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Determination of Free Hole Concentration in Ferromagnetic $Ga_{1-x}Mn_xAs$ Using Electrochemical Capacitance-Voltage Profiling

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ABSTRACT

We demonstrate that electrochemical capacitance voltage profiling can be used to determine the free hole concentration in heavily p-type doped low-temperature-grown GaAs films. This provides a simple and reliable method for measuring the hole concentration in ferromagnetic $Ga_{1-x}Mn_xAs$ semiconductor alloys. The method overcomes the complications that arise from the anomalous Hall effect term which affects standard transport studies of carrier concentration in conducting ferromagnetic materials. Specifically, we find that the maximum Curie temperature of about 111 K found for our $Ga_{0.91}Mn_{0.09}As$ samples corresponds to a hole concentration of 10^{21} cm^{-3}.

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Ferromagnetic $Ga_{1-x}Mn_xAs$ thin films grown by low temperature molecular beam epitaxy (LT-MBE) have recently been attracting a great deal of attention [1,2]. Curie temperature as high as 110K has been achieved for these thin magnetic semiconductor films for Mn content x ranging from 0.05 to 0.09 [2-4]. In this material the Mn^{++} ions reside on the Ga sublattice and act as acceptors. The high concentration of free holes in turn mediates long range ferromagnetic coupling between the Mn ions. It has been shown that the Curie temperature of this ferromagnetic system can be expressed by the Zener model in the form [5],

$$T_C = CN_{Mn}p^{1/3}, \tag{1}$$

where N_{Mn} is the concentration of uncompensated magnetic (Mn) spins that are coupled by indirect ferromagnetic interaction, p is the hole concentration, and C is a constant specific to the host material. It is seen from Eq. (1) that in order to increase T_C one has to increase the concentration of uncompensated Mn^{++} ions, N_{Mn}, and/or the hole concentration, p. Alternatively, it has also been proposed that the ferromagnetic coupling between Mn^{++} ions is mediated by holes localized on adjacent ions [6].

Two key parameters common to most proposed models explaining the indirect ferromagnetic coupling and predicting the Curie temperature in $Ga_{1-x}Mn_xAs$ are the free hole concentration and the concentration of uncompensated Mn^{++} ions [5,6]. One of the long standing problems impeding the analysis of these hole-mediated magnetic interactions that underlie the ferromagnetism in III-Mn-V semiconductor alloys has been the difficulty to reliably determine the hole concentration. The Hall effect which is commonly used to measure the concentration of charge carriers in semiconductors cannot be applied at normally available magnetic fields to materials like $Ga_{1-x}Mn_xAs$ because of the presence of the *anomalous Hall effect* (AHE), a feature characteristic of conducting ferromagnets [3,7]. Specifically, the Hall resisitivity ρ_{Hall} of ferromagnetic materials depends on the magnetization, and can be expressed as

$$\rho_{Hall} = R_o B + R_s M \qquad (2)$$

where R_o is the normal Hall coefficient, B the magnetic flux density, R_s the anomalous Hall coefficient, and M is the magnetization. Ohno *et al.* had performed Hall effect measurements at very high magnetic field of 27 T and very low temperature of 50 mK where the magnetization M saturates and therefore the magnetic field dependence of ρ_{Hall} is dominated by the standard Hall term in Eq. 2 [8]. However, even under such extreme conditions, reliable measurement of the free hole concentration is still not straightforward, since the presence of negative magnetoresistance in this regime indicates that magnetization M is still not completely saturated [8].

In this paper we show that the free hole concentration in ferromagnetic $Ga_{1-x}Mn_xAs$ thin films can be reliably measured using the electrochemical capacitance-voltage (ECV) method. To demonstrate this, we first use ECV profiling to measure the hole concentration in a series of nonmagnetic p-type $Ga_{1-y}Be_yAs$ layers grown by LT-MBE, and compare these results with Hall effect data obtained on the same samples. Additionally, valuable information has also been obtained from comparison of ECV and Hall data observed on non-ferromagnetic $Ga_{1-x-y}Mn_xBe_yAs$ layers that were grown in conditions very similar to those used for the growth of ferromagnetic $Ga_{1-x}Mn_xAs$ layers.

