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Role of defects in magnetic properties of Fe-doped SnO_2 films fabricated by the Sol–Gel method

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This paper obtains the room temperature ferromagnetism in $Sn_{1-x}Fe_xO_2$ films fabricated by the Sol–Gel method. X-ray diffraction results show that Fe doping inhibits the growth of SnO_2 and Fe^{3+} ions occupy the Sn sites. The measurement of resistance excludes the free carrier inducing ferromagnetism. Moreover, the temperature dependence of magnetization has been better fitted by the Curie–Weiss law and bound magnetic polaron (BMP) theory. An enhancement of ferromagnetism is achieved by annealing the samples with $x = 7.1\%$ in H_2, and a decrease of oxygen flow rate. All these results prove that the BMP model depending on defects can explain ferromagnetism in diluted magnetic oxides.

Keywords: diluted magnetic oxides, BMP model, defects
PACC: 8140R, 7510, 7155

1. Introduction

Because of the combined magnetic and transport properties in dilute magnetic semiconductors and the potential technological applications in spintronic devices such as spin transistors, spin light-emitting diodes, very high-density nonvolatile semiconductor memory, and optical emitters with polarized output, a growing effort is directed at studies of magnetic semiconductors with practical ordering temperature. Recently, ferromagnetism above room-temperature has been reported in transition metal-doped SnO_2 of rutile structure.[1−4]

It is believed that ferromagnetism is based upon the interactions between magnetic impurities, which can be mediated either by oxygen, hydrogen or by free carriers.[2] However, Nomura *et al*[1] report that defects can be perhaps the main source of ferromagnetism even in the presence of the magnetic iron ions, according to Mössbauer measurements.

In this paper, we have prepared SnO_2: Fe films with different concentrations by using a simple and economic method, the sol–gel method, and give a systematic analysis about the relation between ferromagnetism and oxygen vacancies or hydrogen. Qualitative fitting of the M–T curve of Fe-doped SnO_2 film was done in order to clarify the mechanism for magnetic ordering.

2. Experiments

$SnCl_4{\cdot}5H_2O$ and $FeCl_3{\cdot}6H_2O$ as starting materials were dissolved in a mixed solution of distilled water and alcohol. After refluxing at 80 °C and aging, the coating solution was prepared. The solution was dropped on rotated Si (111) substrate, and then a film was formed by spin-coating and dried at low temperature. By repeating this process, a precursor film with expected thickness was made and annealed at 500 °C for 2 hours in air. Under the same technological conditions, films with various Fe concentrations (0%, 2.3%, 3.9%, 7.1% and 12.8%) were fabricated. A series of annealing processes with the same annealing temperature (400 °C) and time (30min) but different atmospheres (oxidizing, hydrogenating) was performed in order to test the effect of oxygen and hydrogen on the formation of magnetic semiconductors for these samples whose ferromagnetism vanished in an Ar atmosphere.

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The composition was determined by inductive coupled plasma. The thicknesses of the samples were measured to be 140–220 nm by using an ellipse polarimeter. The crystal structures of Fe-doped SnO_2 were investigated by x-ray diffraction (XRD). A vibrating sample magnetometer (VSM) and superconducting quantum interference device (SQUID) were used to study the magnetic properties.

3. Results and discussions

Figure 1 (a) shows the XRD pattern of the Fe-doped SnO_2 film with $x = 12.8\%$ grown on Si (111) substrate. The crystal structure of all Fe-doped SnO_2 films is similar to that of undoped SnO_2 film without Fe oxides or other impurity phases, indicating that doping does not change the tetrahedron rutile structure of SnO_2. Using the Scherer formula of the Hall method $\beta \cos(\theta)/\lambda = 0.9/D + 4e\sin(\theta)/\lambda$, where β is full width at half maximum (FWHM) of SnO_2 diffraction peaks and e is mean strain, we can make a rough estimate of the average size of grains (D). From Fig.1(b), we can obtained that the grain size reduces from 14.5 nm for $x = 2.3\%$ to 5 nm when $x = 12.9\%$ with increasing x, indicating that Fe doping inhibits the growth of SnO_2, which is consistent with the result[1] of the Nomura group. The lattice constant c (calculated based on (110), (200), (211) peaks) decreases with Fe concentration from 3.201 Å (1 Å=0.1 nm) for undoped SnO_2 film to 3.185 Å for Fe-doped SnO_2 film with $x = 12.8\%$, which can be understood if we take into account the size of the ion radius of the Fe ion (0.64 Å), which is smaller than that of the Sn ion (0.71 Å) in octahedral coordination.[1] This result implies that Fe^{3+} ions occupied the Sn sites.

