Hydrogen Control of Ferromagnetism in a Dilute Magnetic Semiconductor

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We show that upon exposure to a remote dc hydrogen plasma, the magnetic and electronic properties of the dilute magnetic semiconductor $Ga_{1-x}Mn_xAs$ change qualitatively. While the as-grown $Ga_{1-x}Mn_xAs$ thin films are ferromagnetic at temperatures $T \lesssim 70$ K, the samples are found to be paramagnetic after the hydrogenation, with a Brillouin-type magnetization curve even at $T = 2$ K. Comparing magnetization and electronic transport measurements, we conclude that the density of free holes p is significantly reduced by the plasma process, while the density of Mn magnetic moments does not change.

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Today's microelectronics relies on electronic charges to process and store information. Recently, the advantages of using electronic spins for such purposes have been realized, and a new class of semiconductor magnetoelectronic or spintronic devices is emerging, such as spin light emitting diodes [1,2] or spin transistors [3]. Moreover, spintronic devices offer a solid state approach to quantum information processing [4]. Dilute magnetic semiconductors (DMS), which combine magnetic ordering with the versatile properties of semiconductors [5,6], are considered to be key ingredients of such devices.

$Ga_{1-x}Mn_xAs$, which we investigate here, is a prototype III-V DMS. It is well established that the incorporation of Mn atoms on substitutional Ga sites yields not only localized magnetic moments, but also itinerant holes, as Mn is a shallow acceptor in GaAs [7]. Both the localized moments and the holes are crucial for the ferromagnetic properties of the DMS, as the holes are thought to mediate the exchange interaction between the localized moments [7,8]. Accordingly, a particular benefit of DMS materials such as $Ga_{1-x}Mn_xAs$ is the possibility to control their ferromagnetic properties by tuning the density of mobile charge carriers [9]. We show that the incorporation of hydrogen electrically passivates the Mn acceptors and removes the holes crucial to the itinerant ferromagnetism. Thus, such a hydrogenation allows us to control or pattern the ferromagnetic properties of the magnetic semiconductor in a nonvolatile way.

The $Ga_{1-x}Mn_xAs$ thin films studied were deposited on (100)-oriented, semi-insulating GaAs wafers using low-temperature molecular beam epitaxy [10]. As usual for $Ga_{1-x}Mn_xAs$ films, the nominal Mn content x was determined from high-resolution x-ray diffraction (XRD) assuming a lattice constant of 0.598 nm for (the hypothetical) cubic MnAs and the validity of Vegard's law [7,10]. The samples were deuterated using a remote dc plasma at a pressure of 0.3 mbar for 168 h [11]. During the plasma process, the samples were heated to 170 °C, well below the growth temperature of 250 °C. Deuterium was chosen as the hydrogen isotope in this study due to its lower natural abundance, which allows background-free chemical analyses. All $Ga_{1-x}Mn_xAs$ samples investigated, with Mn contents between $x = 0.037$ and $x = 0.051$ and therefore somewhat different ferromagnetic properties in the as-grown state, have shown nearly identical behavior upon deuteration. Here, we focus on one particular sample, which consists of a 300 nm thick, undoped GaAs high-temperature buffer grown at $T = 585$ °C, followed by a 200 nm thick, undoped GaAs low-temperature buffer layer and the 320 nm thick $Ga_{0.963}Mn_{0.037}As$ layer, both deposited at $T = 250$ °C.

The deuterium concentration in the samples after the plasma treatment was studied by secondary ion mass spectroscopy (SIMS). The profiles were taken with a Cameca 5 spectrometer, using Cs as primary ions and detecting Mn as a positive and D as a negative ion. The depth profiles obtained for the sample with $x = 0.037$ are shown in Fig. 1. While the D concentration was determined quantitatively using an appropriate calibration standard, no such standard was available for Mn in GaAs. Therefore, the Mn profile shown has been normalized to the nominal content determined by XRD. However, the Mn concentration estimated from SIMS agrees with these data to better than a factor of 2, which is the typical SIMS error. Figure 1 shows that within experimental uncertainty, the density of D incorporated in the $Ga_{1-x}Mn_xAs$ thin film is identical to the Mn concentration. The same is found in the sample with $x = 0.051$. The high concentration of deuterium in the buffer layers and at the interfaces indicates the decoration of the

