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Disorder enhanced spin polarization of $Zn_{1-x}Co_xO_{1-v}$ concentrated magnetic semiconductor

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Amorphous concentrated magnetic semiconductor $Zn_{0.32}Co_{0.68}O_{1-v}$ (v refers to oxygen vacancies) thin film was investigated by magnetic, electrical transport and Andreev Reflection spectroscopy. At low temperature range, electron in the $Zn_{0.32}Co_{0.68}O_{1-v}$ is strongly localized and electrical transport obeys Efros variable range hopping law. Spin polarization was measured by Andreev Reflection spectroscopy. As high as 64±5% of spin polarization was attained through fitting of modified Blonder-Tinkham-Klapwijk (BTK) theory. This enhanced spin polarization of $Zn_{0.32}Co_{0.68}O_{1-v}$ likely relates with structure disorder and high concentration of magnetic cobalt ions which lead to a spin imbalance impurity band in the tail of conduction band. Considering room temperature ferromagnetism and high spin polarization, this material appears to be promising for spintronics device applications.

Introduction

Oxide magnetic semiconductor that combines both semiconducting and room temperature ferromagnetic properties is currently one of most attractive research fields in spintronics.[1] For application of spintronics materials, high spin polarization of charge carrier is of fundamental importance.[2] Many techniques, such as superconducting tunnel junctions, spin-resolved photoemission and Andreev reflection(AR), had been used to study spin polarization of magnetic materials.[3 4 5] Those materials include magnetic metal, half-metal Heusler alloy, III-V group magnetic semiconductors, concentration magnetic semiconductors and semimetal. [5 6 7 8 9] For oxide magnetic semiconductors, many efforts had been toward to understanding of the nature of ferromagnetism, spin-dependent electrical transport (magnetoresistance, anomalous Hall effect.) and magneto-optical effect.[10 11] However, only a few works had reported on the spin polarization of oxide magnetic semiconductors, especially, the direct measurement of the spin polarization by Andreev reflection.[12 13] Yates et al. found that 55% spin polarization only exists in (Mn,Al) co-doped ZnO thin film. In contrast, Panguluri et al. reported 50% spin polarization in undoped In_2O_3 thin film at helium temperature. To clarify the role of transition metal and yield higher spin polarization in oxide magnetic semiconductors, further works still need to be done.

Conventionally, it is acknowledged that the structure disorder is detrimental on spin polarization due to nanoscale coherence length of spin current. Recently, disorder related spin polarization enhancement received a raising interesting in amorphous ferromagnetic metal and magnetic semiconductors. In metal-based spintronics, disorder enhanced spin polarization was reported on CoFeB in magnetic tunneling junctions and Andreev reflection spectroscopy.[14 15] For magnetic semiconductor investigation, Byoughak Lee et al. had theoretically predicted an enhanced spin polarization in impurity bands of $Ga_{1-x}Mn_xAs$ diluted magnetic semiconductor due to formation of Mn clusters which results in strongly polarized bound states.[16] Hu et al. reported long-range ferromagnetic order in non-stoichiometric amorphous $Co_{0.5}Zn_{0.5}O_{1-v}$ ternary transition metal oxide semiconductor in theory and experiment.[17] In particular, cobalt doped ZnO magnetic semiconductor ($Zn_{1-x}Co_xO_{1-v}$) is a notable material for practical application and fundamental physics investigation due to their room temperature ferromagnetism, visible photoconductivity, large Zeeman splitting by sp-d exchange interaction and small spin-orbital interaction (which is important for high spin polarization).[11 18] Over the past decades, most attentions had been put on the origin of long-range ferromagnetism of crystalline doped ZnO and determinate conclusion is coming.[11] Although the emerging effect of disorder on spin polarization of magnetic materials is unquestionable, neither has there been an experimental measurement, nor has the impact of interface on the spin polarization of amorphous $Zn_{1-x}Co_xO_{1-v}$ magnetic semiconductor been investigated.