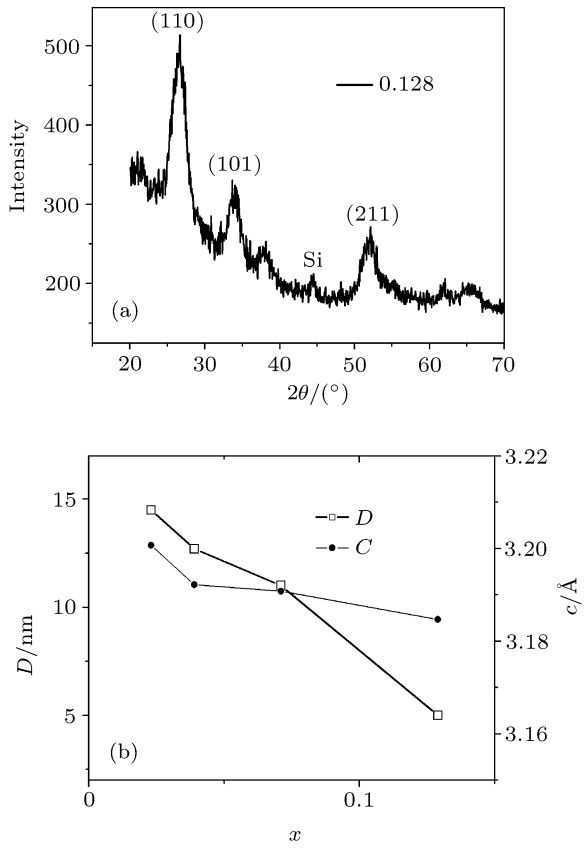


Fig.1. The XRD pattern of the Fe-doped SnO_2 film with $x = 12.8\%$ grown on Si (111) substrate. The Fe concentration dependence on lattice constant c and grain size D.

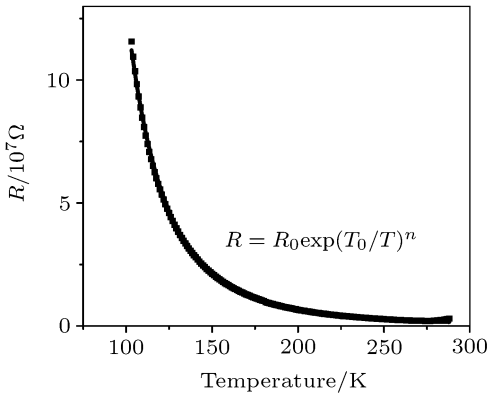


Fig.2. Temperature dependence of resistance (R) in $Sn_{0.964}Fe_{0.046}O_2$ film and the corresponding fitting curve (solid line).

The temperature dependence of the resistance (R) in $Sn_{0.964}Fe_{0.046}O_2$ film is also studied as shown in Fig.2. The resistance increases with the decrease of temperature until 103 K (R is too big to be detected when temperature is below 103 K) and the plot can be well fitted by the equation $R = R_0 \exp(T_0/T)^n$. The value of n cannot be obtained accurately unless more data at low temperature are measured. So it is hard to determine whether Mott's variable range hopping mechanism or thermal activated electron-tunneling can be used to account for the conducting mechanism of the Fe–SnO_2 film. In any case, the electrons were localized owing to the inhomogeneous structure. Also, the resistance increases with the increase of Fe, similar to Co–SnO_2 film,[5,6] showing that the localization was enhanced. This is because of charge compensation owing to Fe doping with fewer electrons or doped elements at the status of deep levels.[7–9] The resistivity of all samples is larger than 560Ω·cm, close to that of an insulator. So, the reduction of electrical diffusion makes the carrier concentration not enough to mediate long range ferromagnetic (FM) interaction

between Fe ions with transition temperatures higher than room temperature.

