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# Tuning the ferromagnetic properties of hydrogenated GaMnAs

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Hydrogenation and post-hydrogenation annealings have been used as a very efficient tool to tune the hole density over a wide range, at fixed magnetic moment concentration in thin GaMnAs layers. Reduction of the hole density resulted in strong modifications of their ferromagnetic properties. In particular, we observed in magneto-transport experiments the decrease of the Curie temperature, along with modifications of the magnetic anisotropy, a behavior predicated by the mean-field theory.

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Carrier-induced ferromagnetism in diluted magnetic semiconductors is mediated by the exchange interaction between the delocalized carriers and the magnetic ions.[1] In GaMnAs, due to the Mn acceptor character, it is thus expected, and it has been predicted[2, 3] and demonstrated,[4, 5] that the ferromagnetic properties, as the Curie temperature ( $T_C$ ), strongly depend on the hole density ( $p$ ) and the precise shape of the valence band. In particular, [2, 3] have predicted a strong influence of the carrier density on the magnetic anisotropy, leading to the re-orientation of the easy axis at low  $p$  for a given epitaxial strain.

A better understanding of the influence of the carrier density on the ferromagnetic properties would require data obtained from experiments in which the density can be tuned over a large range for a given Mn concentration. However, in GaMnAs,  $p$  is fixed, a few  $10^{20} \text{ cm}^{-3}$ , by the number of incorporated Mn ions, since they both act as magnetic moments and acceptors, even so donor defects have been shown to compensate partially the substitutional Mn atoms.[6] It is therefore difficult to separate both contributions, hole density and Mn concentration, to the ferromagnetic phase. Several techniques have been reported in GaMnAs such as co-doping with Sn donors[7] or post-growth annealing which allow the control of  $p$  for a rather fixed Mn concentration.[8] However these techniques are limited either to a single hole density or to a rather narrow range of densities (from  $5 \times 10^{19}$  to  $1 \times 10^{20} \text{ cm}^{-3}$  in the case of Ref. 8).

Having shown recently[9, 10] that hydrogen effectively neutralizes Mn in GaMnAs, we have used hydrogenation as a very efficient way to strongly reduce  $p$  by neutralizing the Mn atoms, while keeping a constant number of magnetic moments. This technique was also recently proposed and experimentally demonstrated by an independent study.[11, 12] Here, using subsequent thermal annealing, we were able to remove gradually H atoms from the neutralized GaMnAs layer and to recover the

hole density and so the ferromagnetic phase. This technique allows the fine tuning of  $p$  over a large range. In this letter we report on the dependence of GaMnAs magnetic properties on  $p$ , adjusted by means of hydrogenation. The results presented here were obtained from magneto-transport experiments.

Hydrogen has been widely used in p-doped GaAs to neutralize acceptors (A).[13] Hydrogenation is performed by exposing the sample to H or deuterium plasmas. Monoatomic H atoms diffuse into the doped layer and form electrically inactive H-A complexes. In GaMnAs, hydrogen incorporation and Mn neutralization were evidenced by secondary ion mass spectroscopy and by local vibrational mode spectroscopy respectively.[9, 11] In this study, the sample consists of a 50 nm thick  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  layer grown on (001) undoped GaAs substrates at around  $260^\circ\text{C}$ . The manganese concentration is estimated to be  $x \simeq 6 - 7\%$ . Prior to hydrogenation, the sample was annealed under nitrogen atmosphere for 1 hour at  $250^\circ\text{C}$  to strongly reduce and homogenize the concentration of highly mobile interstitial Mn atoms, insuring that the subsequent modifications of the magnetization were due to the H neutralization only (the decrease of interstitial atoms was checked using the technique presented in ref. 14). The sample was then hydrogenated during 3 h at  $130^\circ\text{C}$  using a direct exposure radio-frequency H plasma (13.56 MHz,  $80 \text{ mW.cm}^{-2}$ , 1 mbar). Also, the Hall bars were processed before hydrogenation to avoid the neutralization of the GaMnAs regions underneath the Ti/Au layers insuring good ohmicity of the contacts. Optimization of temperature and duration was done by monitoring the change of the resistance of the device before and after hydrogenation. After hydrogenation, values larger than  $40 \text{ M}\Omega$  were obtained similar to semi-insulating GaAs substrate resistance, giving an upper limit for  $p$  of  $6 \times 10^{16} \text{ cm}^{-3}$  assuming a mobility of  $5 \text{ cm}^2/\text{V/s}$  (from Ref. 12) This indicates that H atoms are highly mobile in the GaMnAs layer and efficiently passivate Mn atoms, even at such low temperature. Higher hydrogenation temperatures, above  $170^\circ\text{C}$ , resulted, for the same exposure times, to lower device resistance, so lower H incorporation. Last, a reference sample was ob-

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tained by covering it with a GaAs substrate during exposure to the plasma, to prevent hydrogenation.

