Compensation-dependence of magnetic and electrical properties in Ga$_{1-x}$Mn$_x$P

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We demonstrate the control of the hole concentration in Ga$_{1-x}$Mn$_x$P over a wide range by introducing compensating vacancies. The resulting evolution of the Curie temperature from 51 K to 7.5 K is remarkably similar to that observed in Ga$_{1-x}$Mn$_x$As despite the dramatically different character of hole transport between the two material systems. The highly localized nature of holes in Ga$_{1-x}$Mn$_x$P is reflected in the accompanying increase in resistivity by many orders of magnitude. Based on variable-temperature resistivity data we present a general picture for hole conduction in which variable-range hopping is the dominant transport mechanism in the presence of compensation.

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Dilute magnetic semiconductors (DMSs), where a few atomic percent of magnetic ions are randomly incorporated into a semiconductor host species, represent a remarkable workbench for the study and demonstration of spintronic functionalities.$^1$ They are not only a means to an end but very exciting materials in their own right, exhibiting many striking phenomena whose interpretation and modeling are extremely challenging – from the ferromagnetic exchange itself to the radically different degree of hole localization. Furthermore, we present a picture for hole conduction by variable-range hopping (VRH) in Ga$_{1-x}$Mn$_x$P.

In this letter we present the first systematic study on the electrical and magnetic effects of hole compensation in Ga$_{1-x}$Mn$_x$P. We utilize the amphoteric nature of native defects$^{13-15}$ to investigate a very wide range of $x$ without significantly changing $x$. A similar method has recently been applied to Ga$_{1-x}$Mn$_x$As and we find surprising similarities between the materials despite the radically different degree of hole localization.

The samples for this study were prepared by II-PLM. A GaP (001) wafer – doped n-type; $n \sim 10^{16-10^{17}}$ cm$^{-3}$ – was implanted with Mn$^+$ at an energy of 50 keV and an angle of incidence of $7^\circ$ to a dose of $2 \times 10^{16}$ cm$^{-2}$. Samples with approximate side lengths of 6 mm were cleaved along (110) directions and individually irradiated with a single $\sim 0.4$ J cm$^{-2}$ KrF laser pulse ($\lambda = 248$ nm, FWHM = 18 ns), homogenized to a spatial uniformity of $\pm 5\%$ by a crossed-cylindrical lens homogenizer. They were subsequently subjected to 24 h HCl etching to remove residual surface damage. These parameters have been used previously to produce samples with $x \approx 0.038$. For our samples, $x$ is defined as the peak substitutional manganese (Mn$_{Ga}$) fraction – occurring between 20 and 30 nm below the surface – as determined by a combination of secondary ion mass spectrometry (SIMS) and ion beam analysis (IBA).$^{17}$ Compensating defects were then introduced into samples by consecutive irradiations with Ar$^+$ at an energy of 33 keV and an angle of incidence of $7^\circ$, which according to simulations$^{18}$ yield a vacancy depth profile similar to the typical Mn distribution.

The characterization of several identically prepared Ga$_{1-x}$Mn$_x$P samples was carried out by SQUID magnetometry. All measurements were conducted in zero-field cooled conditions along the [110] in-plane magnetic easy axis,$^{19}$ and the diamagnetic background was removed by linear fitting of variable-field magnetic moment $m(H)$ data up to $H = \pm 50$ kOe at $T = 5$ K. They revealed an average saturation moment per Mn$_{Ga}$ of $m_{sat}^\text{obs} = 3.7 \pm 0.4 \mu_B$ in agreement with previous values.$^7$ Temperature-dependent magnetic moment

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m(T) data at H = 10 Oe revealed T_C = 50 ± 1.5 K, which is in line with both previous experimental and theoretical results. Variable-temperature sheet resistance \( \rho_s(T) \) measurements showed similar agreement between samples.

To confirm their structural integrity, samples were characterized after various irradiation doses. Using IBA, we found that the sheet concentration of MnGa, \( c_s \), remains constant within experimental errors and by SIMS that the Mn distribution is unaffected. High-resolution transmission electron microscopy and atomic force microscopy similarly show no qualitative changes with ion irradiation. Notably, even the sample with the highest irradiation dose shows no traces of secondary phases.

In order to track the degree of compensation, control samples were processed in parallel by implanting Zn\(^{+} \) – a hydrogenic acceptor in GaP – to a dose of \( 1 \times 10^{16} \) cm\(^{-2} \). On these, direct measurement of the hole concentration as a function of irradiation dose is possible using the Hall effect. From this data we have determined a hole removal rate of \( 1.1 \pm 0.1 \times 10^{3} \) holes per Ar\(^{+} \), or \( 2.2 \pm 0.2 \) holes per vacancy when taking into account the simulations. Using this information, we calculate the relative sheet hole concentration \( \Delta p_s \), defined as the difference in the sheet hole concentration \( p_s \) between the unirradiated reference and the irradiated sample.

