Ferromagnetism in Oxide Nanowires: Role of Intrinsic Defects

Shyamsundar Ghosh,1 Gobinda Gopal Khan1 and Kalyan Mandal1

1Department of Condensed Matter Physics and Material Sciences, S. N. Bose National Centre for Basic Sciences,
Block JD, Sector III, Salt Lake City, Kolkata 700 098, India.

Abstract. In this report, we have investigated the origin of defect-induced room-temperature ferromagnetism in pure SnO2 and ZnO nanowires (NWs) with average diameter ~ 50 nm, prepared by template assisted route. Photoluminescence (PL) and electron paramagnetic resonance (EPR) spectroscopic measurements show the singly ionized oxygen vacancy is inducing ferromagnetism in pure SnO2 NWs whereas cation (Zn) vacancy is found to responsible for the ferromagnetic behaviour in pure ZnO NWs. Besides, it is found that the Zn vacancy-induced ferromagnetism in ZnO can be tuned by substituting few percentage of non-magnetic alkali metal like potassium (K) at Zn site. Saturation moment as well as Curie temperature has found to increase significantly with K-doping up to 4 at.% but a decrease of ferromagnetic response is observed for higher K-doping. X-ray photoelectron spectra show that K+1 ions substitute at Zn site and thus introduce hole through which a ferromagnetic interaction between Zn vacancies can be mediated. The direct correlation between the Zn vacancy concentration and the corresponding saturation moment indicates that Zn vacancy-induced ferromagnetism in ZnO can be successfully tuned by K-doping that can an exciting approach to prepare ZnO-based dilute magnetic semiconductors for modern spintronic technology.

1 Introduction

The integration of ferromagnetism (FM) in the wide band gap oxide semiconductors has drawn intense research focus in spintronics [1]. Recently, room temperature ferromagnetism (RTFM) has been reported in the nanostructures of wide band gap pristine and different non-magnetic element doped oxide semiconductors like ZnO, HfO2, CeO2, SnO2, In2O3, Al2O3 and TiO2 [2-8]. However the origin of such unexpected FM in different oxides is found to be controversial issue [2-8]. RTFM in the nanostructures and thin films of undoped and non magnetic ion doped oxide semiconductors is attributed to different intrinsic structural defects like oxygen vacancies [2, 5, 6], cation vacancies [8] or even the surface defects [9], where the quantum confined dimensions of the nanostructures should have very important influence [2]. Therefore, the study of the origin RTFM and the tuning of the ferromagnetic properties in the pristine and non magnetic ion doped metal oxide semiconductors are very exciting considering their potential application for modern spintronic and opto-spintronic devices.

In this work, we have studied the origin of the defect-driven RTFM in pure SnO2 and ZnO NWs fabricated by template assisted wet chemical route. We also have prepared non magnetic alkali-ion K doped ZnO NWs in order to control the FM in the ZnO NWs. It is found that the singly ionized oxygen vacancy clusters are responsible for the FM in pure SnO2 NWs. On the other hand, the magnetic interaction between the cation vacancies mediated via holes is attributed to the observed FM in pure and K-doped ZnO NWs.

2 Experimental details

Arrays of SnO2 and K-doped ZnO NWs are fabricated within nanoporous anodic aluminium oxide (AAO) template through wet chemical route. A precursor solution of 0.2 M SnCl4.5H2O and urea dissolved in ethanol is used for the preparation of SnO2 NWs, whereas the undoped and K-doped ZnO NWs are synthesized by dipping the AAO templates in the alcoholic solutions of zinc acetate and potassium acetate. The K-doping concentration was varied by carefully changing the atomic ratio of Zn/K in acetate solution. AAO templates were immersed in these respective mixed solution and left for few days. Then the AAO templates were removed from the precursor solution and annealed in air at 450° C for 2 hrs. The NWs grown inside the pores of AAO template are characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), vibrating sample magnetometer (VSM), photoluminescence (PL) and electron paramagnetic resonance (EPR) spectroscopy. The morphology of the NWs is observed by field emission scanning electron microscope (FESEM).
after dissolving the template partially in NaOH solution to release the NWs.

3 Results and discussion

Figure 1(a) and 1(c) show the FESEM images for pure SnO$_2$ and 4 at.% K-doped ZnO NWs respectively which exhibit the nanowire-like morphology. High resolution FESEM images also show that both the SnO$_2$ and ZnO NWs have the diameter in the range of 40-50 nm which is very close to the pore diameter of AAO template. The XRD pattern of the as grown pristine SnO$_2$ NWs, shown in Fig. 1(d), indicates pure polycrystalline rutile SnO$_2$ structure (JCPDS card no. 41-1445). On the other hand, undoped and K-doped ZnO NWs show hexagonal wurtzite ZnO crystal structure, where the lattice parameters are found to increase almost linearly with K concentration due to the gradual substitution of larger K$^{+}$ ions (151 pm) replacing smaller Zn$^{2+}$ ions (74 pm) inside ZnO lattice. This observation indicates the successful doping of K ions inside ZnO. Two diffraction peaks at 2θ values of 38.48 and 44.84 appear from the doping of K ions inside ZnO. Similar RTFM in different oxides like ZnO, HfO$_2$, SnO$_2$, TiO$_2$ nanostructures is also observed in AAO template. Two diffraction peaks at 2θ values of 38.48 and 44.84 appear from the doping of K ions inside ZnO. Two diffraction peaks at 2θ values of 38.48 and 44.84 appear from the doping of K ions inside ZnO. Two diffraction peaks at 2θ values of 38.48 and 44.84 appear from the doping of K ions inside ZnO. Two diffraction peaks at 2θ values of 38.48 and 44.84 appear from the doping of K ions inside ZnO. Two diffraction peaks at 2θ values of 38.48 and 44.84 appear from the doping of K ions inside ZnO.