The $Ga_{1-x}Mn_xAs$, $Ga_{1-y}Be_yAs$ and $Ga_{1-x-y}Mn_xBe_yAs$ films were grown on semi-insulating (001) GaAs substrates in a Riber 32 R&D MBE system. Fluxes of Ga, Be and Mn were supplied from standard effusion cells, and As_2 flux was produced by a cracker cell. Prior to film deposition we grew a 450 nm GaAs buffer layer at 590°C (i.e., under normal GaAs growth conditions). The substrate was then cooled down for the growth of a 3 nm thick low-temperature (LT) GaAs, followed by either a 110 nm $Ga_{1-x}Mn_xAs$ layer, or 230 nm thick layer of either $Ga_{1-y}Be_yAs$ or $Ga_{1-x-y}Mn_xBe_yAs$. The As_2:Ga beam equivalent pressure ratio of 20:1 was used. We used substrate temperatures of 265ºC for LT-$Ga_{1-x}Mn_xAs$ growth, and 270ºC for the growth of $Ga_{1-y}Be_yAs$ and $Ga_{1-x-y}Mn_xBe_yAs$.

Hall effect measurements were performed at room temperature using either the Van der Pauw or the six-probe geometry, and magnetic fields up to 7T. Electrochemical capacitance-voltage measurements were carried out at room temperature using a BioRad PN4300 Semiconductor Profile Plotter. The ECV profiling method uses an electrolyte to make a Schottky barrier to the semiconductor surface and at the same time controllably removes the material by electrochemical etching [9]. For all our specimens a 0.2M NaOH: EDTA solution was used as the electrolyte. The C-V measurement technique provides information on the distribution of the net space charge in the depletion region of the semiconductor [9]. Determination of the free carrier concentration using the C-V measurement may be complicated by the presence of deep states in semiconductors [9]. This issue could be especially important in LT-GaAs, which typically contains large concentrations of arsenic antisites [10] and gallium vacancies [11]. In order to establish how the deep states affect the ECV measurements in heavily p-type doped LT-GaAs films, we compare the space charge concentration measured by ECV with the free hole concentration obtained by the Hall measurements on a series of non-magnetic Be-doped LT-GaAs films grown with different Be cell temperatures, and therefore different Be content in the film (from 5 up to 17% of Be). We emphasize that the growth conditions of the Be doped films and undoped $Ga_{1-x}Mn_xAs$ films are very similar and therefore the defects present in both types of films are expected to be similar in nature and quantity.

Figure 1 shows ECV profiles of the ionized acceptor concentrations in two $Ga_{1-y}Be_yAs$ thin films grown, respectively, with Be cell temperature of 1060ºC and 1100ºC. The Be concentrations in these films, estimated from the change in the growth rate between GaAs and $Ga_{1-y}Be_yAs$ and monitored by RHEED oscillations, were $y = 0.06$ and $y = 0.17$, respectively. The free hole concentrations measured by the Hall effect are also given in the figure. The results in Fig. 1 show that the net ionized acceptor concentration measured by ECV agrees to within 15% with the free hole concentration measured by the Hall effect.

To address the possibility that additional deep states may arise specifically from the presence of Mn, we also measure a series of $Ga_{1-x-y}Mn_xBe_yAs$ layers grown under the same conditions as the LT- $Ga_{1-x}Be_xAs$ and LT- $Ga_{1-x}Mn_xAs$ used in this study. We have shown elsewhere [12] that high concentrations of Be in $Ga_{1-x-y}Mn_xBe_yAs$ *suppresses* ferromagnetism, so that hole concentrations can be reliably obtained from ordinary Hall measurements. ECV measurements have yielded results that are nearly identical to the Hall data (within 10%), indicating that the possible error in the hole concentration measured by ECV due to deep-states associated with Mn is below 10%. We thus conclude that the ECV measurements provide a simple and accurate method for measuring the free hole concentration in all heavily p-type doped LT-GaAs, including LT-$Ga_{1-x}Mn_xAs$.

