe delta-doping layer was deposited (sputtering time of target Fe (t_{Fe}) was 15−45 s at deposition rate 0.5−1 nm/min), then Fe layer was covered with growth of cover layer GaAs ~ 10 nm thick. Formation temperature of buffer layer GaAs (T_{buff}) was 400, 200 or 180°C. Deposition temperature of delta-layer Fe (T_{Fe}) and cover layer GaAs (T_{cap}) was 200 or 180°C.

To study the crystalline perfection of samples the method of transmission electron microscope (TEM) was used. Elemental composition of structures was analyzed by method of X-ray photoelectron spectroscopy (XPS). The elements concentration was determined using the relative sensitivity factors [6]. Accuracy of atom concentration determination in used XPS method was 1 at.%. Transportation properties of structures (Hall effect and magnetoresistance) were studied at direct current in van der Pauw geometry. MCD were studied for the geometry of reflection of circularly polarized light from structures surface. The external magnetic field was oriented at right angle to the plane of the structures. MCD effect value was determined in the following way: $(I_l - I_r)/(I_l + I_r)$, where I_l and I_r — intensities of light reflected from sample, light has left and right circular polarization, respectively. Magnetic transport properties and MCD were studied in closed cycle helium cryostat.

3. Experimental results and discussion

Figure 1, *a* shows TEM-image of cross-section portion of structure with Fe delta-doping layer applied for 35 s ($T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 180^\circ$C). In TEM-image GaAs-substrate is evident, as well as layer of low-temperature GaAs (buffer and cover layers) clearly distinguishable from the substrate. In Figure 1, *a* atomic rows are clearly distinguished, they pass from substrate to top of structure, i.e. the deposited layers of low-temperature GaAs are epitaxial. At distance about 30 nm from the interface substrate–buffer on image a horizontal feature is seen, it, probably, is associated with the interface buffer layer — cover layer, where region of Fe delta-doping layer is located. Figure 1, *b* shows TEM-image of region of interface buffer layer — cover layer (region of delta-layer Fe), obtained with large magnification.

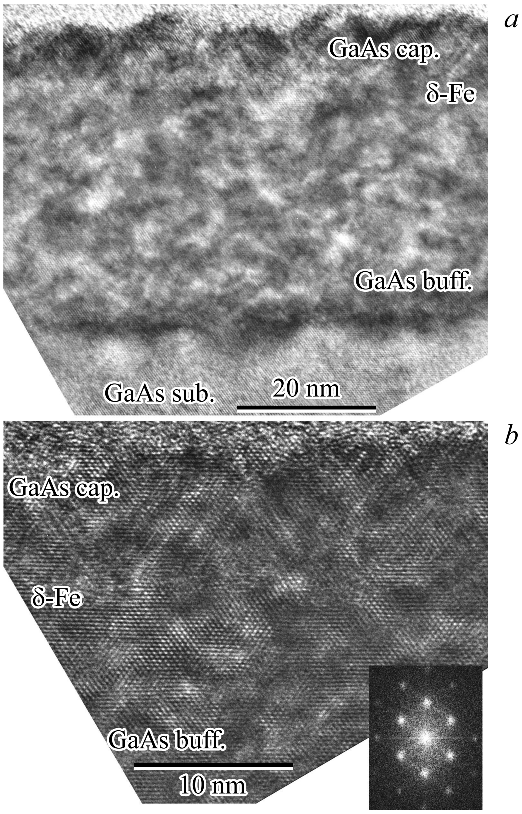

Figure 1. *a*) TEM-image of cross-section of GaAs-structure with Fe delta-doping layer ($t_{\text{Fe}} = 35$ s, $T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 180^\circ$C). *b*) TEM-image of cross-section of region delta-doped with Fe. On the insert: FFT diffraction pattern of this TEM-image.

