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Enhanced annealing effect in an oxygen atmosphere on $Ga_{1-x}Mn_xAs$

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We report on *in situ* resistivity measurements on $Ga_{1-x}Mn_xAs$ during post-growth annealing in different atmospheres. A drop in the resistivity is observed when the $Ga_{1-x}Mn_xAs$ is exposed to oxygen, which indicates that the passivation of Mn interstitials (Mn_I) at the free surface occurs through oxidation. The presence of oxygen can therefore be an important annealing condition for the optimization of $Ga_{1-x}Mn_xAs$ thin films, all the more since the oxidation appears to be limited to the sample surface. Annealing in an oxygen-free atmosphere leads to an increase in the resistivity indicating a second annealing mechanism besides the outdiffusion of Mn_I. According to our magnetization and Hall effect data, this mechanism reduces the amount of magnetically and electrically active Mn atoms. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1886912]

The combination of ferromagnetism with the versatile semiconducting properties in III–V ferromagnetic semiconductors such as $Ga_{1-x}Mn_xAs$ makes them promising for future spintronics applications, in which the spin degree of freedom is used to process and transfer information. The amount of Mn, that has to be incorporated to obtain ferromagnetic $Ga_{1-x}Mn_xAs$ epilayers, is far above the equilibrium solubility limit. Therefore these films have to be grown at low temperatures using molecular beam epitaxy (MBE).[1] When Mn ions are incorporated into GaAs, they do not only introduce magnetic moments but also act as acceptors, providing holes that mediate the interaction between the localized Mn spins. Obtaining higher values for the Curie temperature T_C is therefore not only a matter of increasing the Mn content, but also of achieving a higher free carrier density. The low growth temperatures, however, lead to a high density of As antisite defects (As_{Ga}) and Mn interstitials (Mn_I). It was shown through ion channeling experiments by Yu *et al.* that a significant portion of the incorporated Mn atoms indeed occupies interstitial positions.[2] Both types of defects act as double donors,[3–5] and therefore compensate a fraction of the holes generated by the substitutional Mn_{Ga} acceptor. Moreover, Mn_I tends to couple antiferromagnetically to Mn_{Ga},[6] thus reducing the total magnetic moment. Several authors have reported an enhancement of the hole concentration and T_C upon aftergrowth annealing at temperatures close to the growth temperature.[7–14] The highest T_c values so far were obtained for annealing temperatures T_A just below the growth temperature,[11,14] while long annealing times and higher temperatures result in a reduction of T_C.[7–10,15] The optimization of T_C can be done in a controlled way by monitoring the resistance while annealing,[11] as the high temperature resistivity is correlated with the hole concentration, and therefore with T_C. Yu *et al.* showed strong evidence that this increase of T_C is related to the removal of Mn_I atoms,[2] while Edmonds *et al.* recently identified the underlying mechanism with the outdiffusion of the highly mobile Mn_I to the free surface.[16] It was already suggested by Edmonds *et al.* that at the surface the interstitial Mn atoms may be passivated by oxidation.[16] This mechanism is supported by the capping-induced suppression of the annealing effects.[13,17] In this letter we present evidence that the presence of oxygen is an important parameter for the optimization of T_C through annealing, indicating that the passivation of Mn_I can indeed occur through oxidation.

$Ga_{1-x}Mn_xAs$ films with various Mn contents ($0.03 \leqslant x \leqslant 0.08$) were deposited by standard low-temperature molecular beam epitaxy on semi-insulating epiready (001) GaAs substrates. The growth was performed with a nearly stoichiometric As_2 flux at temperatures typically ≈ 15 °C below the Mn segregation limit, on a 100 nm high-temperature GaAs buffer layer grown under standard conditions, followed by a low temperature GaAs buffer of a similar thickness. The growth was monitored *in situ* by reflection high energy electron diffraction (RHEED), which showed a clear (1×2) reconstruction. The structural quality and the sample thickness of about 40 nm were checked with XRD measurements. Part of the wafer was then chemically etched into Hall bars using photolithography. A small variation of about 3% in the room temperature resistivity was observed in samples that were taken from the same wafer. Post-growth annealing was performed in a tube furnace, which allows a well-controlled atmosphere, consisting of vacuum or a specific gas, for the annealing procedure. The resistance was measured *in situ* in a four probe configuration. Magnetization measurements were performed with vibrating sample magnetometer (VSM) on unprocessed samples with a typical size ~ 30 mm^2.

