

Room Temperature Ferromagnetism of Ni-doped SnO₂ System

Junying Zhang (Corresponding author)

Department of Physics, Hexi University

Zhangye, 734000, China

Tel: 0936-8282065 E-mail: zhangjywang@163.com

Qu Yun

Agriculture University of Hebei

Baoding, 071000, China

Qianghong Wang

College of Electrical Engineering, Xian jiaotong University

Xian, 710049, China

Abstract

A series of Sn_{1-x}Ni_xO₂ films were fabricated by sol-gel method. All samples have pure rutile structure and exhibit room temperature ferromagnetism (RTFM). Magnetic moment per Ni ion decreases with the increase of Ni doping because antiferromagnetic super-exchange interaction takes place in the nearest neighbour Ni²⁺ ions for the samples with high x. The results of the annealing at oxidizing and reducing atmosphere show oxygen vacancies play a crucial role in producing ferromagnetism. This result supports that the origin of RTFM can be explained with Bound magnetic polaron (BMP) model.

Keywords: Oxygen vacancy, Room temperature ferromagnetism, Sol-gel method, Bound magnetic polaron

1. Introduction

Diluted magnetic semiconductors (DMSs) have recently attracted broad interest for their promise in generating and manipulating spin-polarized currents. Optically transparent ferromagnetic DMSs, obtained by doping transition metal ions into wide band gap semiconductors, have received particular attention for integrated opto-electronic materials. (Pearson, 2003, pp.4-6). For practical spintronic applications, ferromagnetic DMSs with Curie temperatures T_C greatly exceeding room temperature are required. After the prediction of RTFM for Mn-doped ZnO of Dietl (2000, p.1020) *et al*, there has been a lot of research following this trend. According to the theory given by K. Sato (2000, p.L556)*et al*, doping transition metal (TM) such as V, Fe, Ni, Co, and Cr into an oxide semiconductor host might introduce RTFM. This prediction has been supported by the recent reports that DMSs fabricated by doping TM into oxide semiconductors, such as TiO₂, ZnO, and SnO₂ etc, exhibit RTFM. (Park, 2002, p.8094. Zhenjun Wang, 2003, p.519. Dana A, 2004, pp.1395-1397. and Ogale, 2003, pp.077206-077208). However, the reports on SnO₂-based DMSs are much less compared to other oxide-based DMSs. (Fukumura T, 2004, pp.64-66. Nguyen Hoa Hong, 2005, p.267 and 2005, pp.1698-1700). SnO₂ along with TiO₂ and ZnO have n-type conduction, which is essential for spintronic devices. Therefore, SnO₂-based system is one of the most promising candidates for RTFM semiconductors. Recently, some research teams have doped Co, Fe, V, Cr or Ni into SnO₂ and obtained large magnetic moment. (Nguyen Hoa Hong, 2005, p.267. 2005, pp.6535-6538 and Coey, 2004, p.1333). Moreover, the magnetization of Sn_{1-x}M_xO₂ (moments per M ions, M = Fe, Mn or Co) is found to decrease with increasing x. (Kimura H, 2002, p.95. Coey, 2005, pp.174-178. and Abraham F, 2002, p.2218), because some antiferromagnetic super-exchange interaction takes place within neighbor M ions through O²⁻ ions (i.e. Fe³⁺-O²⁻-Fe³⁺ super-exchange). (Kimura H, 2002, p.95). Otherwise, the origin of magnetism still remains a question. Comparing with other preparation methods, such as pulsed laser deposition (PLD), molecular beam epitaxy (MBE), sputtering and so on, sol-gel method is lower-cost and easier to control the composition of DMS. In this paper, we report on the magnetism of Ni-doped SnO₂ thin films with different Ni content (from x = 0.016 to x = 0.2) by a simple sol-gel method and obtained polycrystalline structure DMSs.

2. Experimental

SnCl_4 and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled water and ethanol, following by circumfluencing at 80°C for 4 hours and aging for a week, then the solution was acquired. For the film preparation, the solution was spin-coated on Si (111) substrate following by heating at 120°C for 10 minutes. After multilayer-coating, the film precursors were obtained. The precursors of films were calcined at 600°C in air for 1 hour.

The structure was characterized by x-ray diffraction (XRD). The magnetic measurements were performed by a vibrating sample magnetometer (VSM, Lake Shore 7304) with an applied field of 8000Oe at room temperature. The content of nickel element was determined by an inductive coupled plasma emission spectrometer (ICP). X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK II) was employed to test the chemical valence of the elements in the films. In order to remove the surface contamination, the sample surface was sputter-etched for 10 minutes using an Ar^+ sputter gun ($E = 1\text{kV}$, emission current of $18\mu\text{A}$) before testing. An ellipsometer was used to measure the thickness of the films.