In Fig. 1(a-b) we show \( m(T) \) for various \( \Delta p_s \), revealing a monotonic decrease of \( T_C \) with \( \Delta p_s \). Similarly, we observe a decrease of \( m_{\text{sat}} \) with dose as evidenced in Fig. 1(c), consistent with previous studies of donor- or vacancy doping.\(^{1,11,15} \) We point out that this is in contrast to \( m_{\text{sat}} \) being unaffected by hydrogenation,\(^{22,23} \) indicating different mechanisms being involved in passivation versus compensation. The dependence of \( T_C \) on \( \Delta p_s \) is presented in Fig. 2, revealing a virtually linear decline with decreasing hole concentration. We note that the highest irradiation dose of \( 5.77 \times 10^{12} \) cm\(^{-2} \) should be sufficient to fully compensate the Mn acceptors, present at \( c_s = 5.4 \pm 0.3 \times 10^{15} \) cm\(^{-2} \). However, as apparent from Fig. 1(a-d), the films are FM at all irradiation doses, implying that they remain \( p \)-type even for the highest doses. This apparent discrepancy is explained by the amphoteric defect model (ADM),\(^{13,14} \) wherein the defect formation energy strongly depends on the Fermi level \( E_F \), resulting in a saturation of the defect doping-induced shift in \( E_F \) at a material-dependent stabilization level \( E_{FS} \). This effect becomes dominant in our system for \( \Delta p_s > 0.8 c_s \), considerations that are reflected in the error bars where appropriate. Furthermore, the persistence of FM even at these high levels of compensation demonstrates again that the compensation level of as-fabricated films must be very low.\(^{17} \)

Accounting for the ADM-related compensation effects, we observe the relation \( T_C \propto p^\gamma \) with \( 1 > \gamma > 0.5 \) for Ga\(_{1-x}\)Mn\(_x\)P. Remarkably, such dependence of \( T_C \) on \( \Delta p_s \) is nearly identical to that observed in Ga\(_{0.955}\)Mn\(_{0.045}\)As\(^{15} \) films grown by low-temperature molecular beam epitaxy – that is, the trend is identical, barring a certain offset, reminiscent of the similarity in \( T_C(x) \).\(^{24} \) While our \( \gamma \) is in a similar range as a \( p-d \) Zener model prediction for Ga\(_{1-x}\)Mn\(_x\)As of \( \gamma = 0.6-0.8 \),\(^{25,26} \) the model assumption of uniformly distributed delocalized or weakly localized holes does not apply to the Ga\(_{1-x}\)Mn\(_x\)P films in this study.

\( \rho_s(T) \) for Ga\(_{1-x}\)Mn\(_x\)P samples with varying levels of compensation is displayed in Fig. 3. Films become orders of magnitude more resistive with increasing irradiation dose. The generally applied, phenomenological model in Ga\(_{1-x}\)Mn\(_x\)P has been \( \rho = (\sigma_{\text{free}} \exp(-\varepsilon_1/k_B T) + \sigma_{\text{hop}} \exp(-\varepsilon_2/k_B T))^{-1} \).\(^{7} \) Here the first term is attributed to thermally activated hole transport \( \text{via} \) the valence band and the second term to hopping conduction, previously assumed.
to take place between nearest neighbors. This model reproduces the behavior of samples with varying x which have not been intentionally compensated. For the current case of compensated films, however, we find overall better agreement with activated transport of the form $\rho \propto \exp (\epsilon T^x)$ with a temperature exponent of $\lambda \sim -0.5$, separated into a high- and a low-temperature regime characterized by different activation energies $\epsilon$. We attribute the general behavior to hopping conduction, specifically VRH. That this mechanism should dominate even at high $T$ for large $\Delta p_s$ is reasonable as the energetic difference between delocalized states and $E_F$ – here on the order of the Mn acceptor level $\lambda B T$. At $\Delta p_s \lesssim 10^{15}$ cm$^{-2}$, VRH is insufficient to describe fully the transport at high $T$. In this regime, the conduction by holes excited thermally to delocalized states, as described previously, contributes or even dominates. This behavior is qualitatively similar to that observed in insulating, low-doped Ga$_{1-x}$Mn$_x$As and even more so to that in insulating, Sn-codoped Ga$_{1-x}$Mn$_x$As.

In conclusion, the orders-of-magnitude changes in conductivity and the much more subtle changes in the magnetic response upon compensation using Ar$^+$-induced native defects demonstrate the stability of the hole-mediated FM phase in Ga$_{1-x}$Mn$_x$P. While the electrical behavior of Ga$_{1-x}$Mn$_x$P and Ga$_{1-x}$Mn$_x$As at comparable $x$ is dramatically different, these materials display a remarkably similar $T_C$ dependence on both hole concentration and Mn content. This indicates similar mechanisms for inter-Mn exchange in the two systems and places carrier-mediated FM on a continuum of carrier localization in III-Mn-V DMSs.

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See supplementary material at [URL will be inserted by AIP] for SIMS and IBA data.

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