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FAST TRACK COMMUNICATION

Suppression of the magnetic moment upon Co doping in ZnO thin film with an intrinsic magnetic moment

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Abstract

We give experimental evidence for an intrinsic magnetic moment in ZnO films prepared by pulsed laser deposition. In our study using magnetic measurements, we showed that we are able to tune the magnetic moment in ZnO by changing the oxygen content. We also observe that doping of 5% Co in ZnO does not introduce ferromagnetism. All of the arguments are supported by magnetotransport measurements, which reflect mainly the intrinsic properties of the film. It is contemplated in this study that the doping of Co in the ZnO matrix may in fact reduce the magnetic moment which is otherwise present in the pure ZnO.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Dilute magnetic semiconductors (DMS) are becoming important due to possible applications in the proposed semiconductor spintronic [1] devices as spin polarized electron sources [2], to increase the spin injection efficiency as proposed by different groups, since ferromagnetic metallic electrodes pose the issue of conductivity mismatch [3, 4]. Among the oxide based DMS, transition metal doped ZnO is one of the most studied systems due to its predicted ferromagnetic transition temperature above room temperature [5]—along with a few others, like transition metal (TM) doped TiO_2, SnO_2 etc. However the experimental findings from different groups are sometimes vastly contradictory. While many groups report room temperature ferromagnetism of Co doped ZnO [6–8], there are many other groups reporting the absence of ferromagnetism [9–11]. This suggests that the properties of these materials are highly process dependent and the origins of ferromagnetism in these materials are still under debate. There is a lot of discussion going on about the extrinsic and the intrinsic origins of ferromagnetism in TM doped oxide semiconductors. It has been shown very recently that intrinsic ferromagnetism is observed in pure TiO_2 films [12]. However this and the reports on ferromagnetism in HfO_2 [13] have been challenged by other experimental groups pointing out the possible pitfalls in these experiments [14, 15]. In order to give further insight into this problem we have carried out an extensive study on both ZnO films as well as Co doped ZnO films. In this communication, we show conclusively with the help of magnetic measurements and magnetotransport studies that doping with transition metal is not a prerequisite for observing magnetic moments in ZnO film. In addition we emphasize the fact that the doping of the transition metal in the ZnO matrix in fact lowers the magnetic moment of the pure ZnO film. Also we are able to tune the magnetic moment in the pure ZnO film by appropriate oxygenation.

2. Experimental details

We have studied the magnetic and the magnetotransport properties of ZnO films and 5% Co doped ZnO films prepared under specific conditions. Films are deposited using pulsed laser deposition (KrF, 248 nm) on *R*-plane sapphire substrate. Target materials are made by first reducing the nitrate solution/s using a soft chemical route and then by sintering the precipitate. During deposition of films the substrate

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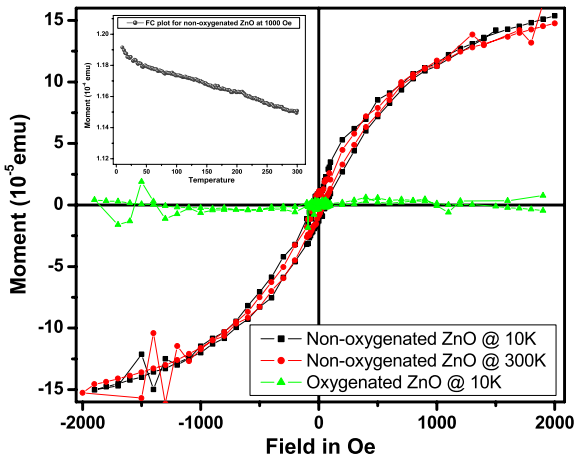

Figure 1. Magnetization plot for the oxygenated (10 K) and non-oxygenated (10 and 300 K) ZnO films. The inset shows the field cooled M versus T data for the non-oxygenated ZnO.

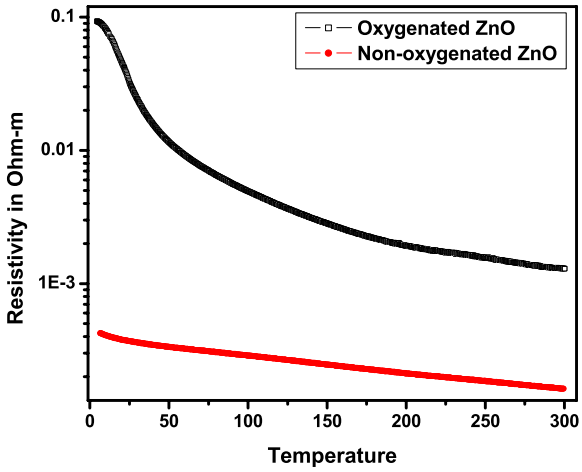

Figure 2. Resistivity plot as a function of temperature for oxygenated and non-oxygenated ZnO films.

temperature is kept at 500 °C, with the laser energy ∼5 J cm^{-2} in O_2 atmosphere. The typical film thickness is ∼30 nm. In DMS materials the possibilities for ferromagnetism are carrier induced [16–18], defect induced [19] and oxygen vacancy induced ferromagnetism [20] as predicted by different groups. So we have tuned the oxygen content in these films in our present study to see its effect on the magnetic properties. After deposition, these films are annealed with or without oxygen atmosphere, for both doped and undoped ZnO. Henceforth the samples are termed oxygenated or non-oxygenated. Magnetization measurements are carried out using a Quantum Design MPMS unit and the magnetotransport measurements are carried out using a Janis superconducting magnet system.

