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We inform an opportunity of a laser synthesis of the diluted magnetic semiconductors on the basis of germanium and silicon, doped by manganese or iron till 10 - 15 at. %. Thin 50 - 110 nanometers thickness layers Ge and Si were grown on heated up to 200 - 480ºC monocrystal substrates of gallium arsenide or sapphire. The content of a 3*d*-impurity was measured by x-ray spectral method. The ferromagnetism of layers, high magnetic and acceptor activity of Mn in Ge, of Mn and Fe in Si were appeared in observation at 77 - 500 K of Kerr effect, abnormal Hall effect, high hole conductivity and anisotropic ferromagnetic resonance (FMR). On the FMR data the Curie point of Ge:Mn , Si:Mn on GaAs substrates and Si:Fe on Al_2O_3 were not lower 420, 500 and 220 K, respectively.

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1.Introduction

Diluted magnetic semiconductors (DMS) based on diamond-like crystals doped with 3d iron-group impurities with ferromagnetic ordering of the spins of 3d ions are promising materials for spintronics. Previously Danilov et al. [1, 2] demonstrated the possibility of the laser synthesis of 30 - 100 nm in thickness epitaxial layers of DMS GaSb:Mn and InSb:Mn with the Curie temperature T_C above 500 K and of InAs:Mn with T_C no lower than 77 K. DMS based on elementary Ge and Si semiconductors doped with 3d-impurities are of particular interest for spintronics, due to compatibility with the most wide-spread silicon solid electronics. Epitaxial Ge:Mn layers with 5% manganese were obtained by Park et al by the molecular beam epitaxy method [3]. The ferromagnetism was manifested in nonlinear and hysteresis dependence of the magnetization and anomalous Hall effect (AHE) on the magnetic field up to a temperature 116 K. In [4] the ferromagnetism in thin silicon layers with 0.8 at % of the ion implanted manganese was observed up to temperature 400 K.

In the present work we report first successful application of laser deposition for synthesis of 50 - 100 nm Ge and Si layers, supersaturated with manganese or iron. The iron and manganese concentrations were up 10 - 15 at % and the samples manifested considerably more high-temperature ferromagnetic spin ordering than previously reported. The ferromagnetism of films has been confirmed by the observation AHE, ferromagnetic resonance (FMR) and Magnitooptic Kerr effect (MOKE) at temperatures 77 - 500 K.

Iron and manganese as dopants were chosen on the basis of our previous investigation of regularities in recharge levels of 3d-atoms in diamond-like semiconductors [5]. Analysis of the similar regularities for the 3-d impurities in the A^3B^5 semiconductors shows, that GaSb, InSb and InAs are favorably over, e.g., GaAs as a base of the DMS, due to a lower electron work function in the first case [2, 3]. Manganese substituted for Ga or In in these compounds has a high spin state favorable for the ferromagnetism. It also has high acceptor activity even at low temperatures and is efficient source of holes for a valence band of a crystal. It is important for the Ruderman-Kittel-Kasuya-Yosida (RKKY) ferromagnetic exchange interaction between magnetic ions. According to the family of levels for 3d substitution ions in Ge and Si, the most preferable situation for maximal spin $S = 5/2$ and $S = 4$ and ferromagnetic spin ordering occurs for iron and manganese.

2. Results and discussion

Ge:Mn, Si:Mn, and Si:Fe layers were deposited on a single crystal wafers of semi-insulating gallium arsenide or sapphire by laser sputtering. The substrate was heated to 200 - 480 ºC. A pulsed AYG:Nd laser was used for sputtering of the semiconductor and metallic (Mn or Fe) targets. The laser radiation wavelength is 1.06 μm, a pulse energy is 0.2 J, and a pulse duration is 12 ns. The DMS layer thickness was ranged from 30 to 200 nm. The content of 3d-impurity was controlled by the x-ray spectrum analysis with the electron excitation. A He-Ne laser with a wavelength 0.63 μm was used for the MOKE investigations at 293 K. The FMR was studied at a frequency of 9.3 GHz in the temperature range 77-500 K for various orientations of the external magnetic field. Field value was up to 0.66 T. The differential Hall effect was measured at 77-293 K in a weak alternating magnetic field with amplitude of $5\cdot10^{-3}$ T and a frequency of 50 Hz in combination with a magnetic field slowly varying within ±0.4 T, both fields are perpendicularly oriented to a sample plane.