In this paper, amorphous concentrated magnetic semiconductor (CMS) $Zn_{0.32}Co_{0.68}O_{1-v}$ thin film is studied by magnetic, electrical transport and Andreev reflection spectroscopy. Through Andreev reflection spectroscopy, it has been revealed that

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spin polarization of $Zn_{0.32}Co_{0.68}O_{1-v}$ is as large as 64%±5% which is larger than that of crystalline $Zn_{1-x}Co_xO_{1-v}$ magnetic semiconductor and metal cobalt reported.[12, 13] Such enhanced spin polarization can be attributed to strong exchange interaction that is correlated to the structure disorder and high concentration of magnetic cobalt ions in amorphous $Zn_{0.32}Co_{0.68}O_{1-v}$.

Experimental methods

The concentrated magnetic semiconductor $Zn_{0.32}Co_{0.68}O_{1-v}$ thin film was deposited by alternating sputtering 5Å Co layers and 5Å ZnO layers 30 periods at 20℃ on glass substrate in pure Ar atmosphere with 0.5Pa sputtering pressure. The relatively low temperature growth and alternating deposition are a thermal nonequilibrium process, which guarantees a high solubility of cobalt in CMS and to prevent formation of metallic cobalt cluster. A similar preparation process was described for $Ti_{1-x}Co_xO_{2-v}$ and $Zn_{1-x}Co_xO_{1-v}$ CMS thin film deposition in refs. 19 and 20. Transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS) studies in these films indicate that the composition of $Zn_{1-x}Co_xO_{1-v}$ and $Ti_{1-x}Co_xO_{2-v}$ CMS thin film is uniform at nanometer scale but maybe inhomogeneous at the sub-nanometer scale. On the other hand, as the thickness of ZnO less than 1nm, x-ray diffraction （XRD）and TEM results suggest that the microstructure of $Zn_{1-x}Co_xO_{1-v}$ CMS thin film is in an amorphous state but containing small crystal grains with average size 4-6 nm.[19 20 21] However, no metallic Co clusters, CoO insulator clusters or ZnO tunneling boundary were detected within whole film, which is different from tunneling granular film with similar deposition process.[22] The magnetic and electrical measurements of $Zn_{0.32}Co_{0.68}O_{1-v}$ films were carried by alternating gradient force magnetometer (AGM) and van der pauw method, respectively.

In order to probe spin polarization information of $Zn_{0.32}Co_{0.68}O_{1-v}$ CMS and excludes the existence of metallic Co or CoO cluster, planar junctions of $Zn_{0.32}Co_{0.68}O_{1-v}$ (30nm)/Pb (500nm) were fabricated on glass substrates defined by shadow mask and the spin polarization was obtained through Andreev reflection spectroscopy. At first, a 30 nm thickness Ag stripe was sputtered as bottom electrode. Then $Zn_{0.32}Co_{0.68}O_{1-v}$ thin film with 30nm thickness was deposited. Finally, the sample was transfer into another ultra-high vacuum chamber without air expose and a crossed Pb stripe with 500nm thickness was grown by thermal evaporation. The growth rate of Pb film was larger than 3nm/s and chamber pressure was kept below $1x10^{-4}$Pa during Pb film deposition. The effective junction area is $0.1*0.1mm^2$ and junction resistance varied from several ohms to tens ohms. There are two points deserved to mention during junction fabrication process. The first one is for the $Zn_{0.32}Co_{0.68}O_{1-v}$ CMS thin film growth, the last layer is not ZnO but 5Å Co in order to get good ohmic contact with superconducting Pb. The second one is that resistivity of $Zn_{0.32}Co_{0.68}O_{1-v}$ film is of order of mOhm*cm; it served as conducting electrode rather than insulating barrier. The differential conductance spectra G(V)=dI(V)/dV, were measured by standard lock-in technology at liquid-helium temperature and the amplitude of the ac modulation was kept sufficiently small in order to avoid heating and other spurious effects. All differential conductance spectra were normalized by the conductance above gap voltage. We also fabricated thicker $Zn_{0.32}Co_{0.68}O_{1-v}$(60nm)/Pb(500nm) junctions and consistent measurement results are obtained suggesting the spin polarization is not an interface effect and thickness independence.