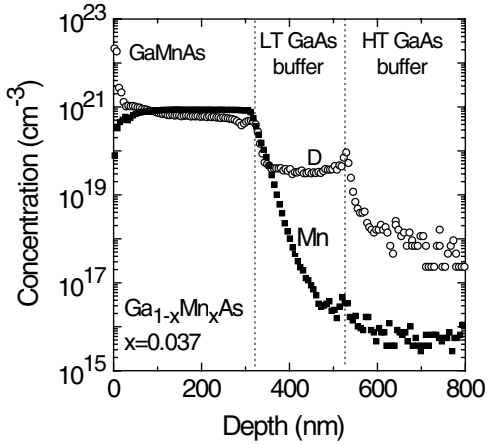

FIG. 1. Secondary ion mass spectroscopy (SIMS) depth profiles of deuterated $Ga_{0.963}Mn_{0.037}As$. Within the experimental uncertainty, D is incorporated into GaMnAs with the same concentration as Mn.

large number of structural defects [12] in these parts of the sample with deuterium. The tails originating at the interfaces are caused by forward implantation during SIMS and are a typical SIMS artifact.

Deuterium incorporation at this concentration drastically changes the magnetic properties of $Ga_{1-x}Mn_xAs$ as shown in Fig. 2. In the as-grown films, the magnetization $M(H)$ as a function of the externally applied magnetic field H exhibits the hysteresis characteristic for ferromagnetism below the Curie temperature, which is $T_C \approx 70$ K for $x = 0.037$. In contrast, the ferromagnetism completely vanishes in the deuterated samples and is replaced by a paramagnetic magnetization, as shown in Fig. 2(b).

The effect of hydrogen on nonmagnetic semiconductors has been studied extensively. It has been found that hydrogen or deuterium form complexes with many defects and dopants, and thereby passivate their electronic properties. In particular, this passivation was determined to work quantitatively with acceptors in a variety of semiconductors, including Be, Mg, or Zn in GaAs [13,14]. Since the transition metal atoms Mn and Zn have nearly the same size, the formation of the corresponding D-acceptor complex should also be possible sterically in $Ga_{1-x}Mn_xAs$. Using Fourier-transform infrared absorption spectroscopy, virtually identical vibrational modes characteristic for acceptor passivation were, in fact, observed in deuterated GaAs:Mg, GaAs:Zn, and $Ga_{1-x}Mn_xAs$ [15,16]. Indeed, our investigation of the electronic properties indicates that electrically inactive complexes are also formed upon the deuteration of $Ga_{1-x}Mn_xAs$. In the as-grown sample, the metallic conductivity typical for ferromagnetic $Ga_{1-x}Mn_xAs$ is found (Fig. 3), with the characteristic conductivity minimum near T_C conventionally attributed to spin-dependent scattering [17]. Upon deuteration, the low-temperature dark conductivity is reduced by more than 9 orders of magnitude, and at high temperatures, the typical

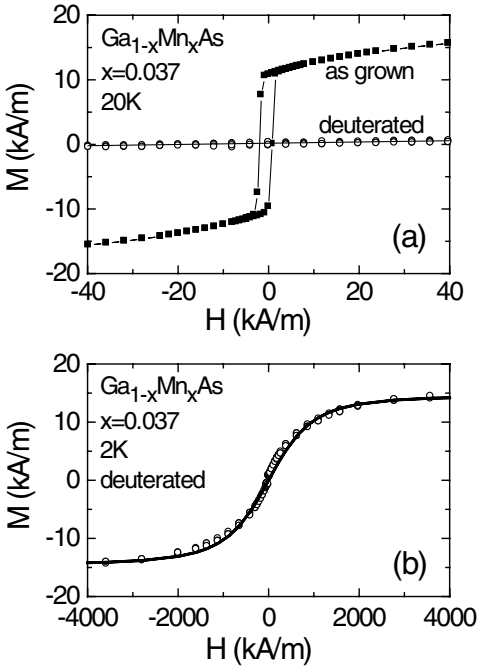

FIG. 2. (a) Comparison of the dc magnetization $M(H)$ loops of $Ga_{0.963}Mn_{0.037}As$ in the as-grown state (full squares) and after deuteration (open circles) at $T = 20$ K with the external magnetic field in the plane of the thin film. The ferromagnetic hysteresis present in the as-grown film vanishes after the deuteration. (b) Magnetization of the deuterated sample at $T = 2$ K and for a much broader range of magnetic fields H (open circles). The data are best described by a Brillouin-type magnetization, with $g = 2$ and $J = 5/2$ (thick straight line) expected for Mn atoms with a $3d^5$ configuration (Mn in its oxidation state 2+).

