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Ferromagnetism above room temperature in bulk sintered gallium phosphide doped with manganese

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Abstract

Evidence for ferromagnetism in bulk sintered gallium phosphide (GaP) doped with 3% manganese, having a Curie temperature of 600 K considerably higher than previous observations, is obtained using ferromagnetic resonance (FMR) and AC magnetization measurements. The field position and line width of the resonance showed a strong temperature dependence characteristic of FMR spectra. A non-resonant derivative signal centered at zero field was also observed starting at 600 K further confirming high temperature ferromagnetism. AC magnetization measurements also show the existence of ferromagnetism at high temperature.
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1. Introduction

Semiconducting switching elements in logic circuits involve transport of holes or electrons induced at specific voltages. On the other hand storage of information employs a separate magnetic material in which magnetic field alignment of micrometer long and nanometer wide magnetic particles is the basis of the storage mechanism. In recent years there has been considerable interest in combining both the storage and transport into one material by developing magnetic semiconductors consisting of alloys of a magnetic ion such as Mn^{2+} and a semiconducting material. In such materials the magnetic field induced orientation of the spin of the charge carriers would be the basis of information storage. Ferromagnetism at 110 K has been observed in GaAs doped with manganese [1]. More recently, there have been reports of ferromagnetism above room temperature in GaMnN, GaMnP made by molecular beam epitaxy which will make large scale production expensive [2–4]. The highest Curie temperature reported to date is above 400 K in Mn doped ZnO [5]. The origin of ferromagnetism in these compounds is not totally understood. It has been proposed that the exchange interaction between the dopant spins is mediated by the holes or electrons [6]. In the ferromagnetic state there is a splitting of the valence and conduction band depending on the spin orientation of the charge carriers. The model predicts that hole doped semiconductors will have higher Curie temperatures than electron doped materials.

Here we report ferromagnetic resonance (FMR) and AC magnetization evidence for ferromagnetism in GaP hole doped with 3% Mn and made by a simple inexpensive sintering process.The Curie temperature of the material is 600 K much higher than any previous observation. FMR is a highly sensitive and well established method of studying and verifying the existence of ferromagnetism in a material [7].

2. Experimental

The ferromagnetic resonance measurements were made using a Varian E-9 spectrometer operating at 9.2 GHz with 100 KHz modulation. The temperature of the sample was controlled by flowing heated or cold nitrogen gas through a doubled-walled quartz tube, which is part of an ADP Heli-Tran system, and which is inserted through the center of

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the microwave cavity. The sample was contained in the quartz tube and located at the center of the cavity. The magnetization was obtained by measuring the magnetic field dependence of the AC susceptibility at 350 KHz using a method similar to that described by Clover and Wolf [8]. The system consists of an HP 204C LC oscillator modified to have an external coil. The sample is contained in the coil, which is in a cryogenic dewar between the poles of a magnetic. The change in the frequency of the oscillator, which is proportional to the change in susceptibility, is measured using a HP 5314 frequency counter. The magnitude of the saturation magnetization is obtained by comparing the measurements with frequency shifts of a sample of known magnetization such as iron.

The GaP used was examined by electron paramagnetic resonance (EPR) prior to processing to insure no magnetic impurities were present in the material. No evidence for any magnetic impurities was found. EPR is sensitive to magnetic species to one part per 10 billion. The samples were synthesized by thoroughly mixing in the ratio 0.03 molecular weight MnO_2 to one molecular weight gallium phosphide having 99.999 purity and then grinding the mixture using a mortar and pestle. The samples in the form of pressed pellets contained in an alumina boat were sintered at 500 °C in an oven for 4 h in air followed by rapid quenching to room temperature. The sintered samples were examined by X-ray diffraction employing a Scintag X-ray instrument using the Cu Kα line. Fig. 1 shows the powder X-ray diffraction spectra. The lines at the top of the figure are those expected for pure gallium phosphide. The peaks in the doped sample occur at the same scattering angles as pure GaP and no impurity lines are evident in the data. The absence of impurity lines is particularly important indicating that the GaMn alloy, which is ferromagnetic at room temperature, is not present or is MnP, which has a Curie temperature of 291 K. Because the XRD lines occur at the same values in the doped and undoped GaP it is suggested that the manganese is not forming clusters in the lattice. Clusters in the lattice would likely result in an expansion of the lattice parameters and a change in the scattering angles in the XRD data. This conclusion is further supported by scanning electron microscope measurements of the samples, which show no evidence for Mn clusters in the sample. While Mn is not ferromagnetic in the bulk there is some evidence that Mn nanoclusters can be ferromagnetic although there is no evidence they can be ferromagnetic above room temperature [9]. The ferromagnetism discussed below is likely not from ferromagnetism in the clusters but rather from a dilute distribution of Mn in the sample.