Results and discussion

Fig. 1(a) shows the magnetization hysteresis loop of $Zn_{0.32}Co_{0.68}O_{1-v}$ thin film measured at 300K. The sample shows room temperature ferromagnetism where magnetization saturates at H=3000 Oe and Hc is about 100 Oe (Inset of Fig. 1(a)). Fig. 1(b) shows negative temperature dependence of resistivity at magnetic field 0 Oe and $6×10^5$ Oe, respectively. The increasing R with decreasing temperature suggests the semiconductor conducting property, which has been proved by theory and experiment.[17] LnR-$T^{-1/2}$ fitting of resistance-temperature (inset of Fig.1 (b)) suggests the electrical transport obeys Efros variable range hopping (VRH) in the low temperature range.[22] The conducting electrons are strongly localized and transport dominated by electron hopping from the initial localized occupied state *i* to the final vacant state *j* due to thermal activation. It deserves to note that negative magnetoresistance of $Zn_{0.32}Co_{0.68}O_{1-v}$ indicates the spin polarized carriers due to strong coupling between them and localized magnetic moments.[20]

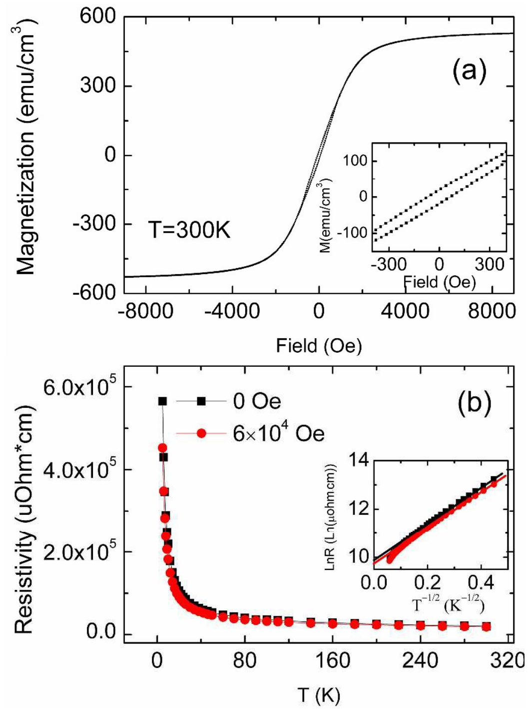

Fig. 1. (a)The magnetization hysteresis loop of $Zn_{0.32}Co_{0.68}O_{1-v}$, the inset shows magnification of low field loop. (b) The temperature dependence of resistivity of $Zn_{0.32}Co_{0.68}O_{1-v}$, the inset is LnR-$T^{-1/2}$ fitting.

Moreover, no anisotropic magnetization or magnetoresistance was observed in $Zn_{0.32}Co_{0.68}O_{1-v}$ thin film for magnetic field applied to parallel or perpendicular to the plane. The isotropy in magnetization and magnetoresistance are consistent with amorphous microstructure while anisotropy had been reported in Co nanoparticle embedded ZnO or granular thin films.[23]

For spintronics devices application and fundamental physics investigation, it is very important to get the spin polarization information directly, especially for carriers which are localized at low temperature. Fig.2(a) shows a representative normalized differential conductance spectroscopy and fitting of modified Blonder-Tinkham-Klapwijk (MBTK) theory of $Zn_{0.32}Co_{0.68}O_{1-v}$ /Pb junction measured at temperature T=2K.[24, 25] The obvious suppression of subgap conductance suggests a moderated spin polarization in $Zn_{0.32}Co_{0.68}O_{1-v}$ thin film. Through the best fitting to the spin polarized BTK theory, P=64% with a certainty better than 5% was obtained. This 64% spin polarization of $Zn_{0.32}Co_{0.68}O_{1-v}$ thin film excludes determinately the possibility of cobalt metal cluster at the interface of $Zn_{0.32}Co_{0.68}O_{1-v}$ /Pb because it is larger than that of metal Co (35%).[5,12] More important, this result reveals that amorphous $Zn_{0.32}Co_{0.68}O_{1-v}$ with high concentration cobalt ions does enhance the spin polarization which maybe related the enhanced strength of exchange interaction between cobalt ions.