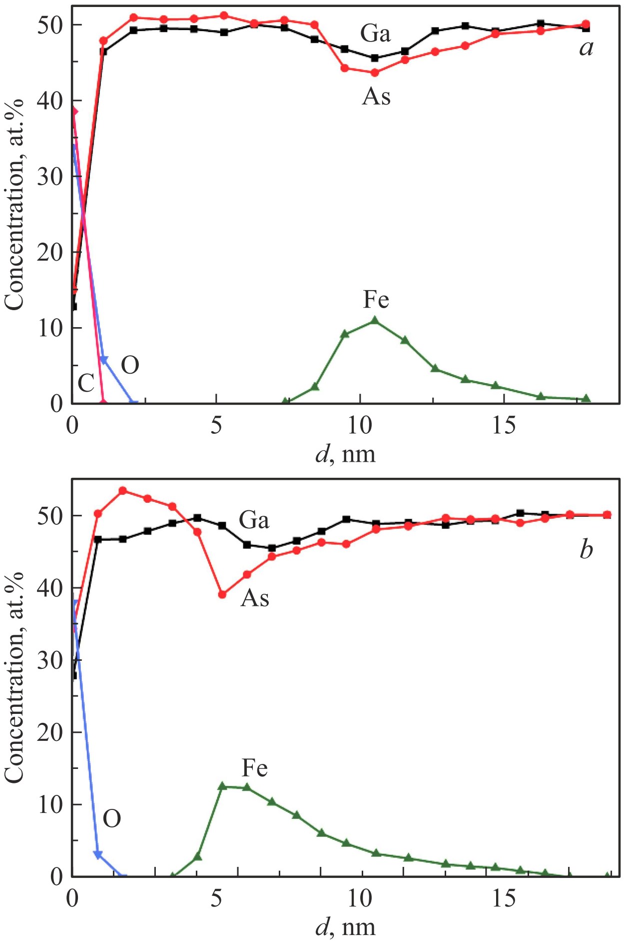

Figure 2. Profile of elements distribution through depth for GaAs-structures with Fe delta-doping layer. *a*) Structure with $t_{\text{Fe}} = 35$ s, $T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 180^\circ$C. *b*) Structure with $t_{\text{Fe}} = 45$ s, $T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 200^\circ$C.

Image shows that cover layer GaAs is epitaxial layer, but contains V-shape regions of microtwins (which is generally characteristic of low-temperature epitaxial layers GaAs [7]). Insert in Figure 1, *b* presents the diffraction pattern obtained by method of fast Fourier transform (FFT) of TEM-image. In FFT diffraction pattern there are only reflexes corresponding to crystalline structure of sphalerite. no additional reflexes (associated with potentially possible second crystalline phase) are observed. Thus, the technological method used makes it possible to obtain epitaxial GaAs-structures with built-in delta-doped with Fe region.

Figure 2,*a* presents XPS-profile of componentry elements distribution through depth for structure with Fe delta-doping layer deposited for 35 s ($T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 180^\circ$C). Half-width of Fe localization region is ~ 7 nm at concentration maximum Fe ≈ 10 at.%. Decreasing of deposition time of Fe delta-layer leads to proportional decrease in Fe concentration. According to XPS-data Fe atoms substitute both Ga atoms, and As atoms (at that As atoms are substituted with somewhat higher probability). Approximately, the equiprobable substitution of Ga and As atoms by Fe atoms was observed by us for bulk-doped epitaxial layers GaAs : Fe [4]. Figure 2,*b* presents XPS-profile of elements distribution for structure with Fe delta-doping layer deposited for 45 s ($T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 200^\circ$C). Increase in Fe sputtering time leads to increase in its concentration in the obtained profile, as well as to predominantly As atoms substitution by Fe atoms in maximum of distribution. Also note that right part of Fe distribution profile, expanded towards the buffer layer. Previous studies showed that diffusion of Fe atoms to side opposite to increase direction is typical of structures A^3B^5, heavily doped with Fe [5]. In spite of similarity of element distribution profiles presented in Figure 1,*a* and *b*, the structures have different electrophysical and magnetic properties, this will be considered further.

Figure 3,*a* presents layer resistance vs. temperature for GaAs-structures with Fe delta-doping layer obtained at different technological parameters. For major of formed structures (for time $t_{\text{Fe}} \leq 35$ s) the characteristic feature is high layer resistance at room temperature ($1-10\,\text{M}\Omega/\text{sq}$), at that conductivity is kept until low temperatures ($10-30$ K). For such structures, like for bulk-doped layers GaAs : Fe [4], the conductivity, probably, is associated with hopping transport of electrons between Fe states in band gap. For structures with higher Fe content in delta-doping layer ($t_{\text{Fe}} = 45$ s) the conductivity has fundamentally another nature. Structures in $t_{\text{Fe}} = 45$ s demonstrate by some orders of magnitude lower layer resistance at room temperature ($\sim \text{k}\Omega/\text{sq}$) and its weak temperature dependence (Figure 3,*a*). Such „metal" nature of conductivity indicates that in such structures carriers transfer, probably, is performed via overlapping regions of intermetallic compounds Fe–Ga–As.