thermally activated behavior of a semiconductor is observed. Room temperature Hall experiments show that the samples are p-type after deuteration. We have not observed any evidence for anomalous Hall effect contributions [7,18] to the Hall resistance in the deuterated samples within the magnetic field range $|H| \leq 1400$ kA/m accessible in our setup. Therefore, we have used the classical Hall formula $\rho_{\mathrm{Hall}} = B/(pe)$ to evaluate our measurements, with the magnetic induction $B = \mu_0 H$ applied perpendicular to the film, the vacuum permeability μ_0, and the charge of the electron e, yielding $5 \times 10^{17} \leq p \leq 5 \times 10^{19}$ cm^{-3} depending on the exact plasma exposure times. At the same time, the activation energy E_a of the dark conductivity is about $E_a \approx (50 \pm 20)$ meV. Considering the known depth of the Mn acceptor level in GaAs at around 113 meV above the valence band [19], this activation energy indicates that some Mn acceptors still remain electrically active and that defects that would lead to a compensation do not influence the charge carrier statistics significantly after the deuteration. Hall mobilities of 5–10 cm^2/V s are found at room temperature and are attributed to dipolar scattering at the Mn-D complexes formed in very large concentration.

The experimental evidence presented above shows that the Mn acceptors can be deuterated quantitatively, leading to a reduction of the hole density by many orders of magnitude. Therefore, one of the two crucial ingredients for the ferromagnetic properties of $Ga_{1-x}Mn_xAs$ films, the charge carrier-mediated exchange interaction between the localized Mn magnetic moments, is removed and the ferromagnetism is destroyed. If a proof for the carrier mediation of the ferromagnetism in $Ga_{1-x}Mn_xAs$ would still be required, the results presented here would provide such definitive evidence. However, the localized Mn magnetic moments should still be present. As shown in Fig. 2(b), the magnetization of deuterated $Ga_{0.963}Mn_{0.037}As$ exhibits the paramagnetic, Brillouin-type magnetization $M(H) = M_{\text{sat}}B_J(g\mu_B\mu_0 HJ/k_BT)$ expected in this case, where M_{sat} is the saturation magnetization, B_J is the Brillouin function, μ_B is the Bohr magneton, g is the g value, T is the temperature, k_B is the Boltzmann constant, and J is the total angular momentum quantum number. The best fit to the experimental data is obtained using the Brillouin function for $g = 2$ and $J = 5/2$, yielding the thick full line in Fig. 2(b). This can be directly understood from the electron configuration of Mn in GaAs, shown in the inset of Fig. 3 both in the as-grown and in the deuterated state. In this simple electron counting picture, a pure $3d^5$ configuration with $g \approx 2$ and $J = 5/2$ [20], corresponding to Mn in its oxidation state $2+$, is expected after deuteration, in agreement with the magnetization experiments. However, $M_{\text{sat}} \approx 15$ kA/m must be assumed in the calculations, which is more than a factor of 2 smaller than $M_{\text{sat}} = xN_0g\mu_BJ \approx 38$ kA/m expected for the nominal Mn content x determined from XRD, with the density $N_0 = 2.21 \times 10^{22}$ cm^{-3} of cation sites in GaAs. Similar discrepancies between the experimentally observed saturation magnetization and the one expected from the nominal Mn content have been reported by others [8,17,21], and have been linked to uncertainties in the determination of the Mn content from XRD [22] or the formation of antiferromagnetically coupled Mn-Mn pairs [12,23]. A Brillouin function with lower values of g and J, which would make M_{sat} compatible with the nominal Mn concentration from XRD, would, on the other hand, not be able to describe the magnetization at low magnetic fields correctly. Nevertheless, it is important to stress that the saturation magnetizations of the as-grown, ferromagnetic film and of the paramagnetic film after deuteration in Fig. 2 are comparable to within 20%. Thus, the density of localized Mn moments is not significantly changed by the deuteration, and the loss of ferromagnetism can be attributed unambiguously to the effective reduction of the hole concentration.

