Magnetic properties of Mn and Co doped $PbPdO_2$

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We report the dramatic change of gapless semiconductor properties by different chemical doping elements of Co and Mn into $PbPdO_2$. The metal-insulatorlike transition temperature $T_{MI} = 100$ K for $PbPdO_2$ shifts to a higher temperature of 150 K by the Co doping and to a lower temperature of 70 K by the Mn doping. Because of the anisotropic band structure with the majority of heavy holes and the minority of light electrons, the transport and magnetic properties are significantly changed by the chemical doping elements. At low temperatures, the Co doping enhances ferromagnetic interactions, whereas the Mn doping favors antiferromagnetic interactions. These results are of great interests because you can control the magnetic ordering as well as manipulate the carrier density by changing the doping elements. These materials could be a good candidate for spintronics applications. © *2011 American Institute of Physics*. [doi:10.1063/1.3554218]

I. INTRODUCTION

The interest in spintronics has been accelerated since the discovery of giant magnetoresistance.[1,2] Materials suited for spintronics applications are those with long spin scattering lengths and high spin polarization. Half metals and magnetic semiconductors are a promising candidate for spintronics application. Half metals are fully spin polarized and metallic, thus they have short spin relaxation lengths. On the other hand, magnetic semiconductors have long spin relaxation lengths but low spin polarization. The magnetic gapless semiconductor is a material in the boundary where a high spin polarization and a long spin relaxation length could be achieved. There exist Hg based gapless semiconductors such as HgCdTe,[3,4] which is toxic and easily oxidized. Recently, $PbPdO_2$ was proposed as an oxide gapless semiconductor.[5] The Co doped $PbPdO_2$ is theoretically proposed to be a spin gapless semiconductor with 100% spin polarization.[5] Similarly by magnetic ion doping, a different type of gapless semiconducting properties can be achieved. In this paper we present the transport, magnetic, magneto-transport properties of Mn and Co doped $PbPdO_2$ samples, compared with those of the native $PbPdO_2$.

II. EXPERIMENTAL

Polycrystalline samples of $PbPdO_2$, $PbPd_{0.9}Co_{0.1}O_2$, and $PbPd_{0.9}Mn_{0.1}O_2$ were produced by sintering high purity powders of β-PbO (99.999%), PdO (99.9%), and the corresponding magnetic oxides of CoO (99%) or MnO (99.9%). The stoichiometric amounts of powders were ground and pressed into a pellet. The 10 mol% excess of PbO was added due to its volatility. The pellet was sintered at the temperature of 700 in air for 12 h. The grinding and heating was repeated several times to improve the homogeneity. The resulting samples were confirmed to be single phased by the x-ray diffraction powder measurements. The lattice parameters were obtained to be $a = 9.455$ Å, $b = 5.460$ Å, and $c = 4.660$ Å in an orthorhombic cell. The crystal structure and lattice parameters are consistent with those reported previously.[6–8]

The transport properties were measured by the Quantum Design physical property measurement system (PPMS). The electrical resistivity data were taken in the temperature range between 2 and 300 K using the conventional four probe method. The Hall measurement was performed with the five probe technique by sweeping the magnetic field between −9 and 9 T. For the magnetoresistance measurements, the magnetic field was applied in the transverse direction of the current at several temperatures. The magnetic properties were measured by the means of Quantum Design superconducting quantum interference device-vibrating sample magnetometer (SQUID-VSM). The temperature dependence of magnetic susceptibility was obtained in a field of 1 kOe after zero field cooling and in-field cooling.

