Zn doping induced ferromagnetism in NiO

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Abstract. Here we report the effect of Zn doping in NiO, in thin film form. Thin film with the composition Ni₀.⁹₈ Zn₀.⁰₂ O has been prepared on [001] oriented Al₂O₃ substrate using pulsed laser deposition technique. X-ray diffraction, SEM, and magnetic measurements were performed to investigate the properties of this material. XRD study revealed oriented growth of the film along the [111] direction. To characterize the magnetic behavior of the film, magnetization vs temperature (M-T) and magnetization vs field (M-H) measurements were performed. Anomalous behavior in M-T measurement has been observed in the low temperature region. At the temperature ~ 70 K, Zn doped NiO thin film is showing antiferro to ferro type of transition. This is in contrast to the pure NiO, which remains antiferromagnetic at low temperatures. Observation of isothermal magnetization hysteresis behavior with finite moment confirms ferromagnetism in Zn doped NiO at low temperatures.

1. Introduction
The NiO, a transition metal oxide, has attracted considerable interest because of its special electrical, optical and magnetic properties. NiO adopts NaCl structure and is an antiferromagnetic insulator at room temperature [1]. Stoichiometric NiO is a Mott insulator, but one can increase its p type conductivity by introducing Ni³⁺ vacancies or by doping with cations[2]. Electrical and magnetic properties of the NiO in thin film form strongly depend upon the deposition parameters like substrate temperature and oxygen content during the deposition. Therefore, selection of the proper substrate, growth condition and deposition technique play crucial role in the synthesis of NiO in thin film form. In the past NiO thin films have been fabricated on a variety of substrates by various deposition techniques like pulsed laser deposition, sputtering, chemical methods, spray pyrolysis methods etc [3-5]. It has been reported that as compared to other substrates, film grown on insulating substrates like TiO, SrTiO₃ and Al₂O₃ is more likely to be epitaxial in nature and contain less surface defects [6].

The NiO thin films find various scientific and technological applications. It can also be used as an exchange biased layer. One of its most important uses could be its applicability for spintronic application by doping with a suitable impurity. There has been various reports on the effort to develop NiO based diluted magnetic semiconductor (DMS) system by adding magnetic impurity/atom but there are very few reports on the doping effect of non magnetic impurity in NiO.

In the present work we have used pulsed laser deposition (PLD) technique to grow the thin film with the composition Ni₀.⁹₈ Zn₀.⁰₂ O. In PLD one can easily tune the parameters to grow the
stoichiometric single phase compounds. In this paper we report effect of the Zn doping on the structural and magnetic properties of the Zn doped NiO thin film grown on Al2O3 substrate.

2. Experimental details
Thin film with the composition Ni0.98 Zn0.02O has been prepared using pulsed laser deposition technique using a single phased composite target made out of high purity NiO and ZnO powders. The single phased target was prepared by the standard solid state reaction technique. Final sintering of target material was performed at 1000°C in air at atmospheric pressure for 24 hrs. [0001] oriented single crystal Al2O3 was used as a substrate. A KrF excimer laser source (λ = 248nm, pulse width = 20 ns) was used to ablate the target. During deposition, the laser pulse repetition rate was set at 10Hz. Substrate to target distance was kept at 5 cm. Deposition was carried out under oxygen partial pressure of 1*10^-4 Torr at an optimized substrate temperature (Ts= 450 °C). Nominal thickness of the grown film is ~ 80 nm.

To study the structural properties of the grown thin film X-ray diffraction (XRD) was performed in θ-2θ geometry using Cu Kα source. Magnetic behavior of the thin film was recorded using SQID vibration magnetometer from Quantum Design.

3. Results and discussions
Prior to deposition of the thin film, crystal structure of bulk sample was examined by XRD. Figure 1 presents the XRD pattern of the bulk sample which has been used as a target material. From the XRD pattern it is clear that sample is single phase and do not contain any impurity phases. XRD peak positions matches very well with the values given in JCPDS database (78-0643) for the cubic NiO. Inset of the figure shows the scanning electron microscopy (SEM) image of the bulk target. Quality of the SEM image ensures that prepared target is quite homogenous and very well sintered, suitable for PLD growth process.

![Figure 1](image_url)

Figure 1. X-ray diffraction pattern of the 2% Zn doped NiO bulk target sample sintered at 1000 °C. Inset shows the SEM image of same sample.

