Origin of ferromagnetism in nitrogen embedded ZnO : N thin films

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Abstract
Nitrogen embedded ZnO : N films prepared by pulsed laser deposition exhibit significant ferromagnetism. The presence of nitrogen ions contained in ZnO is confirmed by the secondary ion microscopic spectrum and by Raman experiments, and the embedded nitrogen ions can be regarded as defects. According to the experimental results, a mechanism is proposed based on one of the electrons in the completely filled d-orbits of Zn that compensates the dangling bonds of nitrogen ions and leads to a net spin of one-half in the Zn orbits. These one-half spins strongly correlate with localized electrons that are captured by defects to form ferromagnetism. Eventually, the magnetism of nitrogen embedded ZnO : N films could be described by a bound magnetic polaron model.

1. Introduction
Magnetic ion doped transition metal oxides such as ZnO, TiO\textsubscript{2}, SnO\textsubscript{2}, In\textsubscript{2}O\textsubscript{3} and HfO\textsubscript{2} are candidates for room temperature diluted magnetic semiconductors \cite{1–4} with highly industrial applications in spintronics. The most popular material used is ZnO, which has been investigated in recent years as a transparent conducting oxide (TCO) because of its good electrical and optical properties in combination with a large band gap of 3.3 eV, abundance in nature, and absence of toxicity with a wide variety of applications as electrodes, window materials in displays, solar cells and various optoelectronic devices \cite{5–8}. Various techniques have been used to deposit doped ZnO films on different substrates, including metal-organic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE), pulsed laser deposition (PLD) and spray pyrolysis deposition (SPD). Furthermore, compared with other deposition methods, PLD is characterized by several advantages, such as low substrate temperatures, good adhesion on substrates, and the fact that alloys and compounds of materials with different vapour pressures can be deposited easily. The possible mechanism for magnetic ion doped ferromagnetic oxides has been proposed\cite{9}, called the bound magnetic polaron (BMP) model, which is different from the conducting carriers mediated mechanism of RKKY \cite{10} appearing in III–V diluted magnetic semiconductors \cite{11}. The BMP model is based on the donor electrons being polarized by the magnetic spins of doped ions to form bond states with finite orbital radius. When the dopant density attains a critical value (percolation), the neighbouring orbits overlap to create a spin-split impurity band leading to interesting conducting electricity and magnetism. Recent experiments demonstrate that some undoped and nitrogen embedded transition metal oxides also exhibit ferromagnetism \cite{12, 13}. Similarly, our N embedded ZnO : N films prepared by PLD in a N\textsubscript{2}O partial pressure atmosphere show significant ferromagnetism, similar to the TiO\textsubscript{2} : N films. Perfect ZnO and TiO\textsubscript{2} samples should not show magnetism because the d-orbits of Zn are completely filled. The picture of the mechanism for the undoped transition metal oxides could be different from BMP because there are no magnetic ions doped directly. Therefore, it is an interesting and physically rich problem to study the mechanism of magnetism for the nitrogen (N) embedded ZnO films with no doping of access magnetic ions.
2. Experiment detail and analyses

A reliable method was used to deposit thin films of undoped zinc oxide transparent electrodes on glass substrates by PLD. The ablation PLD targets with dimensions of 1 inch diameter × 0.125 inch thickness were fabricated with high purity (5N) powder by the solid state reaction technique. ZnO : N films were deposited at 150 °C in oxygen or N₂O (99.99%) atmosphere of 150 mTorr on the glass substrates. A double frequency Q switched Nd : YAG pulsed laser operated at 532 nm, pulse duration of about 7 ns and an 18.5 mJ cm⁻² energy density was focused on the target to generate a plasma plume. The target to substrate distance was 5.0 cm. The crystallinity and surface morphology of ZnO films were characterized by X-ray diffraction (Rigaku Multiflex CD3684N diffractometer). The XRD data for undoped and ZnO : N films grown at the same substrate temperatures are represented in figure 1. Both films exhibit a highly preferred (0 0 2), 34.2 ° orientation indicating that ZnO films prepared by PLD show good textured growth with the c-axis perpendicular to the substrate that is similar to other reports [14–19]. Inspection of Raman shift is an indirect method to probe the possible embedded nitrogen in our films. It has been proposed by Wang et al that the access peaks at 275 and 582 cm⁻¹ in an unpolarized Raman spectrum are most probably caused by the existence of embedded N in ZnO structure [20].

