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GROWTH AND ELECTRICAL PROPERTIES OF PHOSPHORUS DOPED $Zn_{1-x}Mn_xTe$ CRYSTALS*

LE VAN KHOI, J. JAROSZYŃSKI, B. WITKOWSKA
A. MYCIELSKI, R.R. GAŁĄZKA
Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warsaw, Poland
AND J. CISOWSKI
Department of Solid State Physics, Polish Academy of Science
Wandy 3, 41-800 Zabrze, Poland

The high pressure Bridgman technique was used to grow $Zn_{1-x}Mn_xTe$:P crystals. Under the N_2 pressure of 30 atm., we obtained the p^+-$Zn_{1-x}Mn_xTe$ single crystals 8–10 mm in diameter, with free-carrier densities as high as $p \approx 8\times10^{18}$ cm^{-3} and the room temperature conductivity $\sigma(\mathrm{RT}) \approx 30\ \Omega^{-1}\mathrm{cm}^{-1}$. Magnetoresistance measurements were carried out down to 1.3 K and up to 6 T. In $Zn_{1-x}Mn_xTe$:P a strong increase in the acceptor binding energy as well as an immense ($\rho(0, 1.3\ \mathrm{K})/\rho(6\ \mathrm{T}, 1.3\ \mathrm{K}) > 10^3$) negative magnetoresistance are observed, by contrast, not seen in diamagnetic ZnTe:P. It is shown that these effects come from the formation of bound magnetic polarons and their destruction by an external magnetic field.

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1. Introduction

The exchange interaction in semimagnetic semiconductors (SMS) is characterized by exchange constants for the conduction and valence bands. In SMSs based on wide-gap II–VI compounds the exchange constant for the valence band is much greater than the one for the conduction band [1], therefore fabrication of p-type doped SMSs with high hole concentrations opens the door to enlarge the electric and magnetic effects in the wide gap II–VI SMSs [2]. In this paper we report on the growth and on results of the magnetotransport measurements of phosphorus doped $Zn_{1-x}Mn_xTe$ crystals.

2. Experiment

The high pressure Bridgman technique was used to grow $Zn_{1-x}Mn_xTe$ crystals doped with phosphorus. Manganese mole fractions x range from 0 to 0.05. Zinc phosphide (Zn_3P_2) was used as a doping material (0.05 wt.% or less). The Zn, Te, MnTe mixture was heated up to 1400°C for 24 hours in order to melt it completely. The ampoule was then pulled down through a furnace at the various speeds:

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1.5, 2.5, 5 mm/h. The temperature gradient in the growth region was $\approx 60°C/cm$. The N_2 pressure in the chamber was kept at about 30 atm. during growth. The growth was finished when the top of the ampoule reached a temperature below 1100°C. After growth, crystals were cut to about 1 mm thick slices and polished. They were then cut into bars with typical dimensions of $10 \times 1.5 \times 0.8$ mm^3 and etched in a *ca.* 5% solution of bromine in methanol. Ohmic contacts were formed by the chemical deposition of gold. The Hall effect and magnetoresistance measurements were carried out over the temperature range from 1.3 K to 300 K and in magnetic fields up to 6 T.

3. Results and discussion

The best crystals were obtained when the ampoule shift rate was kept at 1.5 mm/h. All grown crystals exhibit p-type conductivity. Typical results of the electrical characterization (Hall concentration, conductivity and mobility) are shown in Table.

TABLE

x	$T = 300$ K $B = 5$ kGs			$T = 77$ K $B = 5$ kGs		
	p cm^{-3}	σ $(\Omega$ cm$)^{-1}$	μ cm^2/(V s)	p cm^{-3}	σ $(\Omega$ cm$)^{-1}$	μ cm^2/(V s)
0	8.5×10^{18}	26	21	1.1×10^{19}	28	16
0.01	7.7×10^{18}	26	23	6×10^{18}	23	24

One can see from Table that phosphorus is a very efficient p-type dopant for $Zn_{1-x}Mn_xTe$ crystals. Room temperature carrier concentrations were about $20 \div 40\%$ of added phosphorus atoms. Two samples were selected for detailed magnetoresistance studies: ZnTe:P and $Zn_{0.99}Mn_{0.01}Te$:P. As it can be seen from Table their electrical parameters at the room temperature are almost the same.

In Fig. 1 we present resistivity as a function of temperature. One can see that the resistivity of the ZnTe:P sample is temperature independent. This result indicates the formation of an impurity band and the metallic behavior in terms of metal-to-insulator transition (MIT). At the same time in paramagnetic $Zn_{1-x}Mn_xTe$:P a striking influence of localized Mn spins on $\rho(T)$ is seen. In this case, resistivity increases with decreasing temperature, with the activation energy $E_a \approx 1$ meV. The temperature dependence of resistivity indicates the temperature driven transition towards the insulating side of MIT and possible increasing of E_a with decreasing temperature. Such behavior cannot be explained by thermally activated band transport. according to the previous findings in p-CdMnTe and n-CdMnSe [3, 4] such $E_a(T)$ behavior can be explained, if one takes into account the formation of bound magnetic polarons (BMP). As it is well established, mutual exchange interaction between Mn and bound hole spins leads to the spin-splitting of the acceptor state increasing its binding energy. The polaron characteristic energy is given by [5]