The formation of Mn-H complexes upon hydrogenation resulted in a strong increase of the resistivity, due to the large reduction of the hole density. Thermal annealing has been used in hydrogenated p-doped GaAs to break the A-H complexes, to remove the H atoms from the layer, resulting in the re-increase of the hole density. In GaMnAs, however, the maximum annealing temperature is limited by the tendency of GaMnAs to deteriorate at temperatures above 300°C. Nevertheless our experiment indicated that temperatures as low as 190°C are sufficient to get large removal of H atoms within a few hours. Figure 1 shows the resistivity evolution with annealing time for both hydrogenated and reference samples, monitored *in situ* during the annealing under nitrogen atmosphere (annealings under vacuum gave similar results). The reference sample exhibits almost no change as Mn interstitial atoms play a minor role, since they were stabilized during the pre-annealing, giving a first indication that the magnetic moment concentration remains constant during the post-hydrogenation annealing. On the opposite, the hydrogenated one shows a very large decrease of the resistivity, by more than two orders of magnitude. After ~3000 min, the resistivity reaches the value measured for the reference sample within 10 % (the usual deviation for these Hall bar devices), indicating i) that most of the H atoms left the GaMnAs layer and ii) that the hole density recovers its original value (an increase of the mobility is quite improbable).

Post-hydrogenation annealings offer a very practical and non-destructive way to precisely tune the hole density, over a large range by adjusting the annealing time. At this point, we would like to underline the difficulty to determine accurately the hole density, because of the anomalous Hall effect contribution. So at the present, we do not have such information. High magnetic fields measurements[15] or Raman spectroscopy[16] may solve this issue. However, this determination could be further hampered at low densities, when crossing the metal-insulator transition.

Change of the carrier density induced large changes in the magnetic properties of GaMnAs. Here, we investigated them through the temperature dependence of the sheet resistivity and the anomalous Hall effect, which both require sufficient carrier density. In particular, this type of experiments does not give access to the regime where the ferromagnetism disappears,[10, 11] since it occurs at vanishing  $p$ , where transport measurements are not applicable. Magnetic measurements, which require great care to avoid parasitic signals, especially for such thin layers, will be presented elsewhere. Several pieces of the same sample, respectively labeled a, b, c, d and e, were annealed for different post-hydrogenation annealing times, 11, 13, 19, 24 and 3000 min, respectively, thus corresponding to different hole densities. The temperature dependence of the resistivity is presented in Fig. 2 along with the one measured for the reference sample.

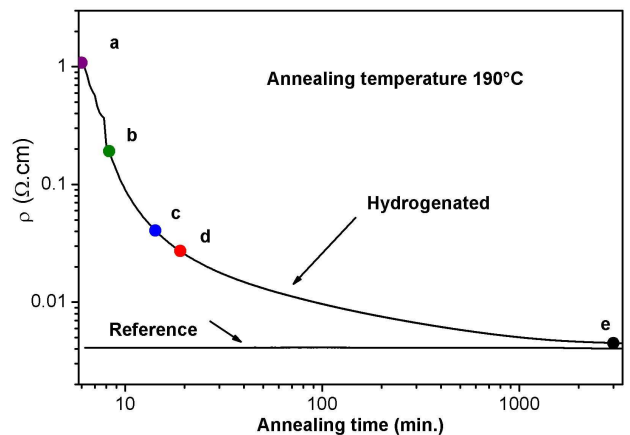


FIG. 1: (Color online). Experimental temporal evolution of the resistivity upon annealing of the hydrogenated a, b, c, d and e and reference pieces, monitored during the annealing at 190°C. The annealing times and resistivities corresponding to the hydrogenated samples reported in this study are represented by the dots.

For high  $p$  (annealings c, d, e and the reference sample), the curves show a clear maximum, followed by a moderate decrease at lower temperature, suggesting a metallic behavior. At lower  $p$  (annealings a and b), the curves exhibit a bump as the resistivity strongly increases at low temperature, indicating an insulating character. These peaks or bumps correspond approximatively to  $T_C$ . [1] As expected, post-hydrogenation annealings resulted in increasing  $T_C$  with increasing annealing time, since the hole density is progressively restored when H atoms leave the GaMnAs layer. After 11 and 13 min, a bump is seen around 25 K, while longer annealings yield, respectively  $T_C = 58$  and 80 K after 19 and 24 min. After 3000 min annealing, the Curie temperature is identical to the one measured for the reference sample,  $T_C = 130$  K, indicating complete recovery of the ferromagnetic phase observed prior to hydrogenation.