Simple annealing of $Ga_{1-x}Mn_xAs$ at temperatures around or somewhat below the growth temperature can also affect the magnetic properties. Both a quenching of the ferromagnetic ordering [21] and an improvement of the ferromagnetic properties [24] were reported after various annealing steps. Using spin wave resonance measurements, which are a very sensitive probe of the exchange interaction between the Mn moments [25], we found that annealing our samples at 170 °C in vacuum for 168 h does lead to a very small increase of the ferromagnetic exchange as expected from Ref. [24], in complete contrast to what is observed after exposure of $Ga_{1-x}Mn_xAs$ to the deuterium plasma at this temperature. Therefore, the effects discussed above are clearly due to the incorporation of deuterium, and not to an annealing during the plasma treatment.

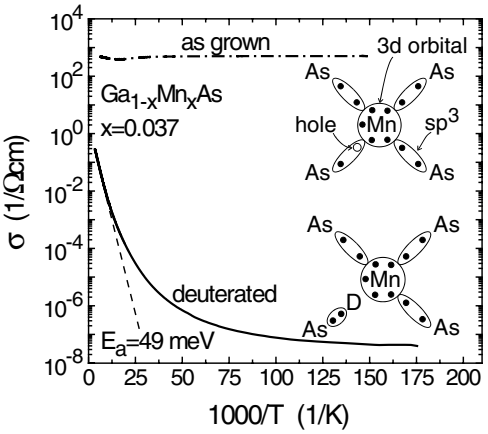

FIG. 3. Temperature dependence of the dark conductivity of $Ga_{0.963}Mn_{0.037}As$ before and after deuteration. The as-grown film exhibits a nearly temperature-independent, metallic conductivity (dash-dotted line). In contrast, deuterated $Ga_{1-x}Mn_xAs$ is semiconducting (full line), the dark conductivity being activated with $E_a \approx (50 \pm 20)$ meV at high temperatures (dashed line). The insets show an electron-counting picture of the Mn acceptor in GaAs, in which the valence electrons are depicted as full circles in the $4sp^3$ and $3d$ orbitals. Mn incorporated on a substitutional Ga site acts as an acceptor. An electron from the GaAs valence band is thus required to saturate all bonds, resulting in a delocalized hole not shown. Upon deuteration, all bonds are saturated without the need for valence-band electrons. This explains the drastic reduction of the density of free holes and the configuration of Mn after the deuteration.

Annealing experiments [21,24] are a first step towards an independent control of the density of itinerant holes and of Mn magnetic moments, and thus of the ferromagnetic properties of the DMS. Other approaches have been put forward, such as codoping [26], the growth of quaternary alloys like (Al,Ga,Mn)As with subsequent annealing [27], or the recrystallization of amorphous films [28]. In contrast to these methods, the hydrogenation of DMS that we discuss here is completely independent from the growth process, but nevertheless allows us to change p by several orders of magnitude without the need for a recrystallization or a treatment of radiation damages.

In summary, we have shown that deuteration changes $Ga_{1-x}Mn_xAs$ thin films from a metallic ferromagnetic

state to a semiconducting paramagnetic state. A controlled incorporation of deuterium or hydrogen, e.g., via a plasma process or by low-energy ion implantation together with appropriate masks or focused ion beams, should allow one to tune the hole density and therefore the magnetic properties both laterally as well as in the depth of the thin films. Acceptor-hydrogen complexes have been found to dissociate at temperatures well above the growth temperature of $Ga_{1-x}Mn_xAs$ [11], so that hydrogen incorporation allows a nonvolatile magnetic lithography. This new degree of freedom in the "design" of the electronic and magnetic properties of $Ga_{1-x}Mn_xAs$ enables a number of fundamental experiments into the physics of DMS and opens up new device applications. For example, the orientation of the easy magnetic axes has been predicted to strongly depend on the density of holes for a given, fixed Mn concentration [6]. A laterally structured hydrogenation might allow one to obtain magnetically heterogeneous, but structurally homogeneous thin films. The use of hydrogen to realize ferromagnet-semiconductor or ferromagnet-semiconductor-ferromagnet devices in one single $Ga_{1-x}Mn_xAs$ layer represents another intriguing possibility. The low density of defects expected at the interfaces of such structures might prove crucial for the performance of the devices, in particular concerning the efficient injection of spin-polarized carriers from the ferromagnetic into the semiconducting layer. Finally, the concept of hydrogen control of ferromagnetism is not limited to $Ga_{1-x}Mn_xAs$, but should be applicable to all other diluted magnetic semiconductors where charge carriers mediate the ferromagnetic coupling, including II-VI semiconductors such as $Zn_{1-x}Mn_xTe$: N [29].

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