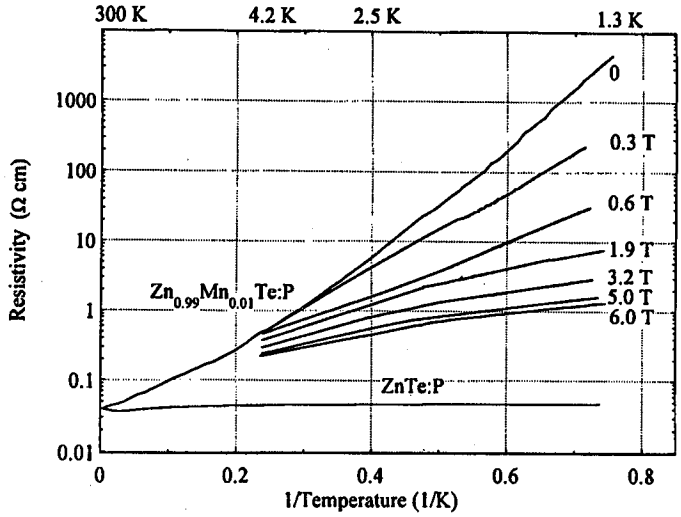

Fig. 1. Resistivity ρ of ZnTe:P and $Zn_{0.99}Mn_{0.01}Te$:P as a function of the temperature at selected magnetic fields.

$$\varepsilon_p(H,T) = \left(\frac{0.8\beta}{g\mu_B}\right)^2 \frac{\chi(H,T)}{32\pi a^3}, \tag{1}$$

where the factor 0.8 describes the orbital quenching of the spin splitting [6], β is the exchange constant of the valence band, $\chi = \partial M_0/\partial H$ magnetic susceptibility of Mn ions system, a is the effective Bohr radius. Because of a very large β value in $Zn_{1-x}Mn_xTe$ ($\beta = 1.09$ eV [7]) ε_p is very high. From Eq. (1) one can evaluate ε_p (0, 4.2 K) ≈ 8 meV for $x = 0.01$, whereas the E_a evaluated from the resistivity slop at 4.2 K equals *ca.* 1.3 meV. It means that the $Zn_{0.99}Mn_{0.01}Te$:P sample is not on the insulating side of MIT, but also does not show the metallic behavior such as ZnTe:P. Following the two-liquid model we deal here with localized spins of holes, which coexist with the Fermi liquid [4]. These spins polarize Mn spins and formation of BMPs does occur. Bound magnetic polarons, in turn, constitute an efficient source of spin–spin scattering, lowering the electrical conductivity. This explains, at least qualitatively, the temperature dependence of resistivity in $Zn_{1-x}Mn_xTe$:P.

Figure 1, as well as Fig. 2, which present resistivity as a function of magnetic field at selected temperatures, show an immense, negative magnetoresistance in $Zn_{0.99}Mn_{0.01}Te$:P sample — $\rho(0, 1.3\text{ K})/\rho(6\text{ T}, 1.3\text{ K}) > 10^3$. At the same time in ZnTe:P sample we deal with a weak (*ca.* 5%) positive magnetoresistance. In terms of MIT this means that applying a magnetic field drives $Zn_{0.99}Mn_{0.01}Te$:P sample back towards the metallic phase. This effect is due to the destruction of BMP and the following suppression of its contribution to the scattering. The external magnetic field induces an alignment of localized Mn spins, thus at a high field the magnetization saturates and $\chi(H,T) \to 0$ in Eq. (1).

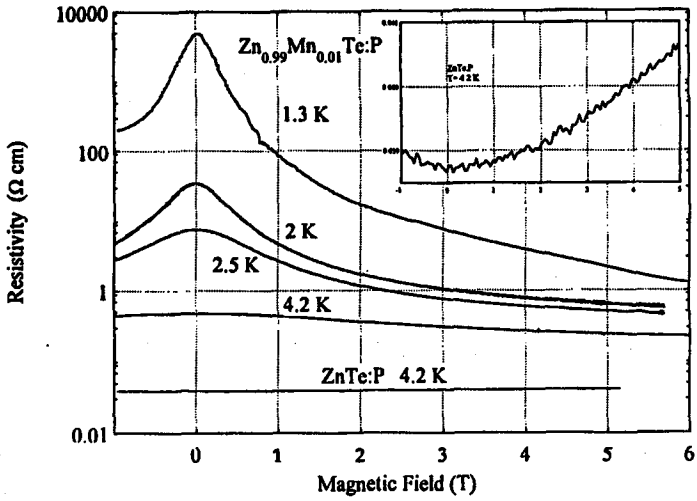

Fig. 2. Resistivity of $Zn_{0.99}Mn_{0.01}Te$:P at 1.3 K, 2 K, 2.5 K, 4.2 K and ZnTe:P at 4.2 K as a function of an external magnetic field. The inset shows the positive magnetoresistance of ZnTe:P sample.

In summary, we have demonstrated that $Zn_{1-x}Mn_xTe$:P crystals with a high hole concentration can be fabricated by the high-pressure Bridgman method, using phosphorus as an efficient dopant. We also show that in the p-type $Zn_{1-x}Mn_xTe$:P the p–d exchange interaction very strongly influences magnetotransport phenomena.

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