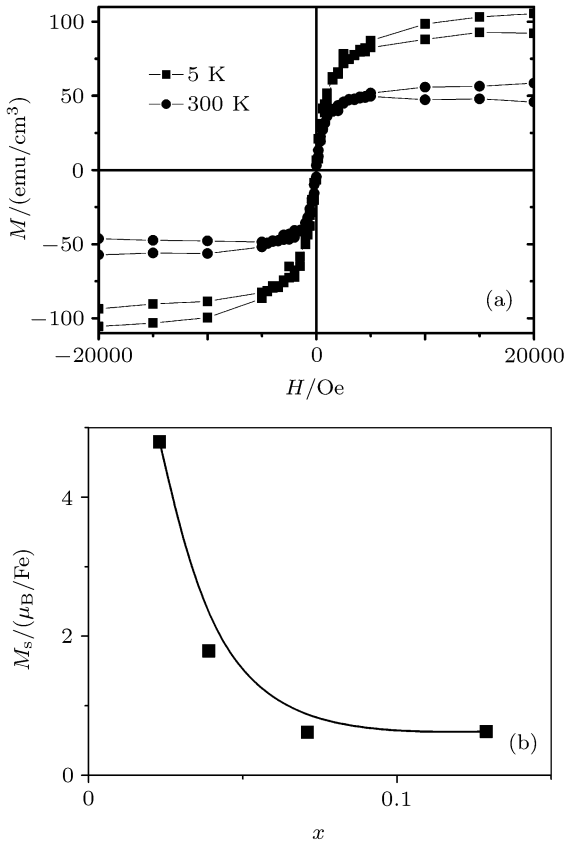


Fig.3. (a) Magnetic field dependence of the magnetization (M–H curves) measured at 5 K and 300 K by SQUID for $Sn_{1-x}Fe_xO_2$ film with $x = 3.9\%$. (1 Oe=79.5775 A/m) (b) The Fe concentration dependence of M_s measured by VSM at room temperature.

Figure 3(a) shows the magnetic field dependence of the magnetization (M–H curves) (the paramagnetic contributions from the sample holder, the sample and diamagnetic contributions from the Si substrate have been subtracted from the data) measured at 5 K and 300 K by SQUID for $Sn_{1-x}Fe_xO_2$ film samples with $x = 3.9\%$. Both hysteresis loops are obvious, showing that the magnetic transition temperature $T_c > 300$ K in the Fe-doped SnO_2 film. The magnetization at 5 K is 90 emu/cm^3, larger than that at 300 K (50.7 emu/cm^3). The origin of room temperature ferromagnetism can be understood in the scheme of the bound magnetic polaron (BMP) model[10] discussed in the following. A defect (such as a hole) and surrounding magnetic impurity ions compose a magnetic polaron through s–d exchange interaction, which leads to ferromagnetic exchange coupling between two magnetic impurities within the polaron. The presence of isolated polarons and isolated Fe^{+3} ions not taking part in polaron formation results in paramagnetism. As the temperature is lowered, the spins of neighbouring polarons become aligned, and clusters of polarons with the same spin appear. The lower the temperature is, the more such 'links' between polarons are established, and the larger the average cluster size is. When a cluster has the dimensions of the sample, the whole sample becomes ferromagnetic. In addition, using VSM measurement at room temperature (all the paramagnetic and diamagnetic contributions have been subtracted from the data), we find that the magnetic moment per Fe obtained (shown in Fig.3(b)) rapidly decreases with the increase of Fe concentration below $x < 7.1\%$; however, for the samples with $x > 7.1\%$, the variation trend is very slow, which is consistent with that of other reports.[5,7] The pure SnO_2 with the same condition is paramagnetic, even annealed in a reducing atmosphere, hence ferromagnetic coupling is introduced by Fe doping, only the defects cannot induce ferromagnetism of SnO_2 system at room temperature.