3. Results and discussion

In figure 1 we have shown the magnetization versus applied magnetic field data for the pure ZnO samples after subtracting the diamagnetic substrate contribution. It clearly shows that the non-oxygenated sample shows a hysteresis characteristic of a ferromagnet with the coercivities of 50 Oe and 35 Oe at 10 K and at 300 K respectively. The remanences at 10 K and 300 K are 1.2 × 10^{-5} emu and 8.6 × 10^{-6} emu respectively. The moment in the oxygenated film is very close to the measurement limit of the instrument and it is mostly diamagnetic in nature. This suggests that the origin of the ferromagnetism in this film is not extrinsic and we can tune the magnetic property by properly tuning the oxygen content in the film. This immediately points to the fact oxygen deficiency is definitely playing a major role in the magnetic property. But further study is required to comment on the origin of ferromagnetism: whether it is carrier induced or defect induced or produced by oxygen vacancies pushing the Zn into the interstitials giving rise to ferromagnetism [21]. The inset of figure 1 shows the field cooled magnetization versus temperature data, measured at 1000 Oe external field, for the non-oxygenated sample. The magnetization value shows a minor drop up to 300 K which suggests that the

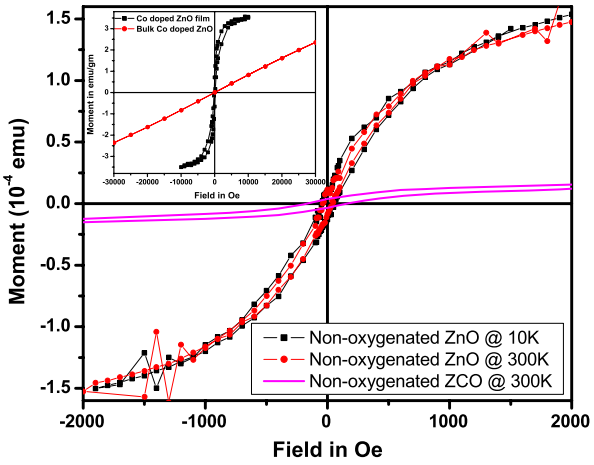

Figure 3. Field dependent magnetization of non-oxygenated ZnO film and non-oxygenated 5% Co doped ZnO film showing that Co doping decreases the magnetic moment. The inset shows magnetization comparison of the doped paramagnetic target material and the ferromagnetic film deposited using the same target.

sample is in the ferromagnetic saturation region and the T_C of this material is well above room temperature. Transport measurements are carried out to check the conductivity of these films. Figure 2 shows the resistivity plots for the undoped sample which reveals that the resistivity is increased by approximately two orders of magnitude in the oxygenated film. Reduction in the resistivity in the oxygen deficient film is quite expected because oxygen vacancies lead to increase in the carrier concentration which increases the conductivity.

Films of Co doped ZnO samples are also made by a similar deposition method. 5% Co doped ZnO target is used for laser ablation. The magnetization versus applied field plot in figure 3 shows a comparison plot of the non-oxygenated undoped ZnO sample and doped sample. Although these films also show hysteresis with higher values of coercivity (∼160 Oe), the remanence (∼3.65 × 10^{-6} emu) and the saturation moment are much less than for the undoped samples. This plot clearly suggests doping essentially suppressing the moment of the

undoped sample by at least an order of magnitude. This suggests that Co doping does not introduce ferromagnetism. This is in agreement with the recent XMCD results of Gacic *et al* [22] which show paramagnetism for the Co in ZnO matrix. Unlike for undoped samples there is not much difference in magnetic properties for the doped samples before and after oxygen treatment and the saturation moment does not change much from 10 K measurement to 300 K measurement. The inset of figure 3 shows the magnetic moment comparison between the doped bulk sintered target material and the film prepared from this target material. It is clearly seen that the bulk material is paramagnetic while the films show ferromagnetic nature with a very low moment. This must point to the fact that doping of Co may be introducing defects which are not fully annealed out even after oxygenation. Here one suspects that the ferromagnetic moment in Co doped ZnO arises from the parent ZnO matrix. Although the inset of figure 3 shows clear hysteresis of the doped film, our study suggests that the undoped compound is a better candidate since it has a moment at least one order of magnitude higher than the doped one's.