III. RESULTS AND DISCUSSION

The temperature dependence of resistivity for Co and Mn doped $PbPdO_2$ is plotted in Fig. 1, where the inset represents the data of the native $PbPdO_2$. The resistivity data show a metallic behavior ($d\rho/dT < 0$) at high temperatures and insulating behavior ($d\rho/dT < 0$) at low temperatures for all the samples. The absolute resistivity value of $PbPdO_2$ is 1 order of magnitude higher than those of the two doped $PbPdO_2$. For the un-doped $PbPdO_2$, the transition temperature where the resistivity changes from metallic to insulating behavior is $T_{MI} = 100$ K, which is changed into 150 K for the Co-doped $PbPdO_2$ and 70 K for the Mn-doped $PbPdO_2$. In the temperature range showing the insulating behavior, the resistivity data could not be fitted by the Arrhenius form.[9] This implies that the increase of resistivity at low temperatures does not result from a thermally activated behavior due to opening a bandgap. The origin of the

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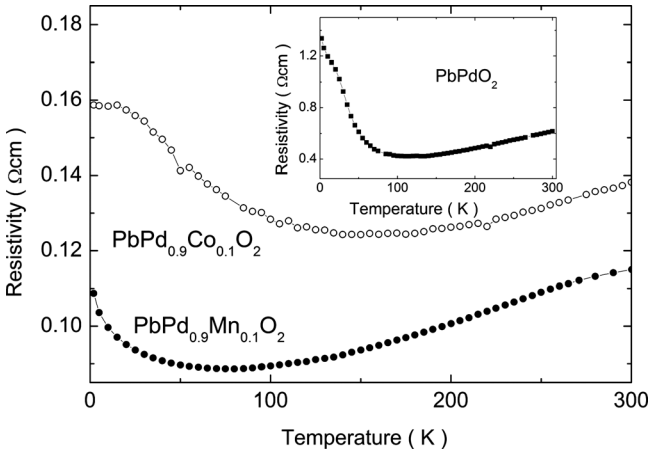

FIG. 1. Temperature dependence of electrical resistivity for Co and Mn doped $PbPdO_2$. The inset shows the resistivity data of un-doped $PbPdO_2$.

existing T_{MI} can be found by the Hall measurements, which give the information of charge carrier type and carrier density. Thus, we measured the Hall voltage as a function of temperature. The positive slope of the Hall voltage versus magnetic field curve yields *the p-type carriers, i.e. holes*. Assuming one carrier model, the carrier density is estimated to be $n = 4.82 \times 10^{17}/cm^3$ for $PbPdO_2$ at room temperature. By Co doping the carrier density is increased by 1 order to $5.13 \times 10^{18}/cm^3$, while the Mn doping case gives an almost similar value of $5.97 \times 10^{17}/cm^3$ to that found in the native $PbPbO_2$. From the obtained carrier density, we could calculate the mobility because the electrical resistivity is determined by the carrier density and its mobility. The calculated mobility of $PbPdO_2$ is 21 cm^2/Vs, which is decreased into 8.8 cm^2/Vs for the Co-doped sample and is increased into 90.88 cm^2/Vs for the Mn-doped sample. This result shows that the increase of carrier density by the Co doping diminishes the mobility by increasing the scattering points. The increase in mobility of the Mn doped sample without the change of carrier density suggests that the Mn doping injects different type of charge carriers, i.e. electrons with high mobility. It is predictable that the $PbPdO_2$ has two different carrier types with a large number of heavy holes and a small number of light electrons. With this scenario we can understand the temperature dependence of resistivity. As the temperature is lowered, the carrier density shows a minimum at T_{MI} where the mobility shows a maximum. The resistivity behavior is governed by the electrons with relatively high mobility, even though the majority carriers are heavy holes.

Figure 2 shows the temperature dependence of magnetic susceptibility measured in a field of 1 kOe. $PbPdO_2$ is basically diamagnetic except the low temperature regime where the magnetic susceptibility increases. This is of particular interest because $PbPdO_2$ is expected to be nonmagnetic. Small amounts of oxygen vacancies or spin-orbit coupling can be the origin of the ferromagnetic component at low temperatures.[10] This low-temperature ferromagnetic component is also observed in the Co-doped samples. The insets of Figs. 2(a) and 2(b) demonstrates the ferromagnetic component in addition to the diamagnetic and paramagnetic backgrounds for $PbPdO_2$ and Co-doped sample, respectively. The