The structures with formation time of Fe delta-layer equal to 25 and 35 s are characterized by negative magnetoresistance up to temperature ~ 150 K. Figure 3,*b* presents curves of magnetoresistance at different temperatures for structure with $t_{\text{Fe}} = 35$ s and $T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 180^\circ$C (magnetic field is applied at right angle to plain of samples). A pronounced negative magnetoresistance with a trend to saturation with magnetic field greater than 2000 Oe indicates spin-dependent scattering of charge carriers. For structures with high resistance ($t_{\text{Fe}} = 15-35$ s) we failed to register authentically Hall EMF, this indicates the very low mobility of charge carriers — significantly below $1\,\text{cm}^2/(\text{V} \cdot \text{s})$, as a result of hopping transfer of electrons between deep states of Fe in band gap. Such magnetic transport properties were observed for the bulk doped epitaxial layers GaAs : Fe [4].

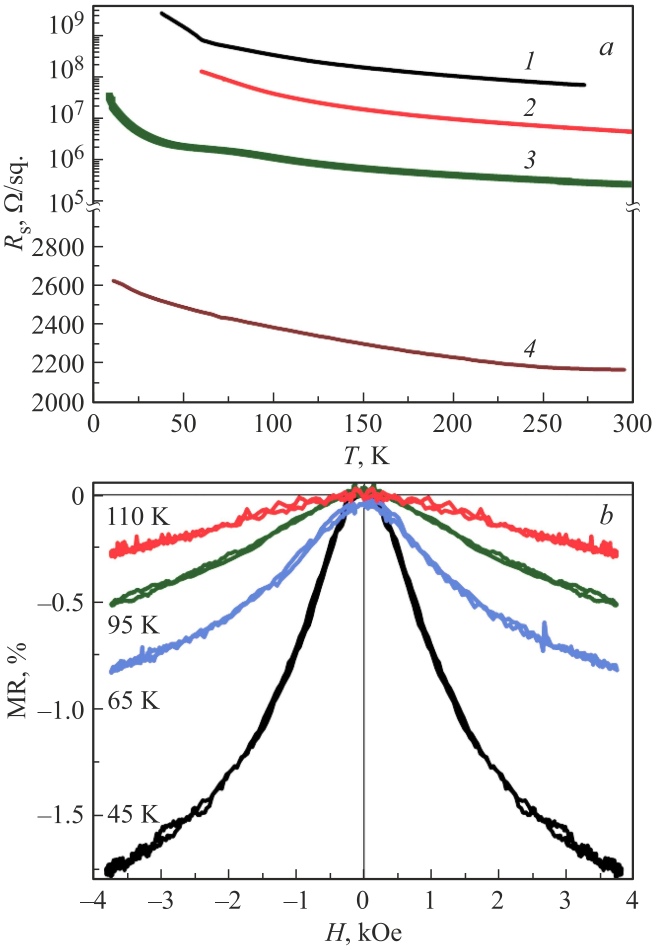

Figure 3. *a*) Temperature dependences of layer resistance of structures with Fe delta-doping layer. Curve *1* — structure with $t_{\text{Fe}} = 15$ s, $T_{\text{buff}} = 500^\circ$C, $T_{\text{Fe}} = T_{\text{cap}} = 200^\circ$C. *2* — structure with $t_{\text{Fe}} = 25$ s, $T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 200^\circ$C. *3* — structure with $t_{\text{Fe}} = 35$ s, $T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 180^\circ$C. *4* — structure with $t_{\text{Fe}} = 45$ s, $T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 200^\circ$C. *b*) Magnetoresistance (MR) at different temperatures for structure with $t_{\text{Fe}} = 35$ s, $T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 180^\circ$C.

Figure 4 presents The Hall resistance vs. magnetic field at different temperatures for structure with „metal" nature of conductivity ($t_{\text{Fe}} = 45$ s and $T_{\text{buff}} = T_{\text{Fe}} = T_{\text{cap}} = 200^\circ$C). Feature of such structures with increased concentration of Fe in region of delta-layer is pronounced Hall anomalous effect up to temperature about 160–180 K, but the magnetoresistance is expressed weakly. Value of magnetoresistance by more than order of magnitude is below at same temperatures, as compared to structures with semiconductor nature of conductivity.