3. Result and discussion

Fig.1 shows TG-DTA curves of the dried SnO_2 gel. Two weight losses were observed at about $70\text{--}100^\circ\text{C}$ and $110\text{--}150^\circ\text{C}$ in the TG curve. The first weight loss may be from the evaporation of water and alcohol and the following weight loss by the combustion of resultant organics. Two small and sharp exothermic peaks were found at 90°C and 130°C respectively which were accompanied by the weight loss mentioned above. Any other weight loss in TG and any peak in DTA were not observed over 600°C , confirming that the organic materials were burned out at 600°C .

Fig.2 shows the XRD patterns of $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ films prepared at different temperatures ($T = 300^\circ\text{C}$, 600°C , and 800°C) in air for 1h. We can see that the intensity of diffraction peaks increases and the FWHM become narrow when annealing temperature increases. This result shows well crystallization of the sample at higher calcined temperature. The crystallization of the sample calcined at 300°C is poor because the organism can not completely burn out at lower temperature.

Fig.3 shows the XPS spectra for $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film, in which the adventitious C1s peak at 285.3eV binding energy. The two distinct peaks located at 853.9eV and 862.1eV with a separation of 8.2eV are identified with the binding energies of Ni^{2+} . This excludes the possibility of the formation of Ni clusters, since the binding energy difference of metal nickel is 17.4eV . Based on above analysis, we confirm that Ni ions in our samples have a chemical valence of $2+$. The binding energy of Sn3d (486.6eV and 494.7eV) and O1s (530.3eV) demonstrate that the valence of tin and oxygen in $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film are $4+$ and $2-$, respectively.

The magnetic properties of $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ films calcined at different temperature were shown in Fig.4, where the contribution from the diamagnetism of substrates was deducted. It is seen that $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film annealed at 600°C has a ferromagnetic moment of $0.63\mu_{\text{B}}/\text{Ni}$ and coercivity H_c of 200Oe , and the $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film annealed at 300°C has a ferromagnetic moment of $0.3\mu_{\text{B}}/\text{Co}$. But when the annealed temperature was 800°C , the ferromagnetism of $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film disappeared.

Considering that poor crystallitation for the samples calcined at 300°C , we chosen the calcining at 600°C for all the samples with different x. For all samples, the calcining at different temperature in air provided a rich-oxygen atmosphere. Under this condition, we could exclude the existence of the Ni clusters in a large part. Although we can not totally exclude the existence of NiO , it does not contribute to RTFM due to it is antiferromagnetism at room temperature ($T_N = 523\text{K}$).

The origin of RTFM has not been totally understood at present. Carrier-mediated exchange is a well accepted mechanism for the RTFM. (Venkatesan, 2004, p.177208). However, since our films were fabricated by a chemical synthesis method, the resistivity of the film is quite large (close to insulator). The results indicate that the RTFM in $\text{Sn}_{1-x}\text{Ni}_x\text{O}_2$ films does not arise from a carrier-mediated exchange interaction such as RKKY-type mechanism (RKKY: Ruderman-Kittel-Kasuya-Yosida), where a large density of mobile carriers are required to induce FM. In this case, a favorite interpretation on our results can be done in terms of a bound magnetic polaron (BMP) model (Coe, 2005, p.176).

In $\text{Sn}_{1-x}\text{Ni}_x\text{O}_2$ system, when Ni^{2+} ions doped into the host semiconductor SnO_2 , the Ni^{2+} ions substitution for Sn^{4+} ions results in the creation of oxygen vacancies in order to ensure charge neutrality. The presence of a certain concentration of oxygen vacancies plays an important role in conduction of RTFM. An electron trapped in the oxygen vacancy constitutes a hydrogenic orbital. The ferromagnetic exchange coupling takes place among the trapped electron and Ni^{2+} ions in this hydrogenic orbital. The trapped electron and the coupled Ni ions form polaron, and the overlap of magnetic polarons leads to the RTFM. Based on this model, the variation of RTFM

with calcining temperature can be understood as follow.

The magnetic moment of $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film annealed at 300°C is smaller than the film annealed at 600°C . This result could due to the remnant organism which hinders the exchange coupling among Ni^{2+} ions. Thereby, ferromagnetic exchange coupling between Ni^{2+} ions is weaken. On the other hand, the film annealed at 800°C , although has a better structure, but is lack of oxygen vacancy in comparison with the film calcined at 600°C , which results in the disappearance of RTFM.