Figure 4(a) shows the temperature dependence of magnetization for $Sn_{0.961}Fe_{0.039}O_2$ film measured by SQUID in 5000 Oe (1 Oe=79.5775 A/m). The signal from the Si substrate (whose M–H curve was measured by SQUID at 5000 Oe, too) was subtracted. Considering that the M–T curve exhibits temperature variation of magnetization similar to that obtained by a theoretical estimation based on BMP,[10] and paramagnetism resulting from uncoupled spins and isolated polarons, we have fitted the thermal decrease of the magnetization by using

$$M(T)/M(0) = HM(0)C/(T-P) + \gamma[0.86 + K\ln(T_c/T)], \quad (1)$$

where C is the Curie constant, P is the Curie–Weiss temperature, γ is the infinite cluster's volume in the model of overlapping spheres and $K = (a_B^3 n_h)^{1/3}$, whose meaning has been referred to in Ref.[10].

The best fit for the sample is shown by the solid curve in Fig.5. The fitting parameter P is –4.58 K. The negative P indicates the existence of antiferromagnetism in Fe-doped SnO_2 films which may result from the superexchange interaction between nearest neighbour Fe^{3+} ions through O^{2-} for the sample with larger x. Moreover, the existence of antiferromagnetism can explain the decreased moment observed in the Fe-doped SnO_2 system (Fig.3(b)). The separation of the zero field curve (ZFC) and field curve (FC) measured in 100 Oe as shown in Fig.4(b) shows that the transition temperature is larger than 350 K, and

the absence of peaks on ZFC demonstrates that there are no Fe clusters in the samples.

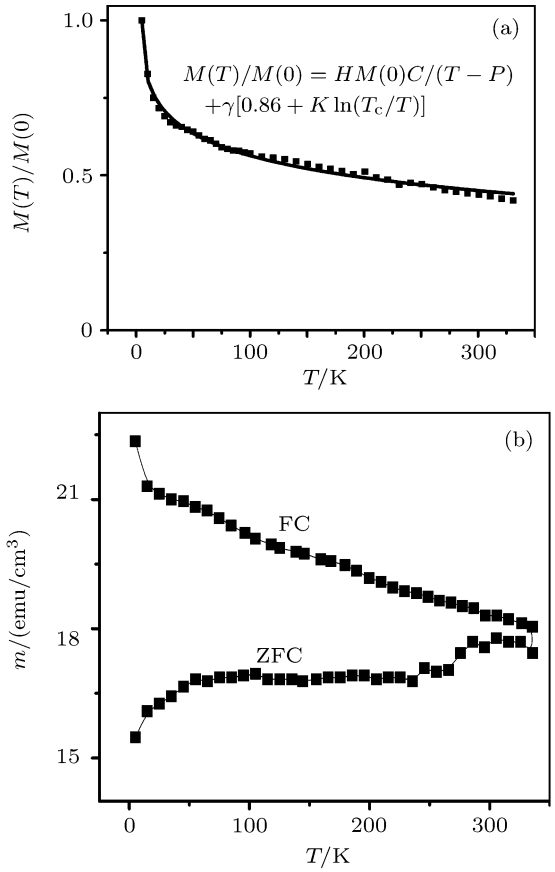


Fig.4. (a) Temperature dependence of magnetization in 5000 Oe. (b) The ZFC–FC curves in 100 Oe for $Sn_{0.961}Fe_{0.039}O_2$ film measured by SQUID, the fitting result of the M–T data is shown by the solid curve.