The observed insensitivity of the ECV measurements to the presence of deep level states could be explained by the argument that, with the relatively low modulation frequency used in the ECV measurements (typically <3kHz), only deep traps at energy levels less than 0.35eV from the valence band maximum are expected to affect the space charge in the depletion region [9]. Therefore the arsenic antisite defects are not expected to affect the ECV measurements, as the second ionization stage of this defect is located at 0.5 eV above the valence band edge [13]. On the other hand, although the energy levels of the Ga vacancy may be located closer than 0.35 eV to the valence band edge, the concentration of these defects is typically only about 10^{19} cm^{-3} in intrinsic LT-GaAs [11], and is expected to be significantly lower in our heavily p-type doped material.

Figure 2 shows the net space charge profiles for three ferromagnetic $Ga_{1-x}Mn_xAs$ samples with x=0.09: as-grown, and annealed at 282°C and 350°C for 1hr in flowing N_2 ambient. The ECV measurements show an increase of the free hole concentration from

$6x10^{20}cm^{-3}$ observed in the as-grown sample to $1x10^{21}cm^{-3}$ for the $Ga_{1-x}Mn_xAs$ film annealed at 282°C. The hole concentration for the sample annealed at 350°C, on the other hand, is very similar to the as-grown sample. Using channeling Rutherford backscattering and particle-induced x-ray emission, we have established the relationship between the change in the hole concentration and the behavior of unstable defects involving highly mobile Mn interstitials in the narrow annealing temperature range [4]. Specifically, we showed that in $Ga_{1-x}Mn_xAs$ samples annealed at 282°C the number of Mn interstitials decreases, causing the concentration of uncompensated Mn^{++} acceptors to grow, in complete agreement with the ECV data of Fig. 2.

The Curie temperatures T_C for the $Ga_{1-x}Mn_xAs$ films are shown in Fig. 3 (upper panel). In the lower panel of Fig. 3 the free hole concentrations measured by ECV are directly compared to the *apparent* free hole concentrations obtained by Hall measurement performed at room temperature at 0.5T. We note parenthetically that, although above T_C the Hall resistivity r_{Hall} is *linear* in magnetic field, it still contains significant latent effects of AHE, as revealed by a strong temperature dependence of r_{Hall}. Note that even at the relatively high temperature of 300K illustrated here the apparent hole concentration determined from the Hall effect is still almost an order of magnitude smaller than the actual hole concentration measured by ECV.

As shown in Fig. 3, we observe a qualitative correlation between T_C and the hole concentration determined by ECV. The increase of T_C from 67 K to 111 K induced by annealing at 282°C scales very well with the corresponding increase in the free hole concentration. This result supports the assertion that the total number of the ferromagnetically coupled spins is related to the concentration of *uncompensated* Mn acceptors, rather than to the total number of Mn atoms [4].

In conclusion, we have found that the net space charge distribution in heavily Be doped low temperature GaAs measured by the ECV method agrees well with free hole concentration obtained by Hall measurements. This establishes that ECV can be reliably used to obtain the free hole concentration profiles in ferromagnetic $Ga_{1-x}Mn_xAs$ grown by the low temperature MBE method, thus circumventing the complications arising from the anomalous Hall effect encountered in conventional transport measurements on this system.