We now turn to the magnetic anisotropy in these samples, since it is expected to strongly depend on  $p$ . Calculations within the mean-field theory[2, 3] have indeed predicted that the magnetic anisotropy in GaMnAs mostly stems from the anisotropy of the carrier-mediated exchange interaction. In particular, the in-plane easy axis, usually observed in GaMnAs layers grown on GaAs, arise from the compressive epitaxial strain, whereas layers under tensile strains generally exhibit an out-of-plane magnetic anisotropy. However recent experiments[8, 17] have shown that for low values of  $p$  and temperature a reorientation of the easy axis, from in-plane to out-of-plane in these cases, occurs, a behavior consistent with mean-field predictions,[2, 3] and related to the filling of the different valence sub-bands. Post-hydrogenation annealings offer a unique opportunity to investigate the modification of the anisotropy upon  $p$  at fixed magnetic moment concentration. Fig. 3 shows the Hall resistivity  $\rho_{Hall}$ , mea-

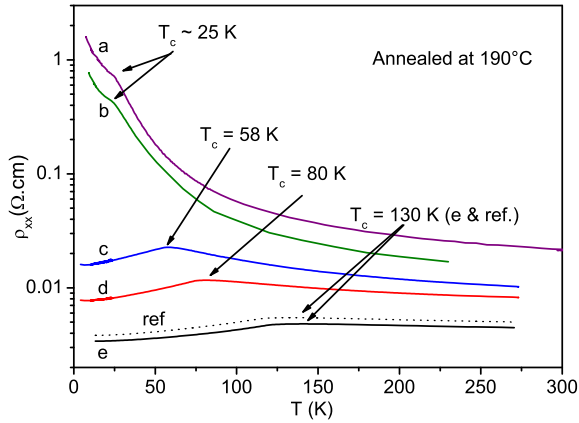


FIG. 2: (Color online). Longitudinal resistivity ( $\rho_{xx}$ ) vs. temperature for post-hydrogenation annealed pieces a, b, c, d, e and the reference sample (dotted line).  $T_C$  is estimated from the resistivity maximum.

sured at 4 K, for the annealed and reference samples. In GaMnAs, the Hall effect is dominated by the anomalous Hall effect which is proportional to the sample magnetization perpendicular to the growth axis.[1] Note that we did not plot  $\rho_{Hall}/\rho_{xx}^\gamma$  with  $\gamma = 1$  as usually found in the literature as the  $p$  dependence of the different spin scattering mechanisms is rather complex.[18] However, this choice has little impact on the shape of the curves in Fig. 3. Sample e, completely depassivated, exhibits, as expected, an almost identical behavior as the reference sample, namely a progressive increase of the Hall resistivity and a saturation at around 0.4 T, which corresponds to the progressive alignment of the magnetization along the hard axis, in this case parallel to the growth axis [001]. Sample b shows an opposite behavior since a hysteresis cycle is seen, indicating that [001] is now an easy axis. Samples c and d exhibit an intermediate regime. Although no clear hysteresis cycle is observed, sample c magnetization first increases progressively and then rapidly saturates at  $\approx 0.15$  T, suggesting that [001] is a less easy axis. Sample d magnetization evolves quite smoothly and saturates at 0.3 T, indicating that [001] is no longer an easy axis. A smaller saturation field however denotes a weaker magnetic anisotropy compared to sample e. Such observations confirm that the magnetic anisotropy is strongly dependent on the hole density. In particular, as predicted by mean-field theories,[2, 3] the anisotropy field is reduced when the hole density is lowered (corresponding to shorter post-hydrogenation annealing time), even leading at lower  $p$  to an easy axis parallel to the growth axis [001].

In conclusion, we have devised a simple technique based on post-hydrogenation annealings of GaMnAs layers to finely tune the hole density, over a large range, at fixed magnetic moment concentration. We have shown, through magneto-transport measurements its ability to

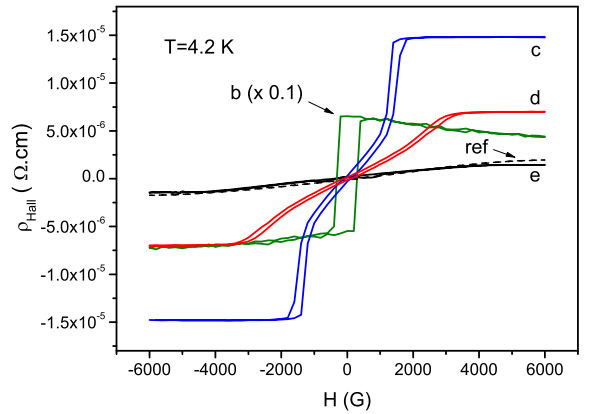


FIGURE 3

FIG. 3: (Color online). Hall resistivity vs magnetic field measured for samples b to e and ref (dotted line). Curves c and d have been corrected for a small planar Hall effect contribution.

investigate in detail the mechanisms responsible for the ferromagnetic phase in this compound, especially the strong dependence of the magnetic anisotropy on the hole density, a specific property of these systems. It should be of great help to assess the validity of the theoretical models, in particular if going beyond the mean-field theory is required or not.

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