For magnetic semiconductors MCD study provides important information. MCD spectral dependences for magnetic semiconductors with intrinsic ferromagnetism shall demonstrate features in regions of energies corresponding to optical transitions in the semiconductor matrix [8,9]. In particular, for ferromagnetic bulk-doped epitaxial layers

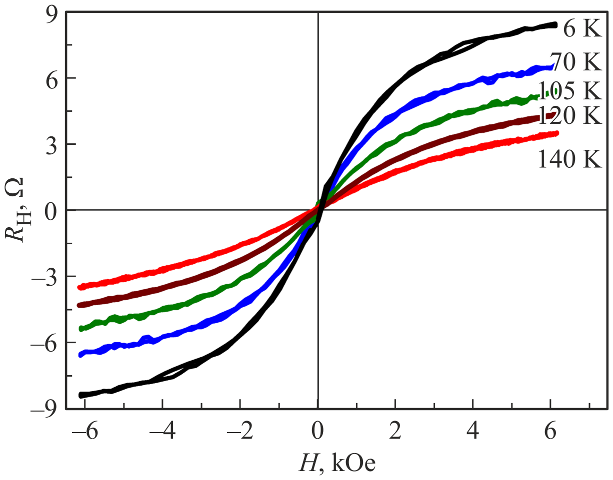

Figure 4. Magnetic field dependences of Hall resistance at different temperatures for structure with $t_{\mathrm{Fe}} = 45\,\mathrm{s}$, $T_{\mathrm{buff}} = T_{\mathrm{Fe}} = T_{\mathrm{cap}} = 200^\circ\mathrm{C}$.

GaAs : Fe significant decrease of MCD value was observed for energies of light quanta below E_g of semiconductor matrix GaAs [4]. Figure 5, *a* presents MCD values vs. magnetic field — MCD(H), at 8 K and different energies of light quanta for structure with $t_{\mathrm{Fe}} = 35\,\mathrm{s}$, $T_{\mathrm{buff}} = T_{\mathrm{Fe}} = T_{\mathrm{cap}} = 180^\circ\mathrm{C}$. At energies of light quanta over E_g the dependences for GaAs have noticeable nonlinear nature with saturation in magnetic field ~ 2000 Oe. At 8 K the dependence MCD(H) is hysteresis dependence. If energy of light quanta decreases below E_g the significant decrease in MCD value is observed. This states that magnetic properties of the structure are determined by the intrinsic ferromagnetism of the magnetic semiconductor GaAs : Fe in delta-doped region. Figure 5, *b* presents dependences MCD(H) for this structure at different temperatures and energy of light quanta 1.8 eV. Analysis of dependences MCD(H) at different temperatures plotted in Arrott coordinates [9] (insert in Figure 5, *b*), indicates that T_C for structure with $t_{\mathrm{Fe}} = 35\,\mathrm{s}$, $T_{\mathrm{buff}} = T_{\mathrm{Fe}} = T_{\mathrm{cap}} = 180^\circ\mathrm{C}$ is abut 70 K. The shape of magnetoresistance curves is in agreement with this conclusion (Figure 3, *b*). Studies of magnetoresistance and MCD for other structures with $t_{\mathrm{Fe}} = 25{-}35\,\mathrm{s}$ indicate that their Curie temperature is below 70–80 K.

Figure 6, *a* presents dependences MCD(H), at 8 K and different energies of light quanta for structure with $t_{\mathrm{Fe}} = 45\,\mathrm{s}$, $T_{\mathrm{buff}} = T_{\mathrm{Fe}} = T_{\mathrm{cap}} = 200^\circ\mathrm{C}$. In contrast to structures with $t_{\mathrm{Fe}} = 25{-}35\,\mathrm{s}$, for structures with an increased Fe concentration in the delta-layer region ($t_{\mathrm{Fe}} = 45\,\mathrm{s}$), the MCD value weakly depends on the energy of light quanta, i. e. there is no spectral feature observed in the MCD effect in the Eg region of the GaAs semiconductor matrix. This is in agreement with transport data for structure with $t_{\mathrm{Fe}} = 45\,\mathrm{s}$ (Figure 3, *a* and Figure 4), and indicates that in this structure the region of some intermetallic compounds Fe–Ga–As, being ferromagnetic, is formed. From temperature dependences of MCD value we can conclude that T_C of this region is 100–120 K (Figure 5, *b*).