In figure 2, two peaks at 440 and 580 cm⁻¹ are those of ideal ZnO structure while the other two peaks at 275 and 582 cm⁻¹ coincide with Wang’s speculation. Secondary ion microscopic spectrum (SIMS) was taken for a 325 Å N-embedded ZnO film, as shown in figure 3, in which the concentration of oxygen is low, indicating a high level of oxygen vacancies was created during the film growth, and that a low concentration of embedded nitrogen was detected. The compositional profiles of Zn, O and N are distributed uniformly throughout the entire film.

The photoluminescence was measured with a He–Cd laser as a light source using an excitation wavelength of 325 nm. Figure 4 is a comparison of PL spectra of the undoped and N-embedded ZnO films. All the spectra consist of two majority bands. The first one, centred at a photon energy of 3.28 eV for the ultraviolet band, corresponds to the radiative recombination of excitons. The second PL bands show a broad orange emission band with a maximum in the range between 2.0
and 2.4 eV. It is possible that the introduction of the impurity atoms changes the potential energy around the impurity and results in the variation of the energy levels of oxygen vacancies. The radiative recombination process responsible for the orange emission would take place between the donors associated with oxygen vacancies and the acceptors associated with the native defects adjacent to the impurity [24–27]. When N₂O dopant is introduced, the PL spectra of N-embedded ZnO thin film show that the formation of the ultraviolet band is suppressed, as indicated in figure 4(b). The suppression of the ultraviolet band could be attributed to the combination with the oxygen species in the films and/or the occupation of N dopant in the interstitial sites. This implies that the N dopants in our films actually behave as donors. The magnetization versus magnetic field at room temperature for a 60 nm thick pure ZnO film is shown in figure 5. One can see that the film is ferromagnetic at room temperature. The observed magnetism in ZnO films is unexpected, because neither Zn²⁺ nor O⁻² is magnetic; thus, in principle, there is no source for magnetism in ZnO. From the electrical results of conducting AFM (CAFM) experiments, the conductivity of the nitrogen embedded ZnO films decreases compared with pure ZnO films, as shown in figure 6. This means that the embedded N ions diminish the transport carrier density. It is reasonable to propose that these embedded nitrogen ions create defects, which capture part of the itinerant electrons. It is based on this capture evidence that we propose the magnetic mechanism described in the next section.

3. Model construction

In the BMP model for transition metal oxides, the defect comes from the oxygen vacancy which could catch one itinerant electron to form a hydrogen-like orbit with a finite radius. When the defects increase to a critical amount, the orbits overlap to form a narrow impurity band. The doped magnetic ions within the radius coverage correlate through the impurity band electrons to become ferromagnetic. Obviously, the important element of BMP, the magnetic ion, does not appear in our ferromagnetic samples. However, we believe the magnetism of undoped ZnO should eventually come from the net spins in the d-orbits. Based on the SIMS and Raman experiment, the N is embedded in our samples. It is seen that, for the valence charges of N, O, Zn and ZnO, every N ion beside a Zn ion leaves an uncompensated dangling bond. In order to stabilize the system, these dangling bonds should be compensated by capturing electrons. When the ion N is beside Zn, one electron in the completely filled d-orbits of Zn possibly jumps to compensate the dangling bond to reduce the total energy leading to a net spin with one half in the d-orbit of Zn and leads to a possibility of ferromagnetism; this picture is depicted in figure 7. Eventually, these nitrogen embedded ZnO : N films representing the magnetism, after the intra carriers jump between the d-orbits of Zn and defects, are equivalent to the magnetic doped ZnO samples in which the magnetic moment is contributed from these magnetic dopants.

4. Conclusion

In conclusion, our nitrogen embedded undoped ZnO shows significant ferromagnetism. The conductivity measured by AFM represents that the itinerant electrons are captured by defects induced by nitrogen ions. According to the experimental results, a model of defect induced magnetism is proposed based on one of the electrons in the completely filled d-orbits of Zn that compensates the dangling bonds of nitrogen ions and leads to a net spin of one-half in the Zn orbits.
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