3.1 Origin of ferromagnetism in SnO$_2$ NWs

Pure SnO$_2$ NWs are found to exhibit RTFM with low saturation moment (~ $10^{-5}$ emu/g) as shown in Fig. 2(a) and (b) for 300 and 80 K respectively. The observed reduction of the saturation moment at higher field is due to dominance of the diamagnetic contribution from the AAO template. Similar RTFM in different oxides like ZnO, HfO$_2$, SnO$_2$, TiO$_2$ nanostructures is also observed in which structural defects like oxygen vacancies [2-6], cation vacancies [8], grain boundaries or interfacial defects [2,9] are attributed to the origin of FM. To investigate the possible defects formation within the SnO$_2$ NWs here, PL spectroscopic measurements are performed using the excitation wavelength of 330 nm of Xe lamp. Figure 2(c) show the normalised PL spectra on the template embedded SnO$_2$ NWs. The AAO template itself provides a broad blue emission centred at 2.90 eV because of the oxygen vacancy related defects [10]. The SnO$_2$ NWs is found to exhibit an emission peak in green-yellow region centred at 2.53 eV. The origin of deep green-yellow emission in SnO$_2$ nanostructures can be originated from different crystalline defects such as oxygen vacancy ($V_O$) and Sn vacancy ($V_{Sn}$) [11]. Due to high formation energy of $V_{Sn}$ it is quite unfavourable to stabilize considerable amount of $V_{Sn}$ defects in the pure SnO$_2$ without any controlled defect engineering [12]. On the other hand, $V_O$ defects can easily grow in SnO$_2$ nanostructures due its low formation energy and often found to exhibit green-yellow luminescence [2,13].

Fig. 2. Magnetic hysteresis loops of pure SnO$_2$ NWs at (a) 300 K and (b) 80 K. Room-temperature (c) PL and (d) EPR spectra of pure SnO$_2$ NWs.

However, three kinds of $V_O$ defects such as neutral oxygen vacancies ($V_O^0$), singly ionized oxygen vacancies ($V_O^-$) and doubly ionized oxygen vacancies ($V_O^{2-}$) can form within SnO$_2$ nanostructures. To investigate the types of $V_O$ defects, EPR spectroscopic measurement for pure SnO$_2$ NWs is conducted and the spectrum is shown in Fig. 2(d). The value of $g$ factor is estimated using the formula $g = \frac{h}{\gamma B}$ which is the magnetic field ($B$) in the Bohr magnetron equal to $9.274 \times 10^{-21}$ erg/Gauss, $h$ is Planck’s constant, $6.626 \times 10^{-34}$ erg-s/cycle and $\gamma$ is the frequency (Hz). The estimated value of $g$ factor for pure SnO$_2$ NWs is found to be 1.988 which is very close to 2. Recently, Özcan et al [14], have shown that the Sn$^{4+}$, Sn$^{2+}$, $V_O^-$ and $V_O^{2-}$ defect states have an even number of electrons and these are EPR-silent singlets. Based on the DFT calculations they also have demonstrated that the $g$ factor around 2.00 can appear because of the $V_O^-$ defects in the SnO$_2$ and this defect is only EPR active [14]. Popescu et al [15] have also attributed the EPR signal with the $g$ factor around 2.00 to $V_O^-$ defects in undoped SnO$_2$ nanostructures. Therefore, our EPR spectroscopy result for the pristine SnO$_2$ NWs suggests that the signal is originated from the $V_O^-$ defects, which are believed to be the recombination centres for the luminescence processes.

$V_O^-$ is found to have magnetic moment [2,5] and can be the possible origin of FM in pure SnO$_2$ NWs. The groups of Coey et al [16] have shown that $V_O^-$ centres...
3.2 Origin of Ferromagnetism in pure and K-doped ZnO NWs

Magnetic hysteresis loops of undoped and K-doped ZnO NWs are shown in Fig. 3(a). Like pure SnO₂ NWs, here also, pure ZnO NWs also found to exhibit RTFM with magnetization higher by almost one order in magnitude compared to pure SnO₂ NWs. Interestingly, saturation magnetization (\(M_S\)) in ZnO NWs is found to enhance with the increase of K-doping concentration up to 4 at.% but then decreases for higher K-concentration. The inset of Fig. 3(a) show the temperature dependent magnetization M(T) curves for undoped ZnO and 4 at.% K-doped ZnO NWs. The estimated values of Curie temperatures (\(T_C\)) of ZnO NWs are also found to enhance with K-doping and 4 at.% K-doped ZnO NWs showed the highest \(T_C \sim 510 \text{ K} \) like \(M_S\).