XRD patterns of $\text{Sn}_{1-x}\text{Ni}_x\text{O}_2$ films (with $x = 0.016, 0.03, 0.09, 0.15$ and 0.2) calcined at 600°C in air for 1h are shown in Fig.5. It can be found that all of the samples show rutile structure of SnO_2 . Furthermore, within the resolution limit of the x-ray diffraction (5%), no additional phases such as Ni clusters, or NiO were seen in the samples. The peak positions do not show any measurable changes. As Ni content increases, the intensities of the peaks decrease and the full width at half maximum (FWHM) of diffraction peaks (110) become broader, indicating the possible changes of crystallite size. Using the Scherrer equation and FWHM, the crystal size can be estimated to be 10, 7, 6.8, 6 and 5.5 nm from $x = 0.016, 0.03, 0.09$ and 0.2 , respectively. This result proves that introducing of nickel dopant inhibits the growth of the grains.

In order to confirm the explanation of the origin of the RTFM in our samples, annealing studies were undertaken to study the dependence of ferromagnetism on oxygen vacancies. The annealing in both oxidizing atmosphere (oxygen flow of 80 sccm and protective gas argon flow of 50 sccm for 5h) and reducing atmosphere (low vacuum atmosphere, 100Pa, for 10min) were used at a low temperature of 200°C . The starting sample for anneals is the as-prepared $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film which was calcined at 600°C for 1 hour in air. As shown in Fig.6, the ferromagnetism of the film disappeared after annealing in oxidizing atmosphere. However, the ferromagnetism of the film recurred in reducing atmosphere, and the magnetic moment is similar to that of as-prepared film. More important, these experiments are reproducible. This behavior can be understood as the rich-oxygen atmosphere compensates the oxygen vacancy in sample and hence induces the disappearance of ferromagnetism while the vacuum annealing results in the increase of the oxygen vacancy which conduces the recurrence of ferromagnetism. The above results confirm that the oxygen vacancies play a crucial role in producing ferromagnetism in $\text{Sn}_{1-x}\text{Ni}_x\text{O}_2$ films.

Fig.6 displays the magnetic hysteresis loops for the films with different x from which it can be seen that all samples have RTFM. The relationship between magnetic moments of films and Ni content gotten from these loops is shown in Fig.7. It is obvious that the magnetic moment drops rapidly with the increase of Ni content. Other authors had reported the similar results in 3d elements doped oxide semiconductor films. (Ogale, 2003, pp.077206-077208 and Y.X.Wang, 2006, pp.042512-042513). One possible explanation is that with the increasing dopant, some antiferromagnetic super-exchange interaction takes place within the neighbor Ni^{2+} ions through O^{2-} ions (i.e. $\text{Ni}^{2+}-\text{O}^{2-}-\text{Ni}^{2+}$ super-exchange), which leads to the reduce of the average moment per Ni^{2+} ion.

4. Conclusions

In summary, a series of $\text{Sn}_{1-x}\text{Ni}_x\text{O}_2$ films were fabricated by sol-gel method successfully. The samples with different Ni content have pure rutile structure and exhibit RTFM. The annealing condition plays an important role in inducing the ferromagnetism in $\text{Sn}_{1-x}\text{Ni}_x\text{O}_2$ samples. The BMP model is a reasonable explanation for RTFM. Magnetic moment per Ni ion decreases with the increase of Ni doping because antiferromagnetic super-exchange interaction takes place among nearest neighbour in Ni^{2+} ions in the samples with high x .

Acknowledgment

This work is supported by National Natural Science Foundation of China (NO.50371034).

References

- Abraham F. Jalbout, Hanning Chen, and Scott L. Whittenburg. (2002). Monte Carlo simulation on the indirect exchange interactions of Co-doped ZnO film. *Appl. Phys. Lett*, 81, 2217-2219.
- Dana A. Schwartz, Kevin R. Kittilstved, and Daniel R. Gamelina. (2004). Above-room-temperature ferromagnetic Ni^{2+} -doped ZnO thin films prepared from colloidal diluted magnetic semiconductor quantum dots. *Appl. Phys. Lett*, 85, 1395-1397.
- Fukumura T, Yamada Y, Toyosaki H, Hasegawa T, Hoinuma H and Kawasaki M. (2004). The ferromagnetism of Co-doped TiO_2 and transition metal-doped ZnO. *Appl. Surf. Sci*, 223, 62-67.
- J. M. D. Coey, A. P. Douvalis, C. B. Fitzgerald, and M. Venkatesan. (2004). Ferromagnetism in Fe-doped SnO_2 thin films. *Appl. Phys. Lett*, 84, 1332-1334.