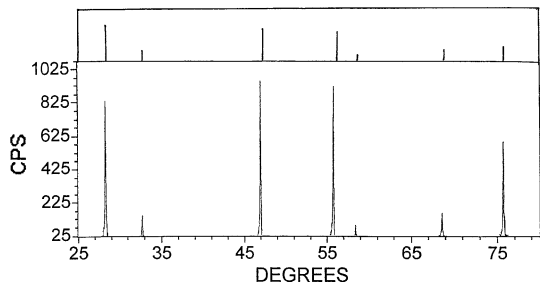

Fig. 1. Powder X-ray diffraction of GaP:Mn. The lines at top show X-ray diffraction pattern for pure GaP.

3. Results and analysis

Fig. 2 shows the Raman spectra of the transverse optical (TO) mode and longitudinal optical (LO) mode in doped and undoped GaP recorded using a JY Horiba confocal Raman spectrometer. No extraneous lines indicative of the presence of impurities were observed. The higher frequency LO mode is down shifted by 4 cm^{-1} in the manganese doped sample. It has been shown in other semiconductors such as GaN that the LO mode is coupled to the plasma mode whose frequency is proportional to the electron carrier concentration [10]. The LO mode has been shown to shift to higher frequencies with increasing electron carrier concentration. The observed decrease in the frequency of the LO mode in the Mn doped GaP indicates a decrease in the electron carrier concentration consistent with hole doping. To further verify this interpretation gallium phosphide was doped with V^{5+} by a similar sintering process described above using V_2O_5. In this material the LO mode increased by 3 cm^{-1} consistent with electron doping of the sample verifying that the direction of the shift of the LO mode is a viable way to determine whether GaP is electron or hole doped.

Fig. 3(a) and (b) show the ferromagnetic resonance spectra at 300 and 104 K, respectively, showing a marked broadening and shift of the of the magnetic field position of the line to lower field as the temperature is lowered characteristic of ferromagnetic resonance spectra. The smaller high field resonance peak at approximately 3100 G, which is temperature independent, is probably due to some unreacted MnO_2 or Mn^{2+} in non-ferromagnetic regions of the sample. Fig. 4(a) and (b) are plots of the temperature dependence of the magnetic field position and line width of the FMR signal above room temperature.

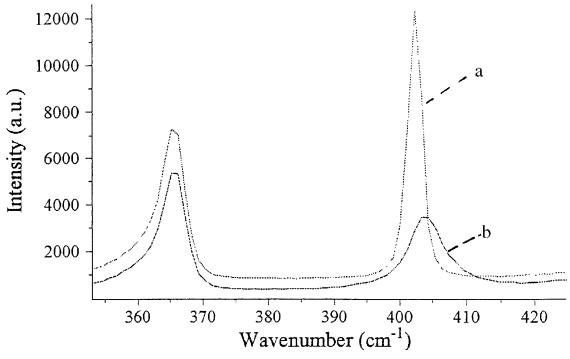

Fig. 2. Raman spectra of the TO and LO mode of doped (a) and undoped (b) GaP showing a downward shift of the LO mode in the doped material.

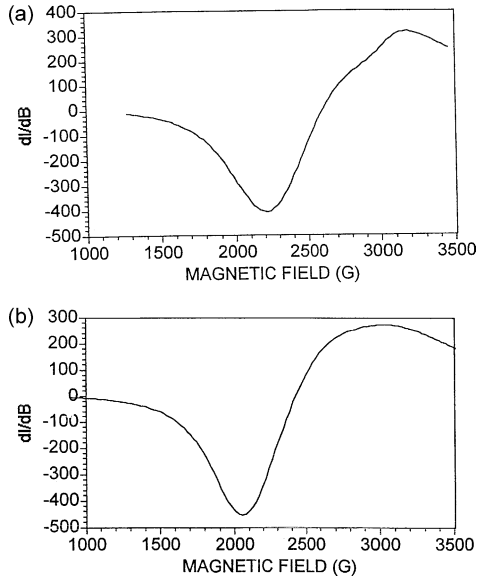

Fig. 3. Ferromagnetic resonance spectra in GaP:Mn at (a) 300 K and (b) 104 K.

These data show clearly that ferromagnetism persists well above room temperature. Such temperature dependent changes in the line width and field position of the resonances would not occur in the paramagnetic state. The strong temperature dependent effects occur in the ferromagnetic state because the field position and line width depend on the magnetization and the anisotropy constant, which are temperature dependent in a ferromagnet. The specific functional form depends on the shape of the sample

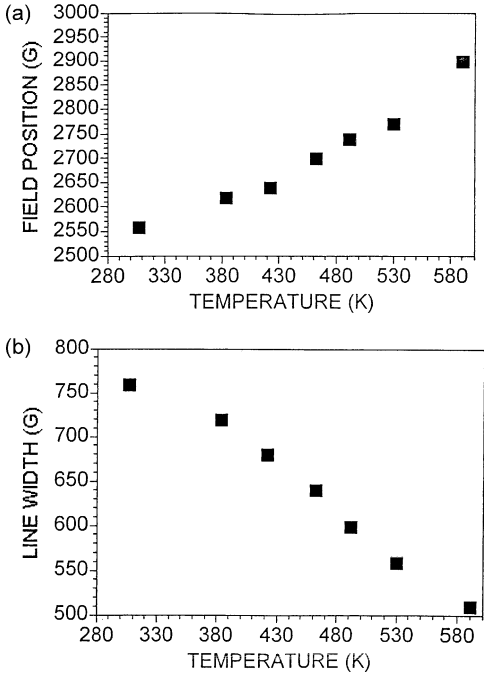

Fig. 4. (a) Temperature dependence of the field position of the resonance above room temperature and (b) the temperature dependence of the line width.