Based on the above analysis, the most appropriate understanding of the ferromagnetism is the BMP model.[7] The spins of the magnetic atoms are parallel through the electrons associated with a particular defect (oxygen vacancy). Based on BMP theory, this could imply that more defects can connect more BMPs together to enhance the ferromagnetic phase and M_s, and vice versa. So, to validate further the BMP model, the samples with $x = 7.1\%$ whose ferromagnetism vanished in Ar annealing atmosphere were annealed in low vacuum and O_2 atmosphere to control the oxygen vacancies to study the effect of oxygen vacancies on ferromagnetism of Fe-doped SnO_2 films. Ferromagnetism first increases when the oxygen flow rate is 5 sccm (standard-state cubic centimetres per minute) as shown in Fig.5(a), showing that the vacuum condition predominates and oxygen vacancies are increased, then gradually decline with increasing oxygen flow rate from 5 sccm to 30 sccm, which is expected since oxygen vacancies reduces gradually when the oxygen flow increases. Similar results have also been observed for Co–SnO_2 insulating films and Ni, Fe–TiO_2 films in vacuum annealing by other groups.[2,11,12] Figure 5(b) compares the hysteresis of $Sn_{0.929}Fe_{0.071}O_2$ films annealed in H_2/Ar whose ratios (R) are 5/95 and 10/90 sccm, respectively, since hydrogenated samples show robust ferromagnetism even above room temperature, obtained in diluted magnetic semiconductors. It is shown that the magnetization with R=10/90 is obviously larger than that of the sample with R=5/95, indicating that hydrogen can contribute to the enhancement of ferromagnetism in Fe-doped SnO_2 films by hydrogenating the dangling bond[13] or forming Fe–H bonds.[14] Charles *et al* found that at low temperature, and low P_{H2}, the hydrogen diffused into the host, filling the oxygen vacancies[15] and we also observe transition metal–hydrogen bonds in other systems (unpublished). So the defects on the centre of the polaron are different from those in the samples annealed in vacuum and an oxygen atmosphere.

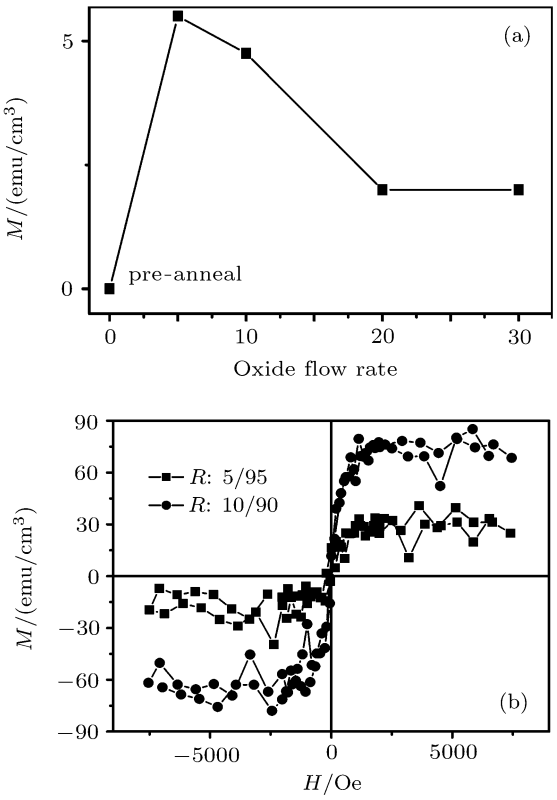


Fig.5. (a) Oxygen flow dependence of M_s for $Sn_{0.929}Fe_{0.071}O_2$ films annealed in vacuum. (b) The hysteresis loops of $Sn_{0.929}Fe_{0.071}O_2$ films annealed in H_2/Ar with ratios (R) 5/95 and 10/90 sccm, respectively.

4. Conclusions

In summary, we investigated the structure, magnetic property of Fe-doped SnO_2 films fabricated by the sol–gel method. The XRD patterns show that Fe doping does not change the tetrahedron rutile structure of SnO_2, and the lattice constant decreases with increasing x, showing that Fe substitutes for the Sn ion in the SnO_2 lattice. The resistance measurement illuminates that the electrons are localized. The origin of room temperature ferromagnetism can be explained by a model based on the interaction between BMPs including Fe ions and defects. So, the decrease of ferromagnetism in $Sn_{0.972}Fe_{0.038}O_2$ film with x is due to the existence of antiferromagnetism for the isolated polarons. The annealing atmosphere studies demonstrate that room temperature (RT) ferromagnetism can be enhanced by the increase of oxygen vacancies and hydrogen diffusion. In contrast, the decrease of the oxygen vacancy concentration by increasing the oxygen flow during annealing in vacuum can obviously degrade the RT ferromagnetism.

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