- J. M. D. Coey, M. Venkatesan and C. B. Fitzgerald. (2005). Donor impurity band exchange in dilute ferromagnetic oxides. *Nature Material*, 4, 173-179.
- K. Sato and H. Katayama-Yoshida. (2000). Material Design for Transparent Ferromagnets with ZnO-Based Magnetic Semiconductors, *J. Appl. Phys*, 39, L555- L558.
- Kimura H, Fukumura T, Kawasaki M, Inaba K, Hasegawa T and Koinuma H. (2002). Rutile-type oxide-diluted magnetic semiconductor: Mn-doped SnO₂. *Appl. Phys. Lett*, 80, 94-96.
- M. Venkatesan, C. B. Fitzgerald, J.G. Lunney, and J. M. D. Coey. (2004). Anisotropic Ferromagnetism in Substituted Zinc Oxide. *Phys. Rev. Lett*, 93, 177206-177209.
- Nguyen Hoa Hong and Joe Sakai. (2005). Ferromagnetic V-doped SnO₂ thin films. *Physica. B*, 358, 265-268.
- Nguyen Hoa Hong, Antoine Ruyter, and W Prellier. (2005). Magnetism in Ni-doped SnO₂ thin films. *J. Phys: Condens. Matter*, 17, 6533-6538.
- Nguyen Hoa Hong, Joe Sakai, W Prellier, and Awatef Hassini. (2005). Transparent Cr-doped SnO₂ thin films: ferromagnetism beyond room temperature with a giant magnetic moment. *J. Phys: Condens. Matter*. 17, 1697-1702.
- S. B. Ogale, R. J. Choudhary, J. P. Buban, and S. R. Shinde. (2003). High Temperature Ferromagnetism with a Giant Magnetic Moment in Transparent Co-doped SnO_{2-δ}. *Phys. Rev. Lett*, 91, 077205-077208.
- S. J. Pearton, C. R. Abernathy, M. E. Overberg, G.T. Thaler, D. P. Norton, N. Theodoropoulou, A. F. Hebard, Y. D. Park, F. Ren, J. Kim, and L. A. Boatner. (2003). Optical and magnetic properties of ZnO bulk crystals implanted with Cr and Fe. *J. Appl. Phys*, 93, 1-13.
- T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand. (2000). Optical and magnetic properties of ZnO bulk crystals implanted with Cr and Fe. *Science*, 287, 1019-1022.
- W. K. Park, R. J. Ortega-Hertogs, J. S. Moodera, A. Punnoose, and M. S. Seehra. (2002). Controlled transformation of paramagnetism to room-temperature ferromagnetism in cobalt-doped titanium dioxide. *J. Appl. Phys*, 91, 8093-8095.
- Y. X. Wang, Hui Liu, Z. Q. Li, X. X. Zhang, R. K. Zheng and S. P. Ringer. (2006). Role of structural defects on ferromagnetism in amorphous Cr-doped ZnO films. *Appl. Phys. Lett*, 89, 042511-042513.
- Zhenjun Wang, Wendong Wang, Jinke Tang, Le Dung, Leonard Spinu, and Weilie Zhou. (2003). Electrical and ferromagnetic properties of Tb-doped indium–tin oxide films fabricated by sol–gel method. *J. Appl. Phys*, 83, 518-520.

Figure captions:

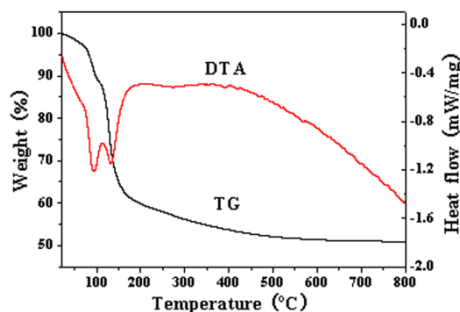


Figure 1. TG-DTA curves of the dried SnO₂ gel.