Both MOKE, and AHE, and FMR measurements have demonstrated the ferromagnetic behavior of Si:Mn layers on GaAs substrate at room temperature. The films of Ge:Mn on GaAs substrate revealed the ferromagnetism in AHE and FMR. In these two DMS the introduction of a 3d-impurity leads to significantly high hole conductivity. The hysteresis of AHE in Ge:Mn, Si:Mn and Si:Fe at 77 K, non-linear dependencies of Hall effect at room temperature was observed in magnitotransport measurements. The concentration of holes p and their mobility μ at 293 K was determined by measurements of resistivity ρ and Hall factor at the maximal field. We obtained the following data: for Ge:Mn (with the x-ray spectral content of manganese N_{Mn} = 13 at %) $p = 6.6\cdot10^{19}$ cm^{-3}, μ = 23 cm^2/V·s, $\rho = 0.004$ Ω·cm, for Si:Mn with N_{Mn} = 15 at %, $p = 7.5\cdot10^{20}$ cm^{-3}, μ = 33 cm^2/V·s, $\rho = 0.00025$ Ω·cm. Evidently in the both cases manganese exhibits a surprising high electric activity as a shallow acceptor with an inserted concentration of holes up to 10 % of Mn content. The acceptor action with a low activation energy is consistent with the expected behavior of manganese in substitution site of Ge or Si. Hence, embedding of a 3d-impurity in a crystal lattice during laser deposition of nanometer layers is significantly different from that in the case of a bulk crystal doping. Previously [6] it was established that in the case of silicon matrix such impurities is mainly dissolved in the interstitial crystal positions with limiting solubility $\approx10^{16}$cm^{-3} and basically shows the donor properties. In our Si:Mn films the concentration of holes ($7.5\cdot10^{20}$ cm^{-3}) is particularly great, and their mobility is one and half time higher than in Ge:Mn films where p is less by one order of value. In both cases the mobility of current carriers is much higher than that in metals.

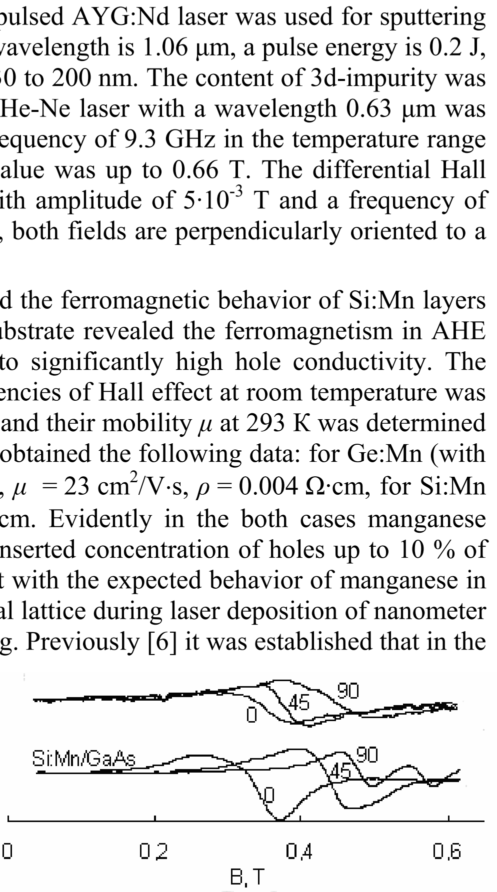

Fig.1 The first derivatives of FMR absorption spectra for Si:Mn 50 nm thick films and for Ge:Mn 75 nm thick film at room temperature. The numbers above the lines are the angles (in degrees) between the sample plane and the magnetic field.

The observed strong anisotropy of the spectra FMR for Ge:Mn and Si:Mn films (Fig.1) indicates the presence of an inner magnetic field comparable with external magnetic field and caused by geometry of a flat sample. The spectra for normal orientation are shown in Fig. 2 for the different temperatures. The single line with a smooth temperature transition (up to ≈ 420 K) from FMR to electronic paramagnetic resonance was observed in the case of Ge:Mn. Such transition is a consequence of the thermal destruction of spin ordering of manganese magnetic ions. As well as in the case of GaSb:Mn the shift FMR field is non-monotonic with the temperature. It has a maximum at 256 K for the case of Ge:Mn. The line amplitude falls down below 256 K.