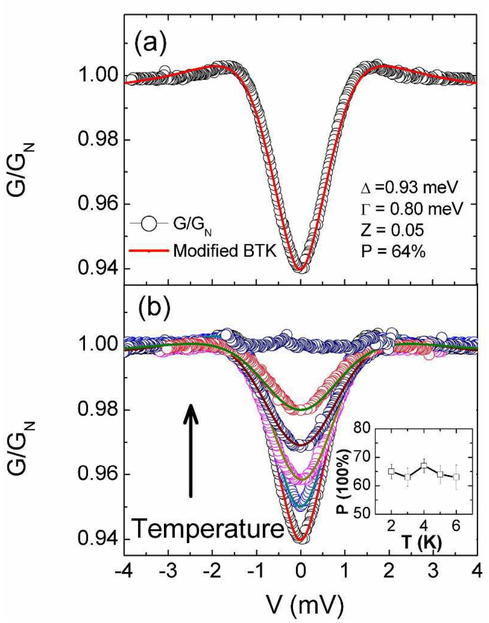

Fig. 2. (a) Normalized differential conductance spectroscopy of $Zn_{0.32}Co_{0.68}O_{1-v}$ /Pb junction measured at T=2K. The junction resistance is 16Ω. The red line is fitting of modified Blonder-Tinkham-Klapwijk (MBTK) theory. (b) Normalized differential conductance spectra (symbols) and MBTK fitting (solid lines) between T=2K and 7.2K. The inset shows temperature dependence of spin polarization with an average P=64%.

In order to get the best fitting to the BTK theory, four physical parameters, including spin polarization P, interfacial scattering barrier strength Z, superconducting gap Δ and inelastic broadening parameter Γ, are used.[24, 26, 27] We emphasize that the fitting is always performed in a straightforward manner with actual measurement temperature. For MBTK fitting of differential conductance spectra at T=2K, Z=0.05, Δ~0.93meV and Γ=0.80 meV are obtained. Consistent with low junction resistance, small barrier scattering strength Z can be qualitatively attributed to the enhanced junction transparence due to a moderated spin polarization.[7,8] The fitting yields the superconducting gap Δ~0.93meV, which is smaller than the bulk BCS gap of Pb~1.3meV, possibly attributed to the suppression of superconductivity due to interface intermixing or exist of magnetic impurity.[25, 28] Here the conductance peaks at ±Δ are absent completely since AR process does not require available quasiparticle states in the superconductor.[7] Based on Zutic and Das Sarma's theoretical results, the spin polarization actually enhances junction transparency of ferromagnet/superconductor junction.[29] Specially, the conductance peaks at ±Δ can be completely suppressed by a moderated spin polarization at the ferromagnet/superconductor interface.[29] Similar conductance characteristics have been confirmed in Andreev reflection spectra of CrO_2 half-metal.[6,30] In order to better understand nature of spectroscopy broadening in our junction, the inelastic scattering parameter Γ is introduced into energy term (E+iΓ) for fitting.[27] This inelastic term Γ is equivalent to the effective temperature ($\Gamma=\sqrt{2}\,T_{eff}$) that is often used in point contact Andreev reflection spectra fitting due to heating effect.[25, 31] Large inelastic scattering term Γ=0.80 meV is obtained which is nearly comparable to the magnitude of energy gap. Considering disordered interface of $Zn_{0.32}Co_{0.68}O_{1-v}$/Pb superconducting junction, cobalt oxide and a large amount of magnetic cobalt ions would results in high inelastic scattering strength at the interface which is also the reason of suppression of superconductivity. The high inelastic scattering leads to spectroscopy broadening and flatting conductance peaks at ±Δ. Furthermore, high inelastic scattering strength can cause spin-mixing effect (spin flips) and dilute the intrinsic spin polarization. Therefore, 64% spin polarization is underestimated and further clean interface is necessary for intrinsic spin polarization measurement and devices application.

We also studied temperature effect on the conductance spectra as shown in Fig. 2(b). As superconducting transition temperature of Pb is approached, the subgap conductance increases gradually. At critical temperature of Pb, Tc=7.2K, the conductance is a constant that is consistent with the good ohmic contact of $Zn_{0.32}Co_{0.68}O_{1-v}$ /Pb junction. As temperature increasing, the spin polarization remains constant in around 64±5% (inset of Fig. 2(b)). The corresponding fitting parameters, Z, Δ and Γ are summarized in Fig. 3(a)-(c). The interfacial scattering barrier strength Z is small while inelastic scattering Γ increases as temperature increasing. The superconducting gap value decreases and can be well fitted by BCS gap law, which is consistent with independence measurement of superconducting of Pb thin film.