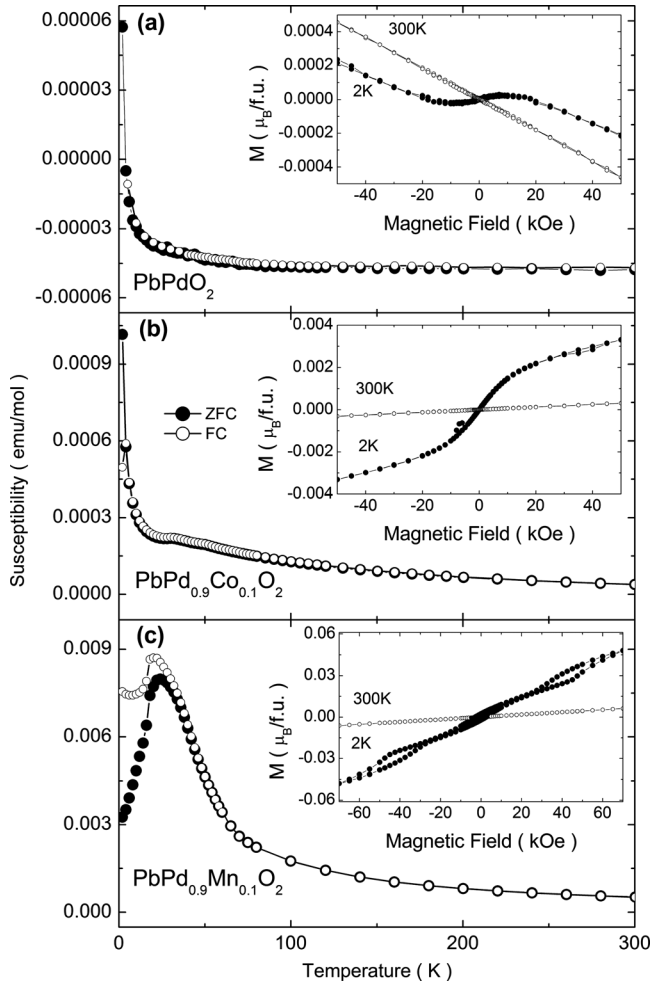

FIG. 2. Temperature dependence of magnetic susceptibility measured in a field of 1 kOe for un-doped, Co-doped, and Mn-doped $PbPdO_2$. The insets represent the corresponding magnetization vs field curves at 2 and 300 K.

high-temperature data of the Co and Mn doped $PbPdO_2$ could be fitted by the modified Curie-Weiss law including a temperature independent susceptibility term,[11,12] whereas those of the native $PbPdO_2$ could not. For the Co doped sample, the effective magnetic moment per Co ion is estimated to be $\mu_{eff} = 4.65\ \mu_B$ and the paramagnetic Curie temperature is $\theta_P = -71.80$ K. The effective magnetic moment is close to the value for the divalent Co ion which is 4.8 μ_B. The sign and magnitude of θ_P can be considered as a measure of dominant magnetic interaction. The negative θ_P value implies antiferromagnetic interactions in the Co doped $PbPdO_2$. However, the low-temperature data show an increase, indicating that the dominant interactions are ferromagnetic. On the other hand, the Mn doped sample gives the effective magnetic moment of $\mu_{eff} = 11.78\ \mu_B$ per Mn ion and the paramagnetic Curie temperature of $\theta_P = 4.65$ K. The much larger value of μ_{eff} is unexpected as the full moment ($= 4.9\ \mu_B$) of Mn^{2+} ion. Even if the Mn is substituted for Pd in $PbPdO_2$, the magnetic behavior may not be described in a simple localized spin picture. The much smaller positive θ_P value represents weak ferromagnetic interactions, but the antiferromagnetic transition is observed at 20 K. The magnetization versus field curve shows a weak ferromagnetic behavior with hysteresis at low fields and a strong metamagnetic