To study the crystal structure of deposited thin film, XRD pattern has been recorded, shown in Figure 2. XRD pattern of the film shows the peaks corresponding to (111) and (222) planes of NiO
along with substrate peaks. No extra peaks corresponding to any other phase or orientation were observed in the spectrum. This confirms the single phase nature and [111] oriented growth of the film. We have calculated particle size of the film using Scherrer’s formula, which is ~ 20nm. Calculate value of lattice parameter is a = 4.15 Å, which is slightly lower than pure NiO.

Figures 3 and 4 illustrate the magnetic property measurements of the grown thin film. Temperature dependent magnetization behavior of Ni$_{0.98}$Zn$_{0.02}$O thin film taken at 500 Oe measuring magnetic field under zero field cooled (ZFC) and field cooled (FC) protocol is shown in figure 3. In FC data, value of the magnetization is seen decreasing with the decreasing temperature but at temperatures below 70 K reverse behavior was observed. This anti-ferromagnetic to ferromagnetic type of transition is prominent in FC data. Observed bifurcation in FC and ZFC data is a feature which is common to the systems having magnetic anisotropy and grain boundary effects.

Figure 4 shows low temperature (10K) M-H behavior of the film after subtracting the substrate contribution. Observed hysteresis, with the finite coercivity of ~ 180 Oe, in film confirms the ferromagnetic like behavior at low temperatures. It has been reported in literature that pure NiO thin films can show weak ferromagnetism even at room temperature. The presence of Ni clusters into NiO lattice, uncompensated spins, and lattice distortion are some of the reasons reported to explain magnetic hysteresis in NiO [7]. However, observation of magnetic hysteresis here in Zn doped NiO film at low temperature may be attributed to the presence of Zn which causes the distortion in NiO as evident from the lattice parameter from XRD pattern. Such distortion can break the anti ferromagnetic interaction in NiO and lead to canted anti ferromagnetic interaction. Similar behavior has been reported for Zn doped NiO nano clusters [8]

4. Summary
Pulsed laser deposition technique was used to grow the Ni$_{0.98}$ Zn$_{0.02}$O thin film on single crystal [0001] oriented sapphire substrate. XRD confirms that the prepared sample is single phase in bulk as well in thin film form and do not contain any impurity. Grown film is oriented along the [111] direction. Magnetic measurements revealed a antiferro to ferro type of transition at ~ 70 K. Low temperature ferro magnetic behavior were further confirm by isothermal hysteresis measurement performed at 10
Present results indicate that presence of Zn in NiO helps in field induced spin canting of the antiferromagnetic sub-lattices which is giving rise to observed magnetic hysteresis. For the better understanding of observed anti ferro to ferro magnetic transition at low temperatures more measurements are under process.

**Figure 3.** Zero field cooled and field cooled magnetization vs temperature behaviour of the Ni$_{0.98}$Zn$_{0.02}$O thin film. Measuring field was 500 Oe.

**Figure 4.** Isothermal magnetic hysteresis loop of the Ni$_{0.98}$Zn$_{0.02}$O thin film at 10K.

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**References**

[1] Fujii E, Tomozawa A, Torii H and Takayama R 1996 *Japan. J. Appl. Phys* 35 L328.
[2] Wu J, Nan C W, Lin Y and Deng Y 2002 *Phys. Rev. Lett.* 89 217601
[3] Nandy S, Goswami K S and Chattopadhyay K 2010 *Appl Surf Sci* 256 3142
[4] Wang H, Wang Y and Wang X 2012 *Electrochem Commun* 18 92
[5] Xia X, Tu J, Zahang J, Wang X, Zahang W and Huang H 2008 *Sol Energy Mater Sol Cells* 92 628
[6] Lee Ju Ho, Kwon Yong Hun, Kong Bo Hyun, Lee Jeong Yong and Cho Hyung Koun 2012 *Cryst Growth Des*. 12 2495
[7] Wongsaprom K and Maensiri S 2013 *Chiang Mai J. Sci.* 40 99
[8] Peck M A , Huh Y, Skomski R, Zhang R, Kharel P, Allison M D, Sellmyer D J and Langell M A 2011 *J. Appl. Phys.* 109 07B518