We have also investigated the magnetotransport properties of these samples. Unlike magnetic measurements, transport data do not depend much on the local foreign impurities and reflect the intrinsic property of the sample. Magnetoresistance is measured keeping the magnetic field perpendicular to the sample at 4.6 K. Figure 4 shows the magnetoresistance $[R(H) - R(0)]/R(0)$ plot at different field values up to 5 T for the oxygenated and the non-oxygenated undoped samples. From the plot we can see that the natures of the MR in these two samples are completely different. The non-oxygenated sample shows pure negative MR for the complete range of the applied field whereas the oxygenated sample shows a small negative MR at low fields and then it changes sign near 1 T and shows a high positive MR value. So there is an intrinsic change in the sample property which changes the magnetotransport property. In figure 2 we have already seen that the carrier concentration and hence also the conductivity is less for the oxygenated sample. This carrier concentration is also responsible for the change in the magnetotransport property of the undoped sample. For the Co doped sample, at low fields the MR has positive slope, but again there is a change in sign of the slope of the curve at around 3 T field—similar to what is observed by Gacic *et al* [22]. In figure 4, symbols are the experimental data points and the continuous lines are the least square fits. We have used the semiempirical formula from Khosla *et al* [23] consisting of both negative and the positive contributions of MR as given below; this fits reasonably well with the present experimental data and it helps us to understand the magnetotransport qualitatively:

$$\frac{\Delta\rho}{\rho_0} = -a^2 \ln(1 + b^2 B^2) + \frac{c^2 B^2}{1 + B^2 d^2} \qquad (1)$$

where

$$a^2 = A_1 J \rho_F [S(S+1) + \langle M^2 \rangle]$$

$$b^2 = \left[1 + 4S^2\pi^2 \left(\frac{2J\rho_F}{g}\right)^4\right] \frac{g^2\mu^2}{(\alpha k T)^2}.$$

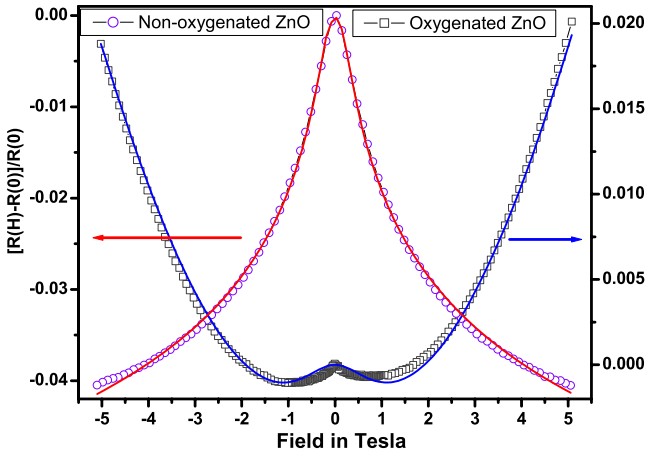

Figure 4. Field dependent magnetoresistance at 4.6 K for the oxygenated and non-oxygenated ZnO films showing clear change in the magnetotransport properties of the film after oxygenation. Points in the plot indicate the experimental data points and continuous lines show the fits to the data using equation (1).

The four fitting parameters a, b, c and d are functions of many other sample properties as shown in the equations. Here $\langle M^2 \rangle$ is the average magnetization, S is spin of the localized magnetic moments, J is the exchange integral, ρ_F is the density of states at the Fermi energy, and A_1 is a measure for spin scattering. Parameters c and d which give saturating positive high field MR are functions of the conductivity and charge carrier concentration—which is again a function of temperature. So to get a proper fitting we have to fit with both positive and negative parts over the complete range. This fitting qualitatively shows that there is an enhancement of the value of fitting parameter a for the non-oxygenated pure ZnO film as compared to the oxygenated sample, indicating that the average magnetization is enhanced in the sample.

4. Conclusion

In conclusion, we have observed large ferromagnetic moments in the non-oxygenated ZnO film. The presence and absence of magnetic moments in the pure ZnO films treated under different conditions show that the many pitfalls [14, 15] pointed out in the literature as a reason for ferromagnetism in doped and undoped ZnO, TiO_2 etc are not valid for our sample. According to our study, 5% Co doping in ZnO, which is predicted to be a DMS material, actually leads to less moment than for the ZnO film. So even without doping with transition metals we can get ferromagnetism by suitably tuning the oxygen content in the film, and Co doping is effectively suppressing the moments of these films. In the magnetoresistance data for the undoped film we see a clear change of sign, which clearly indicates that there is a change in the intrinsic property of the sample between before and after the oxygen treatment. Although at this point of time it is difficult to comment exactly on the origin of the ferromagnetism, we can exclude extrinsic origins like impurity from tweezers or contamination during sample handling etc. Again magnetotransport data support the magnetization results

which suggest that undoped ZnO is a better candidate for room temperature semiconductor spintronic device use than Co doped ZnO. But we have to investigate further to understand the suitability of this material as a spin polarized electron source.

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