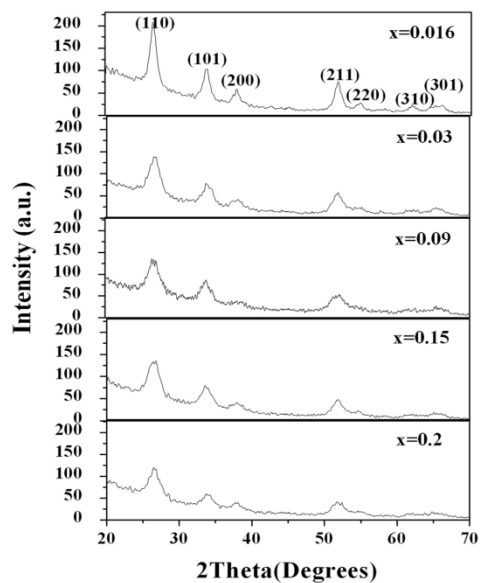


Figure 2. XRD patterns of $\text{Sn}_{1-x}\text{Ni}_x\text{O}_2$ films with different x annealed in air at 600°C .

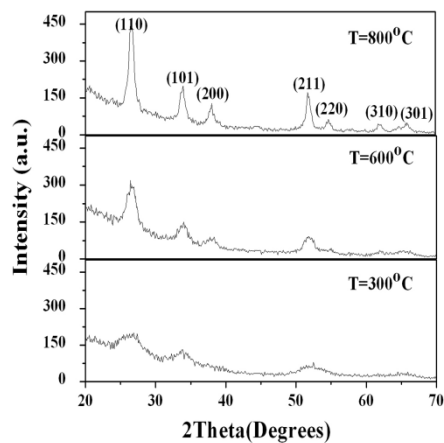


Figure 3. XPS spectra of $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film.

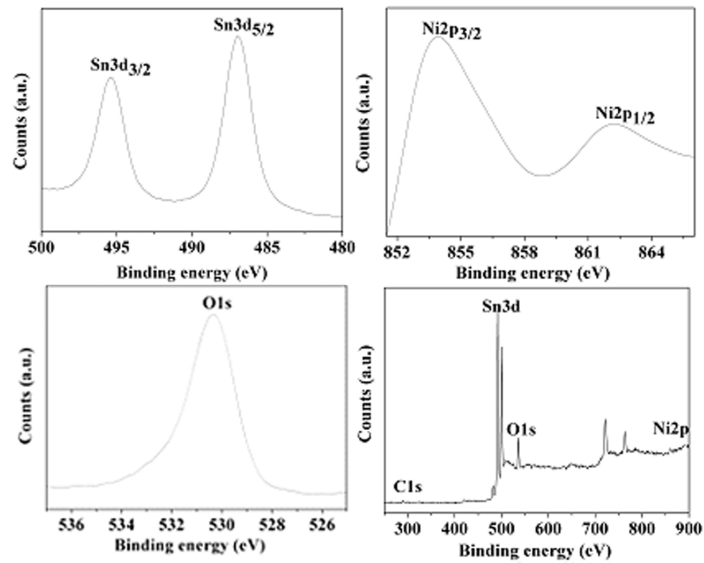


Figure 4. Room temperature hysteresis loops of $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film with different temperature.

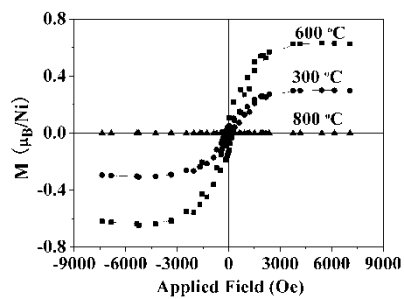


Figure 5. XRD patterns of $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film annealed at different temperature.

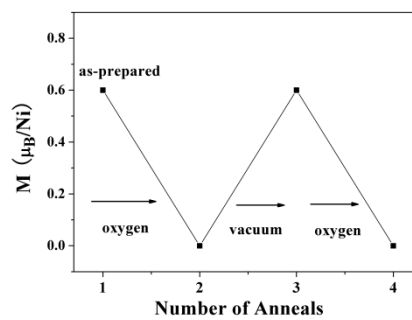


Figure 6. Variation of M_s of $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ film annealed in oxygen and vacuum atmosphere.

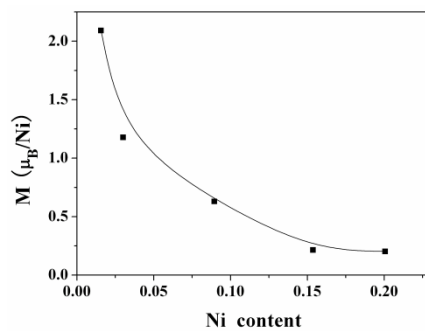


Figure 7. Magnetic moments of $\text{Sn}_{0.91}\text{Ni}_{0.09}\text{O}_2$ films versus Ni content.