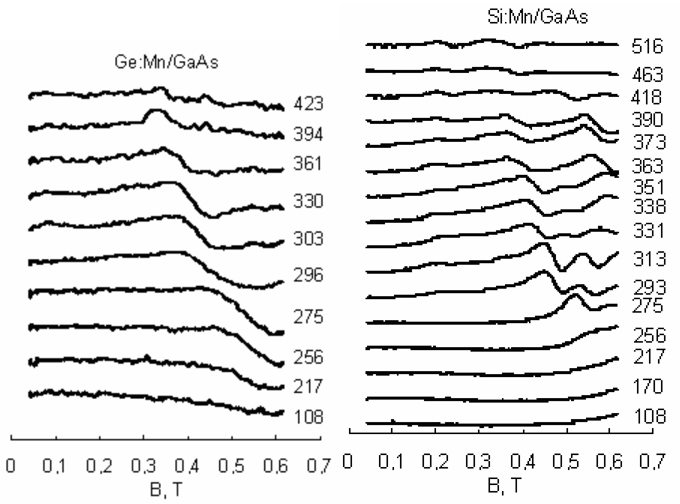

Fig.2 The FMR spectra of the samples Si:Mn and Ge:Mn (the same as in Fig.1), oriented perpendicularly to the magnetic field for different temperatures. The numbers at the right are the temperature in K.

In the case of the Si:Mn the FMR spectrum consists of two or more resonant peaks. It is not a case of a spin waves resonance spectrum, because in the case of the spin wave resonance the amplitudes of the lines have the opposite order with the increase of the external field. The variation of the content of manganese and the thickness of a film lead to the change of the ratio of amplitudes of peaks, but do not change their position. Only one weak ferromagnetic manganese silicide with the Curie point 29 K is known [7, 8] and metal Mn is antiferromagnet. So, most likely, the observable FMR peaks in our Si:Mn samples are caused by the presence of domain structure in DMS films. The FMR of Si:Mn layers take place up to temperatures ≈ 500 K. As in the case of Ge:Mn, there is a temperature shift of FMR lines to smaller fields and a reduction of their intensity. Supposing that each Mn ion has spin 5/2, one can calculate the manganese concentration (N_{Mn}) using the data in Fig. 2, as it had been done in [2]. So we estimate the concentration of magnetic ions of manganese as $2.6{\cdot}10^{21}$ cm^{-3} or 5.9 at % in relation to germanium in Ge:Mn at 256 K. That is that 45 % of Mn atoms show the magnetic activity at 293 K. Similar estimations for Si:Mn give N_{Mn}=$1.8{\cdot}10^{21}$ cm^{-3} for the first FMR peak and $2.8{\cdot}10^{21}$ cm^{-3} - for the second one. The part of magnetically active manganese (≈ 9 at %) is much higher, than in layers Ge:Mn and constitutes 3/5 from x-ray spectral contents of this impurity (15 at %). The shift of FMR lines to the right with a decrease of the temperature shows, that, practically all manganese is probably magnetically active (Fig. 2).

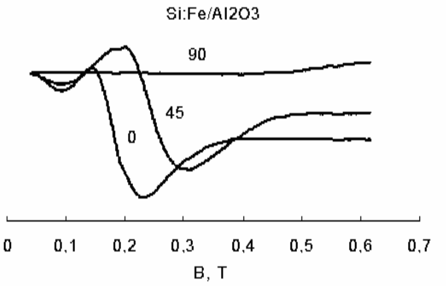

Fig.3 The angle dependencies of FMR for the Si:Fe/Al_2O_3 films at 77 K. The numbers above the curves are the angles (in degrees) between the sample plane and the direction of the magnetic field

Promising results were obtained for Ge:Fe and Si:Fe layers deposited on single crystal sapphire substrates. AHE and FMR are pronounced at 77 K, the FMR of Si:Fe was observed up to 220 K. The ferromagnetism of Si:Fe layers on the same substrates is stronger than that for Ge:Fe layers. The amplitude of FMR spectrum for Si:Fe/Al_2O_3 was five times more intensive, than that for Ge:Mn/Al_2O_3 at thickness about 50 nanometers. Figure 3 shows the strong anisotropy of the spectrum for Si:Fe/Al_2O_3 at 77K. The concentration of magnetically active iron atoms in silicon is near 10^{21} cm^{-3} at 77 K. The layers have a high hole conductivity, the resistivity of Si:Fe layers does not exceed the value 10^{-3} Ω·cm at 77 and 300 K.

Thus, we demonstrated the possibility of laser synthesis of thin layers of elementary semiconductors supersaturated by 3d-impurities Ge:Mn and Si:Mn with the Curie point much higher than room temperature as well as Ge:Fe and Si:Fe with the Curie point not below 77 K and 220 K, respectively. In the nonequilibrium thermodynamics terms laser formation of the supersaturated solid solution of the 3d-impurity in Ge and Si elementary semiconductors is no worse than the ion beam doping used in [4] to form Si:Mn ferromagnetic layers.

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