In system of intermetallic compounds Fe–Ga–As the class of ferromagnetic compounds $\mathrm{Fe_3Ga_{2-x}As_x}$ is known. Depending on concentration x_{As}, T_C for the compound varies in range 350–700°C [10]. Besides, there are different options of ferromagnetic compound $\mathrm{Fe_{1-x}Ga_x}$, with T_C above room temperature, but in such compounds, like in compounds $\mathrm{Fe_3Ga_{2-x}As_x}$, Fe concentration is at least 60 at.% [11,12]. To form the regions with relatively low resistance from such intermetallic compounds, it is necessary to overcome the percolation threshold, therefore, a practically continuous region with thickness of several nanometers containing more 60 at.% Fe shall be formed. This supposition does not agree with XPS results of element analysis for the structure with metal nature of conductivity ($t_{\mathrm{Fe}} = 45\,\mathrm{s}$, Figure 2, *b*). Note also that Curie temperature for the obtained structures with $t_{\mathrm{Fe}} = 45\,\mathrm{s}$ is significantly lower the room temperature (~ 130 K).

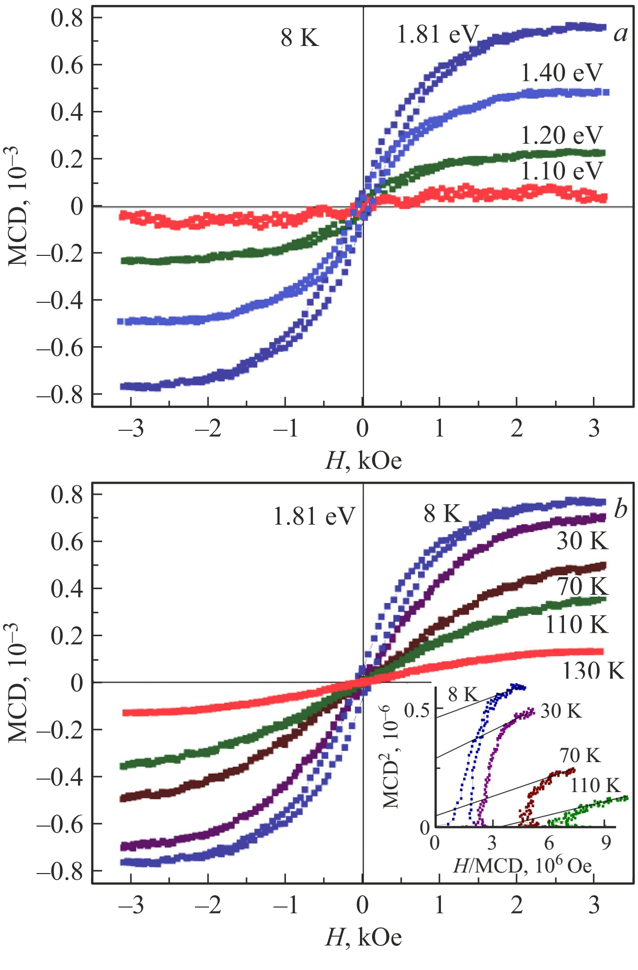

Figure 5. Magnetic field dependences of MCD for structure with $t_{\mathrm{Fe}} = 35\,\mathrm{s}$, $T_{\mathrm{buff}} = T_{\mathrm{Fe}} = T_{\mathrm{cap}} = 180^\circ\mathrm{C}$. *a*) Dependences at 8 K for different energies of light quanta. *b*) Dependences at different temperatures for energy of light quanta 1.81 eV. The insert presents dependences of MCD(H) in Arrott coordinates.