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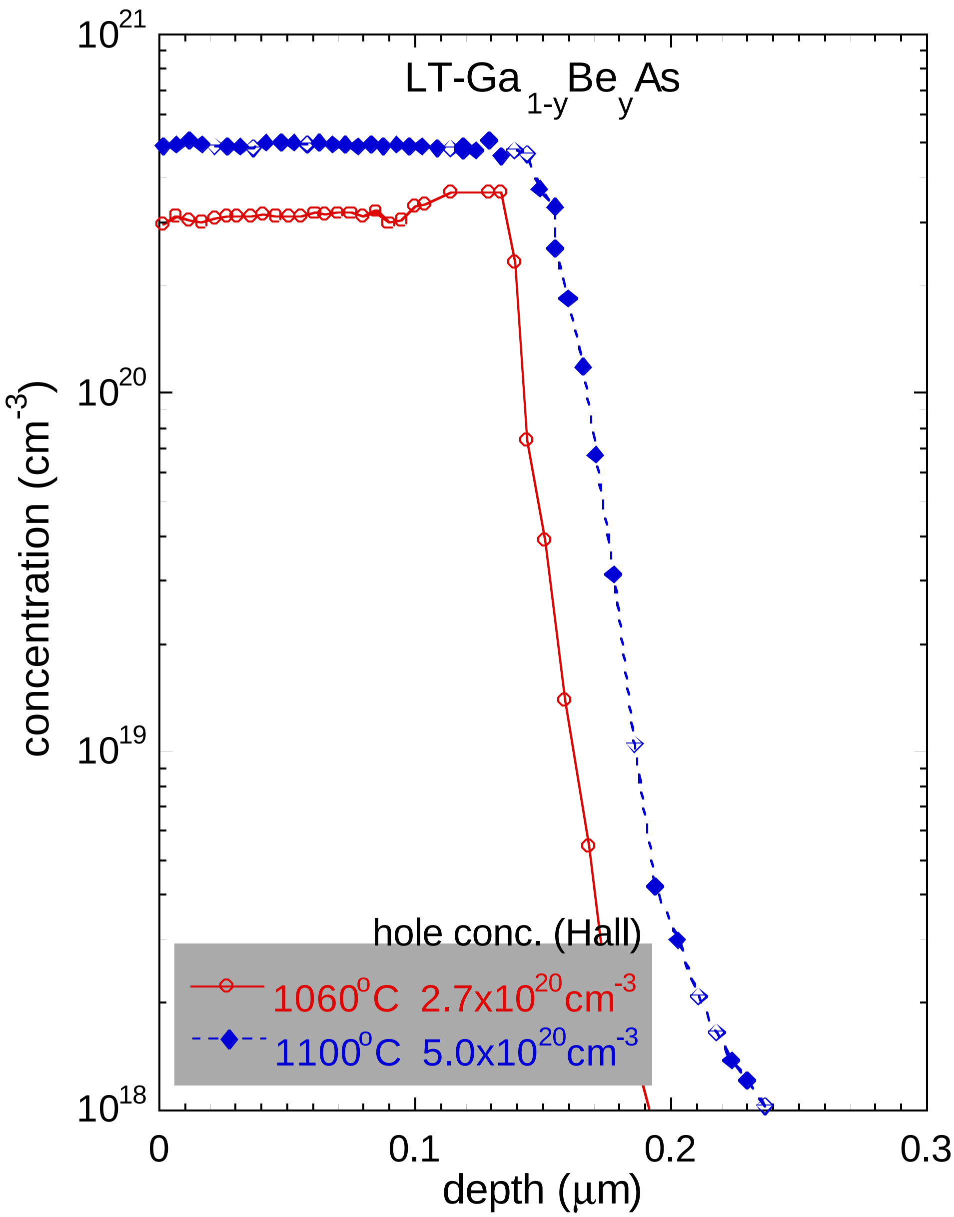
FIGURE CAPTIONS

Fig. 1 The net space-charge profiles measured at room temperature by electrochemical capacitance-voltage measurements (ECV) for two non-magnetic $Ga_{1-y}Be_yAs$ films grown by the low temperature molecular beam epitaxy technique. For comparison, the values of the free hole concentration obtained by room temperature Hall measurements on these films are also listed in the figure.