The substitution of K at Zn site has been confirmed by XPS measurements. Figure 3(b) show the XPS spectrum of Zn 2p core level which display a doublet by XPS measurements. Figure 3(c) show the normalised PL spectra of pure and K-doped ZnO NWs embedded on the AAO template. PL spectra of the template embedded pure and doped ZnO NWs are found to exhibit a broad blue emission centred at 2.90 eV originating due to AAO template [10]. Hence we have neglected the hump like broad blue region for all the K-doped ZnO NWs. It is important to notice that all the doped ZnO NWs show significant green emission (2.42 eV) along with ultraviolet-visible (UV) emission. The emission peak at 3.37 eV corresponds to the near band edge (NBE) electronic transition and/or the free exciton recombination through an exciton–exciton collision process [22]. It is noticeable that K-doping results in the enhancement of intensity of the NBE UV emission which is found to be maximum for 4 at.% K-doped ZnO NWs.

An extra emission peak is found to appear at 3.21 eV with the introduction of K in ZnO. The emission peak near to the ZnO band edge is quite expectable because of the electronic transition from conduction band minimum (CBM) to the shallow \(K_{\text{Zn}}\) acceptor levels [23-24]. The presence of the shallow \(K_{\text{Zn}}\) acceptor states can push the ZnO system from n-type to p-type direction [23]. Looking at the intensity of the peak it is clear that maximum amount of K ions are substituted at Zn site in case of 4 at.% K-doped NWs. For higher K-doping, the substitution process might get saturated and K ions can move to lattice interstitial (\(K_i\)) position which acts as a donor [23-24] and thereby can reduce the p-type nature of ZnO. Therefore, the hole concentration should maximum in the 4 at.% K-doped ZnO NWs compared to the others.

Besides the NBE emission, the K-doped NWs also exhibited significant green emission centred at 2.43 eV. The origin of well known green emission in ZnO nanostructures and thin films is highly controversial. It was previously believed that the oxygen vacancies (\(V_{\text{O}}\)) [25] are responsible for the green emission, but recent in depth studies reveal that Zn vacancy (\(V_{\text{Zn}}\)) is found the origin of the green emission in ZnO nanostructures and thin films [26, 27]. The green emission is attributed to the electronic transition between the CBM and \(V_{\text{Zn}}\) acceptor levels which is found to situated at 0.9 eV above the valance band maxima (VBM) [26, 27]. Therefore, K-doping is found to stabilize more \(V_{\text{Zn}}\) defects in ZnO NWs and the 4 at.% K-doped NWs contains maximum amount of \(V_{\text{Zn}}\) defects as the intensity of the green emission is highest. Similar enhancement in \(V_{\text{Zn}}\)
concentration with Li-doping in ZnO thin films is also observed previously [8].

$V_{Zn}$ is found to have localised magnetic moment originating from the unpaired 2p orbital of O atom nearest the $V_{Zn}$ site [3, 8] and the results so far clearly suggests that they are surely playing a crucial role in inducing FM in K-doped ZnO NWs. In fact, a direct correlation of the $M_S$ and $T_C$ with the green emission intensity ($I_G$) has observed in Fig. 3(d). It is quite interesting to notice that the increase of $I_G$ follows the increase of $M_S$ as well as the $T_C$ of the K-doped ZnO NWs. The magnetic moments of $V_{Zn}$ defects can be mediated through the holes due to $K_{Zn}$ defects and giving rise to a long range ferromagnetic interaction. The 4 at.% K-doped NWs contains maximum amount of $V_{Zn}$ and holes and this is the reason it show the strongest FM. With the increase of K-doping concentration, the advent of K-interstitial defects compensates the acceptor-like defects such as $K_{Zn}$ and $V_{Zn}$ and thereby reducing the overall hole concentration and consequently the strength of FM.

4 Conclusions

In summary, the origin of FM in pure SnO$_2$ and K-doped ZnO NWs has been successfully investigated. Singly ionized oxygen vacancies are found to induce RTFM in pure SnO$_2$ NWs. On the other hand, cation vacancies ($V_{Zn}$) is playing a role in stabilizing FM in ZnO NWs and the FM signature is found to enhance with the substitution of alkali-element K at Zn site. The concentrations Zn vacancies as well as the p-type conductivity of the ZnO NWs are found to increase significantly with K-doping and the FM signature increases consequently. For higher K-doping concentration, the stabilization donor like K-interstitial defects compensate the effects of K-substitutional and Zn vacancy acceptors and thereby reducing the degree of p-type nature which diminishes the related FM consequently. Therefore, the stabilization of defect-induced FM in such oxides can be an exciting approach to prepare new class of magnetic semiconductors for spintronics and opto-spintronics applications.

Acknowledgements

One of the authors (S. G.) thanks Council of Scientific and Industrial Research (CSIR), Government of India, for providing a research fellowship. The above work is supported by the CSIR (INDIA) funded project 03(1178)/10/EMR-II.

References