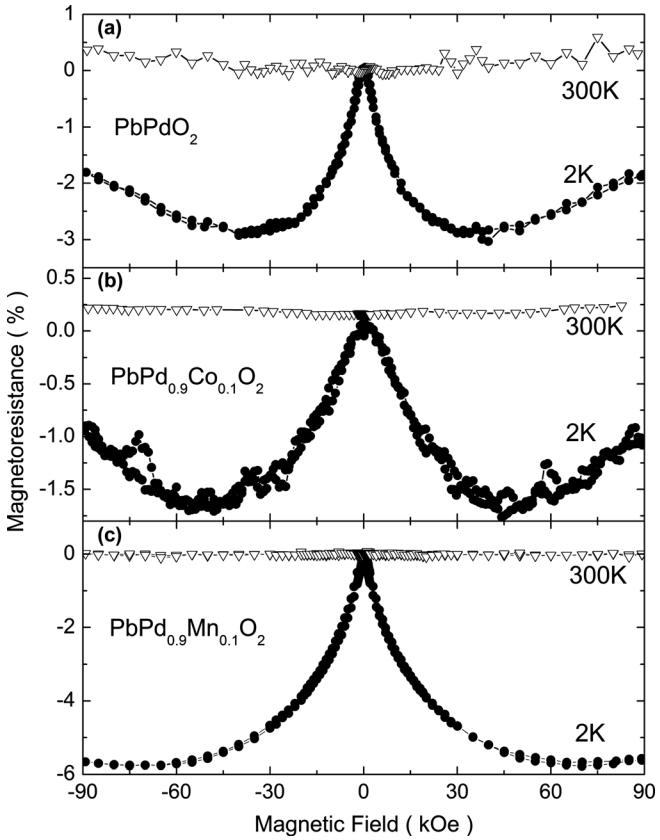

FIG. 3. Magnetoresistance curves as a function of magnetic field applied along the transverse direction of the current at 2 and 300 K.

transition around 50 kOe, as shown in the inset of Fig. 2(c). The metamagnetic transition verifies the antiferromagnetic ordering at low temperatures.

In Fig. 3 is displayed the transverse magnetoresistance data. It is common for all the samples that at 300 K the magnitude of the magnetoresistance is almost constant. The overall trends of the 2 K data are negative magnetoresistance at low fields and positive magnetoresistance at high fields. There seem to be two possible origins which could account for the negative magnetoresistance. Either the magnetic field gives up the quantum interference or weak localization due to the spin-orbit coupling,[13] or the magnetic field increases the mobility due to the spin scattering of carriers in an impurity band.[14] Since the electrical conduction is governed by the light electrons, the increase of mobility with field is more convincing for the negative magnetoresistance. The negative slope disappears with the ferromagnetic component in the magnetization. Thus, we can conjecture that the spin scattering plays an important role in the magnetoresistance behavior. Further studies with single crystals are needed for the magneto-transport mechanism.

IV. CONCLUSION

We have studied the Co and Mn doping effects on gapless semiconductor $PbPdO_2$. The metal-insulator transition temperature $T_{MI} = 100$ K for $PbPdO_2$ shifts to higher temperature of 150 K by the Co doping and to lower temperature of 70 K by the Mn doping. From the electrical resistivity and Hall measurements, the most striking feature is the anisotropic band structure that the majority of charge carriers are heavy holes and minority are light electrons. For the Co-doped $PbPdO_2$, the increase of hole carrier density diminishes the electron mobility because of the more scattering events. On the other hand, the Mn-doped $PbPdO_2$ gives rise to the increase of mobility with no change in the hole carrier density. The magnetic properties are more significantly changed by the chemical doping elements. The Co doped sample exhibits ferromagnetic components at low temperatures, whereas the Mn doped sample favors antiferromagnetic interactions. A metamagnetic transition around 50 kOe is observed in the low temperature magnetization curves because of the antiferromagnetic ordering in the Mn doped $PbPdO_2$. These magnetic behaviors cannot be understood in a framework of simple localized spin picture.

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