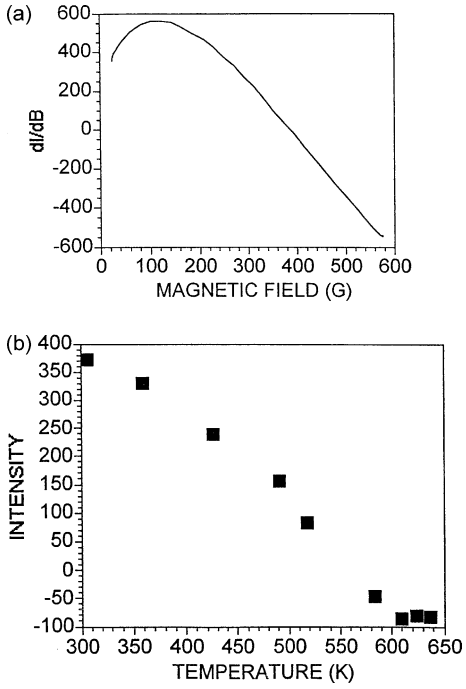

Fig. 5. (a) Low field non-resonant derivative signal recorded at 300 K and (b) temperature dependence of the intensity of the signal showing its emergence at 600 K which identifies the Curie temperature of the sample.

and the orientation of the dc magnetic field. The functional form for a powder, which has a distribution of grain shapes, sizes and orientations, has not been determined. At the Curie temperature the FMR line becomes an EPR line of Mn^{2+} having a g value near the free electron value of 2.0023 corresponding to a field of 3100 G in this experiment. Extrapolating the temperature dependence of the field position in Fig. 4(a) to 3100 G yields a T_c greater than 600 K

Another strong evidence for the existence of ferromagnetism above room temperature is the presence of a non-resonant derivative signal centered at zero field which is shown in Fig. 5(a) at 300 K. This signal is a well established

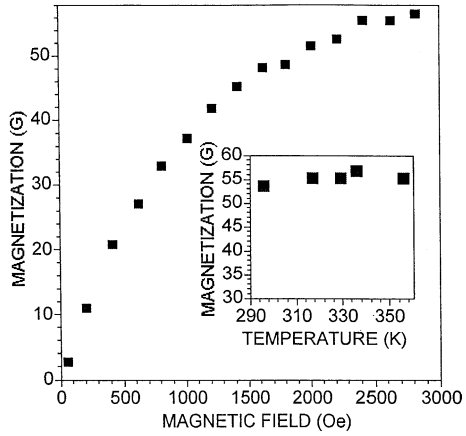

Fig. 6. Magnetic field dependence of the magnetization measured at 300 K. The insert shows a measurement of the temperature dependence of the magnetization at 3.5 kG above room temperature.

indication of the presence of ferromagnetism [11,12]. The signal occurs because the permeability in the ferromagnetic state depends on the applied magnetic field increasing at low fields to a maximum and then decreasing. Since the surface resistance depends on the square root of the permeability, the microwave absorption depends non-linearly on the strength of the dc magnetic field resulting in a non-resonant derivative signal centered at zero fields. This signal is not present in the paramagnetic state and emerges as the temperature is lowered to below T_c. Fig. 5(b) is a plot of the temperature dependence of the signal intensity showing an onset of growth at 600 K which corresponds to Curie temperature of the sample.

Fig. 6 shows a plot of the magnetization of the sample versus applied magnetic field at room temperature providing further support for ferromagnetism in the sample. There is a small hysteresis not shown in the figure indicating the material is a relatively soft ferromagnetic at room temperature. The insert in the figure is a measurement of the temperature dependence of the magnetization at 3.5 kG above room temperature. The independence of the magnetization on temperature up to 360 K is consistent with the high Curie temperature. The small hysteresis rules out the possibility that the ferromagnetism arises from the Mn_xGa_{1-x} alloy which has a large hysteresis at room temperature having a coercive field of 3.15 kOe [13]. Also an MnP impurity cannot account for the results because it has a T_c of 291 K well below the T_c of 600 K observed here [14].

In summary both ferromagnetic resonance and AC magnetization measurements show the existence of ferromagnetism in gallium phosphide hole doped with manganese and synthesized by a bulk sintering process. The onset of the low field non-resonant derivative signal indicates a Curie temperature of 600 K considerably higher than previous observations in materials made by molecular beam epitaxy. The ferromagnetism is believed to arise from a dilute distribution of Mn^{2+} in the sample and not from clusters of Mn^{2+} or other impurities.

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