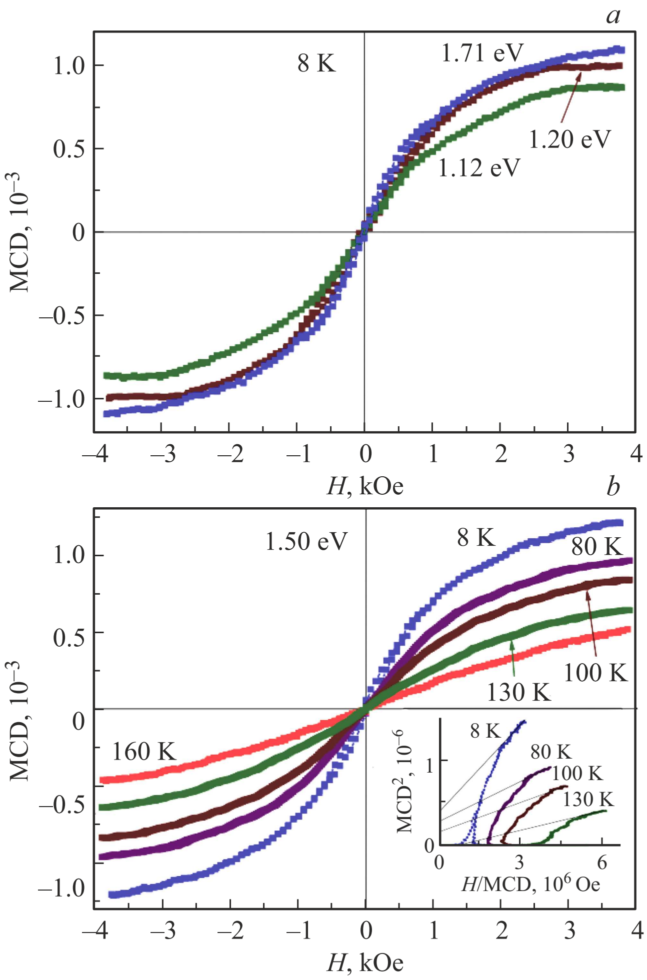

Figure 6. Dependences MCD(H) for structure with $t_{\mathrm{Fe}} = 45$ s, $T_{\mathrm{buff}} = T_{\mathrm{Fe}} = T_{\mathrm{cap}} = 200°$C. *a*) Dependences at 8 K for different energies of light quanta. *b*) Dependences at different temperatures for energy of light quanta 1.5 eV. In insert: curves MCD(H) in Arott coordinates.

According to phase diagram of intermetallic compounds Fe−As, at temperatures blow 800°C in equilibrium conditions the stoichiometric compounds $\mathrm{FeAs_2}$, FeAs, $\mathrm{Fe_2As}$ are formed, and potential formation of phase with Fe concentration over 67 at.% is also possible [13]. The stoichiometric compounds FeAs, $\mathrm{Fe_2As}$ are antiferromagnetics, and compound $\mathrm{FeAs_2}$ — diamagnetic [14]. In publications there low little data on magnetic properties of nonstoichiometric compounds FeAs obtained under equilibrium conditions. So, paper [15] informs about ferromagnetic compound $\mathrm{Fe}_x\mathrm{As}_y$ with Curie temperature ∼ 150 K. Paper [14] informs about formation on GaAs by MBE method of the ferromagnetic epitaxial layers FeGaAs (Fe concentration ∼ 60 at.%, Ga concentration ∼ 1 at.%) with Curie temperature ∼ 400 K. By publication data we can conclude that potentially possible ferromagnetic phase Fe−As shall have Fe concentration at least 50−60 at.%. It was note previously that potentially possible formation of solid layer of such compound with thickness of several nanometers does not agree with XPS data (Figure 2, *b*).

According to obtained results of study of MCD spectral dependence, the obtained GaAs-structures with Fe delta-doping layer deposited for 25 and 35 s, can be characterized as ferromagnetic semiconductor with intrinsic ferromagnetism. Structures with $t_{\mathrm{Fe}} = 45$ s demonstrate formation of some second ferromagnetic intermetallic phase. At that note similarity of Curie temperature for structures of these two types. To determine the reason of difference in transportation and magnetic properties of the obtained structures we planned in-depth examinations of their microstructure.

4. Conclusion

So, by the method of pulsed laser deposition in vacuum it is possible to form conductive ferromagnetic GaAs structures with Fe delta-doping layer. Structures with Fe delta-doping layer deposited for 25 and 35 s, can be characterized as ferromagnetic semiconductor with intrinsic ferromagnetism and Curie temperature 70−100 K. In structures with Fe delta-doping layer deposited for 45 s the formation of second ferromagnetic intermetallic phase with Curie temperature 100−120 K is observed.

Funding

This study was supported by grant of the Russian Science Foundation No. 24-22-00151, https://rscf.ru/project/24-22-00151/.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by I.Mazurov