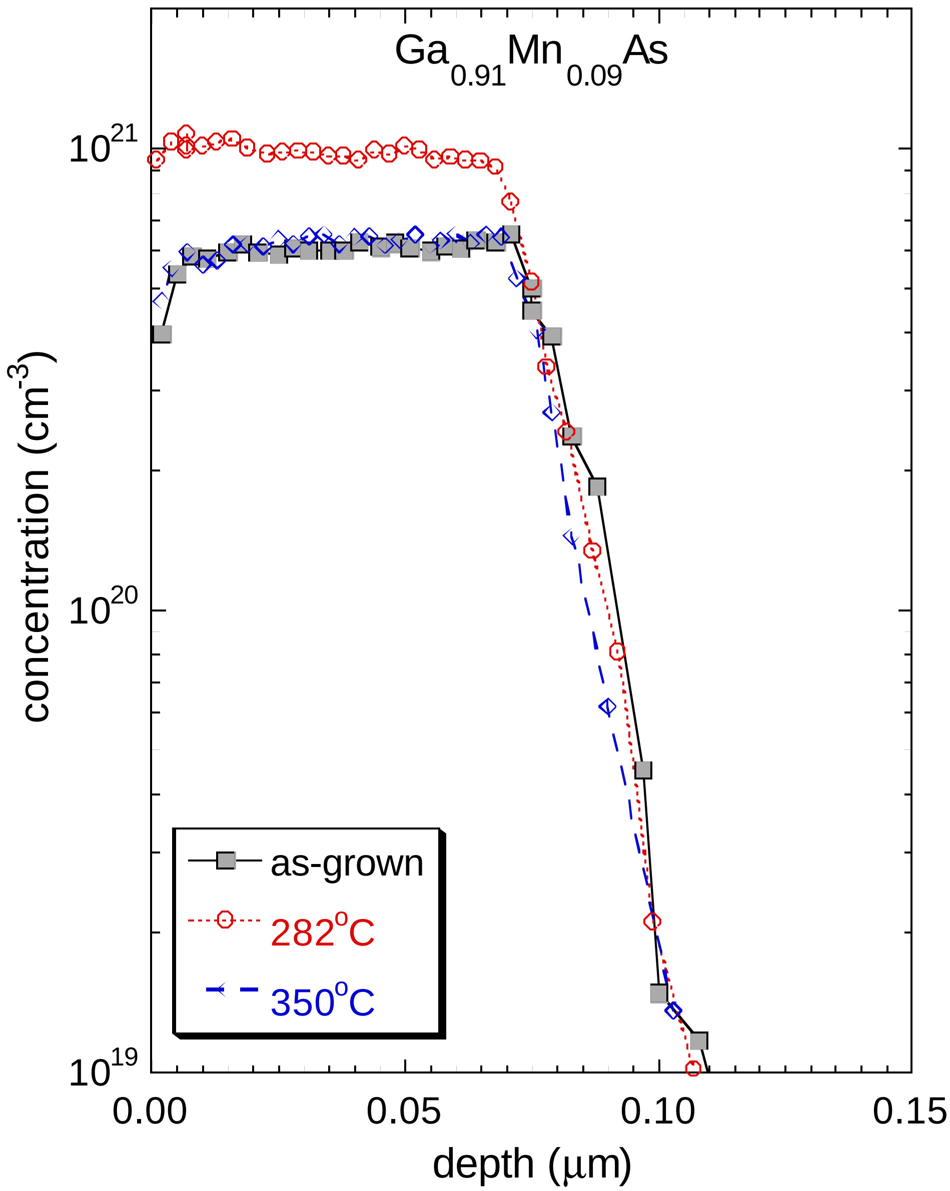
Fig. 2 ECV-measured hole concentration profiles for three $Ga_{0.91}Mn_{0.09}As$ thin films: as-grown, annealed at 282ºC, and annealed at 350ºC.

Fig. 3 Variation of the Curie temperature T_C with the annealing temperature for the $Ga_{0.91}Mn_{0.09}As$ thin films (top panel). The free hole concentrations measured by ECV are directly compared to the *apparent* free hole concentrations obtained by Hall measurement performed at room temperature at 0.5T in the lower panel of the figure.