To investigate the role of oxygen in the annealing process, we have subjected the samples to an aftergrowth annealing procedure in which the atmosphere was initially oxygen-free and after a well defined annealing time the epilayers were exposed to oxygen. To ensure the oxygen-free initial atmosphere, the quartz tube containing the sample was pumped to a vacuum of the order of 10^{-6} mbar, flushed out and filled with forming gas consisting of 99% N_2 gas and 1% H_2 gas. The tube was then sealed, while filled with forming gas at a slight overpressure (≈ 0.1 bar). Within about 20 min the annealing temperature is stabilized with little overshoot

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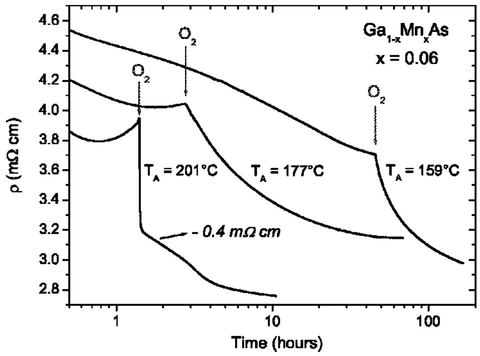

FIG. 1. Resistivity vs annealing time for 40 nm thick $Ga_{1-x}Mn_xAs$ ($x=0.06$) films at 159, 177, and 201 °C, measured in a four probe configuration. The annealing is initially performed in a forming gas atmosphere ($N_2+1\% H_2$). The arrows indicate when the samples were exposed to oxygen. The curve at 201 °C is shifted by −0.4 mΩ cm for clarity.

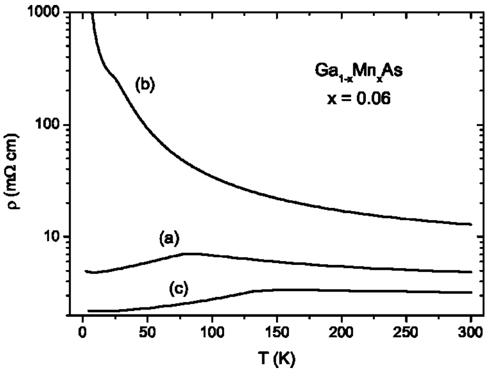

FIG. 2. Temperature dependence of the resistivity of $Ga_{1-x}Mn_xAs$ ($x=0.06$) films (a) as-grown, (b) after annealing with only forming gas (198 °C, 16 h), (c) after annealing in an oxygen atmosphere (190 °C, 70 h).

($\leqslant 1$ °C). After a well-controlled time, the tube containing the sample is exposed to a gentle O_2 gas flow, typically for 5–10 min, maintaining a constant temperature and ensuring an oxygen pressure of the order of 1 bar. During this entire procedure the resistance is continuously monitored. Figure 1 shows the resistivity as a function of time for $Ga_{1-x}Mn_xAs$ ($x=0.06$) at 159, 177, and 201 °C. The resistivity initially decreases with a rate that diminishes with time (note that the time in Fig. 1 is plotted on a logarithmic scale), and then rises again for $T_A=177$ and 201 °C, which will be discussed later. Upon exposure to oxygen a sudden resistivity drop occurs, which is very sharp for $T_A=201$ °C, and shows diffusion-like behavior similar to that reported by Edmonds *et al.*[11,16] A similar drop in resistivity occurs when N_2 gas is used as initial atmosphere or for samples with a different Mn content. These results clearly show that the presence of oxygen enhances the resistivity reduction upon annealing, which corroborates the migration of hole-compensating interstitials to the free surface during the annealing process,[16] where they are passivated through oxidation. This reduction of compensating defects results in the observed increase in hole density and conductivity. The $Ga_{1-x}Mn_xAs$ epilayer itself does not appear to suffer from oxidation, since this would lead to an increase in the resistivity. This is confirmed by low angle XRD measurements on a 235 nm $Ga_{1-x}Mn_xAs$ ($x=0.07$) film, which indicate a natural oxide layer with a thickness of 2 nm, while after annealing in O_2 gas (≈ 200 °C, 80 h) this thickness only increased to about 5 nm.

Fig. 2 shows the resistivity versus temperature for a sample with $x=0.06$, both as-grown (curve a) and after annealing at ≈ 200 °C for 60 h in an O_2 atmosphere (curve c). Both curves show typical behavior for metallic $Ga_{1-x}Mn_xAs$, with a peak at $T_p=82$ K for the as-grown sample, and $T_p=162$ K for the oxygen-annealed one. The peak temperature gives a good estimate of the Curie temperature for the as-grown sample. The direct measurement of T_C with vibrating sample magnetometry gives $T_C=81$ K. However, for the annealed sample T_p is found to overestimate the measured $T_C=133$ K by 29 K, which is a large deviation, even considering the broadness of the resistivity peak.