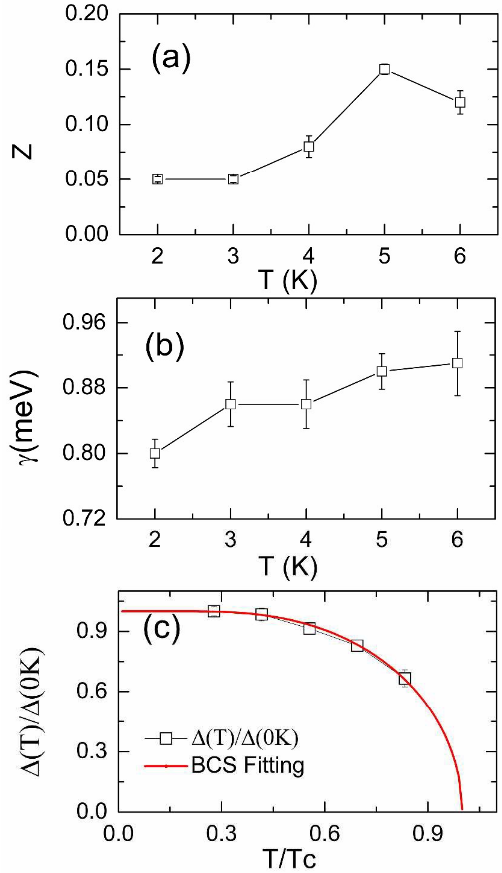

Fig. 3. The temperature dependence of parameters extracted from fitting the data in Fig. 2(b). (a) Interfacial scattering barrier strength Z, (b) inelastic broadening parameter Γ, (c) superconducting gap of Pb. The red line in (c) shows the best fit to the BCS gap law.

The Andreev reflection spectra shows quite clearly that, within the temperature range measured, the spin polarization of $Zn_{0.32}Co_{0.68}O_{1-v}$ can be enhanced by amorphous structure and high concentration of Co ions. The origin of spin polarization of $Zn_{0.32}Co_{0.68}O_{1-v}$, especially in variable range hopping regime, is a matter of considerable important in physics. Recent theoretical research in amorphous transition metal oxide found that high spin polarization and magnetization probably associated with the accommodation of concentrated transition metal atoms.[17] Compare to crystalline structure, there is much more of oxygen deficiencies in the amorphous thin film $Zn_{0.32}Co_{0.68}O_{1-v}$. These oxygen deficiencies offer charge carriers which mediated the ferromagnetic exchange interaction of cobalt magnetic moments. On the other hand, the high concentration of magnetic cobalt ions reduces the distance thus increases the strength of exchange interaction of local cobalt magnetic moments. Oxygen deficiency and high concentration of cobalt ions, both of them result in long range ferromagnetic in cobalt-rich region. Furthermore, the enhanced coupling of electrons and localized magnetic moment leads to a spin imbalance density of states in the tail of conduction band.[17] This spin polarized band structure also is indicated by the negative magnetoresistance in our $Zn_{0.32}Co_{0.68}O_{1-v}$ thin film. However, to clarify the influence of structure disorder on spin polarization of $Zn_{0.32}Co_{0.68}O_{1-v}$, further element-specific electronic structure study, such as x-ray absorption fine structure (XAFS), x-ray magnetic dichroism (XMCD) et al., are needed.

Conclusions

In conclusion, spin polarization of concentrated magnetic semiconductor $Zn_{0.32}Co_{0.68}O_{1-v}$ is probed by Andreev Reflection spectroscopy. The spin polarization is 64%±5% at low temperature in which charge carriers are in strong localization that reflected by Efros variable range hopping transport. We believe the spin polarization of $Zn_{0.32}Co_{0.68}O_{1-v}$ is underestimated due to strong inelastic scattering strength at the interface of $Zn_{0.32}Co_{0.68}O_{1-v}$ /Pb. To elucidate the nature of high spin polarization of localized carrier in concentrated magnetic oxide semiconductor, the correlation of microstructure and electronic structure, may shed some lights on spintronics materials and devices application.

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