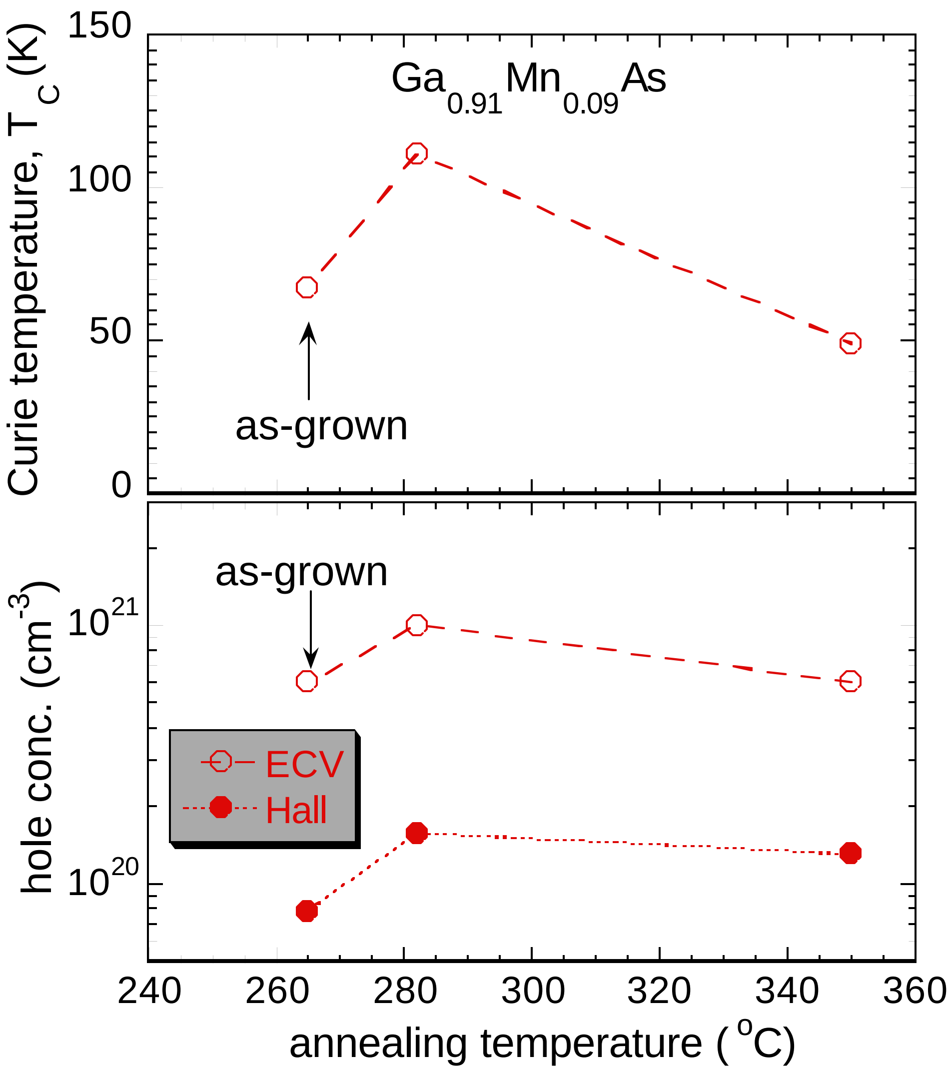
LT-Ga 1-y Be y As
concentration (cm-3)
10^21
10^20
10^19
10^18
0
0.1
0.2
0.3
depth (μm)
hole conc. (Hall)
1060°C 2.7x10^20 cm-3
1100°C 5.0x10^20 cm-3

Fig. 1



Ga0.91Mn0.09As
concentration (cm-3)
10^21
10^20
10^19
depth (µm)
0.00
0.05
0.10
0.15
as-grown
282oC
350oC

Fig. 2



Curie temperature, T C (K)
150
100
50
0
Ga0.91Mn0.09As
as-grown
hole conc. (cm-3)
10^21
10^20
as-grown
ECV
Hall
240
260
280
300
320
340
360
annealing temperature (oC)

Fig. 3