To investigate further the increase in resistivity observed at $T_A=177$ and 201 °C (before exposure to O_2), the same annealing procedure was repeated without oxygen, thus in a forming gas atmosphere. The resistivity of $Ga_{1-x}Mn_xAs$ ($x=0.07$) as a function of time at 198 °C is shown in Fig. 3. The resistivity initially drops, but then quickly increases with a rate that decreases with time. A similar effect is observed for samples with various Mn content and the slowly increasing resistivity was established for annealing times exceeding 100 h. It is unlikely that the increase in resistivity is caused by the passivation of the $Ga_{1-x}Mn_xAs$ layer due to hydrogenation as described recently by Brandt *et al.*,[18] as a similar resistivity curve was observed when annealing in a N_2 gas atmosphere and in vacuum (10^{-6} mbar). The resistivity increase is even observed at $T_A=158$ °C when annealing $Ga_{1-x}Mn_xAs$ ($x=0.04$ and $x=0.08$) in vacuum, albeit only by about 20% after annealing for 120 h. These results are in agreement with the increased resistance observed for long annealing times and higher temperatures.[7–10,15] The resistivity versus temperature for $Ga_{1-x}Mn_xAs$ ($x=0.06$) after annealing in forming gas is plotted in Fig. 2 as curve (b) and shows semiconducting behavior with a slight deviation around 25 K. To determine the carrier type and concentration, Hall effect measurements in dc magnetic fields up to 12 T were performed at 300 K, which is far above T_C so no significant paramagnetic contribution through the anomalous Hall effect was detected. The Hall data revealed positive holes as carriers with a concentration of 4.6×10^{19} cm^{-3} for $Ga_{1-x}Mn_xAs$ ($x=0.06$) annealed in forming gas, which is almost an order of magnitude less than the hole concentration $p=2.0\times10^{20}$ cm^{-3} found for the as-grown sample from Hall measurements at 5 K. The latter value for p was obtained by taking the magnetoresistance contribution to the anomalous

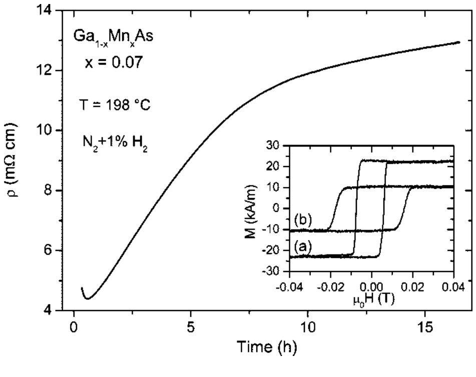

FIG. 3. Resistivity vs annealing time for a $Ga_{1-x}Mn_xAs$ ($x=0.07$) film in a forming gas atmosphere at 198 °C. The inset shows hysteresis loops measured at 5 K for $Ga_{1-x}Mn_xAs$ ($x=0.07$): (a) as-grown, measured along the [100] easy axis; (b) after annealing in a forming gas atmosphere (199 °C, 25 h), measured along the [001] easy axis.

Hall effect into account, by assuming the anomalous Hall coefficient $R_A \propto \rho^2$.

Magnetization measurements performed on $Ga_{1-x}Mn_xAs$ ($x=0.07$) show that the easy axes for as-grown samples are [100] and [010] in-plane, while after a similar annealing treatment in forming gas the easy axis is shifted to the out-of-plane [001] axis, as expected for $Ga_{1-x}Mn_xAs$ with such a low hole concentration.[19,20] When measuring along the easy axis, the magnetic moment shows no significant increase when the magnetic field is raised from 20 mT to 0.5 T, indicating that the samples are in a nearly single domain state at remanence. Macroscopic single domains in $Ga_{1-x}Mn_xAs$ have been established with scanning Hall probe and scanning SQUID microscopy,[21] magneto-optical imaging,[22] and planar Hall effect measurements.[23] Therefore the remanent magnetization M_{rem} along the easy axis at 5 K is a good measure of the saturation magnetization of the $Ga_{1-x}Mn_xAs$ layer. As can be seen from the inset of Fig. 3, M_{rem} has decreased by more than 50% as a consequence of the annealing procedure.

These results show that there is a second mechanism besides the diffusion of Mn_I. This mechanism appears to diminish the amount of ferromagnetically coupled Mn ions, as M_{rem} has decreased, and since the carrier concentration is strongly reduced, this may be due to the removal of Mn from electrically active Ga sites. The fact that the remaining carriers are still found to be *p*-type indicates that Mn_{Ga} ions do not simply move to interstitial positions, as an excess of Mn_I would lead to electrons as carriers. The activation energy for the removal of Mn_{Ga} will be much higher than that for the outdiffusion of Mn_I, which therefore dominates in an O_2 atmosphere. When no oxygen is available, no passivation at the surface can occur, but the relatively mobile Mn_I are still free to migrate through the epilayer. An additional mechanism could be the formation of Mn–As complexes, possibly with Mn_I as an intermediate state. MnAs inclusions were previously observed after annealing at high temperatures (600 °C).[24] The initial decrease in resistivity upon annealing as seen in Figs. 1 and 3 may be due to the passivation of some Mn_I at the natural oxide layer at the sample surface and the limited diffusion of Mn_I to the substrate.

In summary, exposure of $Ga_{1-x}Mn_xAs$ to oxygen during annealing causes a substantial drop in the resistivity, which indicates that the passivation of Mn_I at the free surface occurs through oxidation. The presence of oxygen can therefore be an important post-growth annealing condition for the optimization of this system. Annealing in an oxygen-free atmosphere leads to an increase in the resistivity indicating a second annealing mechanism besides the outdiffusion of Mn_I, which reduces the amount of electrically and magnetically active Mn atoms.

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