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Conductivity modification of ZnO film by low energy Fe^{10+} ion implantation

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ABSTRACT

In this paper we report the structural, optical and electrical behaviours of ZnO films implanted with 300 keV Fe^{10+} ions. From UV–vis spectroscopy it is observed that the band gap of the films decreases after implantation. Photoluminescence yield seems to increase in the implanted samples. From Hall measurements it is observed that the unimplanted sample shows n-type conductivity for the entire temperature range (100–300 K), whereas after implantation the samples show p-type conductivity for ≤200 K. The DC resistivity of the implanted samples is found to be lower than that of the unimplanted sample. We have found that the magnetoresistance of our samples is positive in the temperature range 200–300 K, but it becomes negative below 200 K.

1. Introduction

Zinc oxide (ZnO) is one of the II–VI semiconductor materials with band gap ~3.37 eV at room temperature [1] and large exciton binding energy (60 meV). Thin films of ZnO have very good transparency in UV–vis range. These properties have made this material promising candidate for different opto-electronic devices. Interest in the study of ZnO for device applications has been accelerated after the growth of p-type ZnO layers and fabrication of p–n junction for solar cells [2]. This material almost always exhibits strong n-type conductivity, as most stable point defects in ZnO are donors and they dominate the transport properties of this material [3]. It is very difficult to tailor its electrical conductivity as well as to get low resistive p-type ZnO films. On the other hand, growth of high-quality p-type ZnO is essential for the application of ZnO devices. Several techniques have been reported to prepare p-type ZnO films, for example by doping N [4], In–N [4], P [5] and Na [6]. Some other technique of obtaining p-type ZnO films by thermal oxidation of nitrogen-doped ZnTe layers has also been reported [7]. Ion implantation could also be one suitable technique for solving this problem. Developments of p-type ZnO film at room temperature using As [3] and N [8] ion implantations have been reported. The p-type conductivity has also been achieved for high energy electron beam irradiated Al doped ZnO film [9]. Although modification of ZnO sample with Fe ion implantation is studied by some researchers [10–14], but we have not come across any report on its nature of carriers due to Fe implantation. Potzger and his group [10–13] have studied the effect of Fe ion implantation on ZnO single crystals; they have observed appearance of dilute magnetic semiconducting (DMS) behaviour of their samples due to implantation. In case of Fe implanted ZnO films also Zhang et al. [14] have observed DMS behaviour. Optical properties of such films are important objectives for understanding their usefulness in opto-electronic devices; hence more extensive works on Fe implanted films are still required. In this paper we report the appearance of p-type behaviour of ZnO film (at ≤200 K) by implanting 300 keV Fe^{10+} ions into the film. We started this work with some motivation that since implantation of Fe^{10+} ions will be accompanied by radiation damage; the residual defects caused because of this may bring a favourable change in the electrical properties of ZnO for getting p–type. For this work, the fluence of the iron ions has been varied in the range 3×10^{15} to 1×10^{17} in order to find suitable condition for achieving low resistive p–type ZnO films. A thorough report on the structural, optical and electrical behaviours of the pristine and implanted films has been reported in this paper.

2. Experimental

The ZnO films were prepared using the spin coating method after obtaining sol–gel, which was prepared as follows. Reagent grade (RG) zinc acetate ($Zn(C_2H_3O_2)_2$, 99.99%) was first dissolved in RG isopropanol ($(CH_3)_2CHOH$, 99%) at room temperature. Then diethanolamine ($HN(CH_2CH_2OH)_2$, 99%; DEA) was added to it as a sol stabilizer [15,16]. The molar ratio of DEA to zinc acetate was maintained at 1.0 and the final concentration of the zinc acetate was 0.3 mol/L. The resulting mixture was then stirred at 50 °C for

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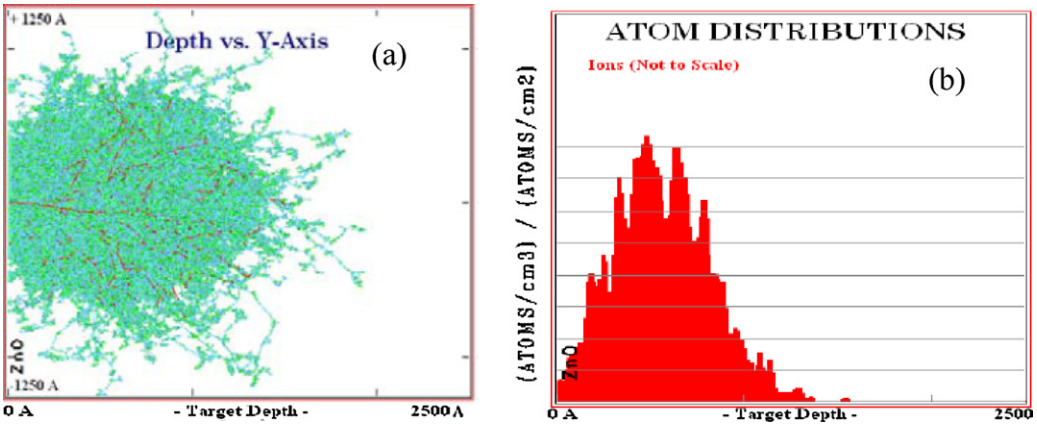

Fig. 1. (a) Monte Carlo simulation of Fe^{10+} implantation in ZnO. (b) Implantation profile of Fe ions as a function of target depth.

2 h to form a clear and transparent homogeneous mixture and upon cooling transparent solution was filtered to remove the possible foreign particulates. Transparent solution was aged for 24 h at room temperature.

Thin films of ZnO were then prepared by spin coating 0.2 ml sol–gel solution onto corning glass substrate of 20 mm × 20 mm × 3 mm size. The substrate was first cleaned with soap water solution and a neutral cleaning agent taken in an ultrasonic bath, after that it was cleaned again with ethanol, chromic acid, ion exchanged distilled water and acetone successively; and then dried with hot air. The clean substrate was placed on the disk of the spin coater and the coating solution (0.2 ml) was dropped on the substrate and spin coated with 3500 rpm for 40 s in air. This process made a precursor film on the substrate. The specimen was dried in air at 80 °C by keeping it on a hot plate for 10 min and then cooled to room temperature. After that it was annealed in air at 500 °C by putting it in a box furnace for 2 h and then slowly furnace cooled to room temperature. By analyzing the cross-sectional view of the grown films using JEOL make scanning electron microscope (SEM), the average film thickness after deposition of three cycles was estimated as ~250 nm.

Crystallographic behaviour of the samples was examined at room temperature by a Bruker D8 Advance diffractometer using CuK_α radiation (1.54056 Å) at a continuous scan rate of 1°/min with resolution 0.1° for the range $20° \le 2\theta \le 80°$ and step size 0.02. Surface morphology and grain growth of the material were studied using SEM, equipped with Oxford INCA energy dispersive X-ray (EDX) spectrometer. The thin film samples were implanted with Fe^{10+} ions from electron cyclotron resonance (ECR) based low energy ion implantation facility at Variable Energy Cyclotron Centre, Kolkata, India. The Fe^{10+} ions were implanted into the n-type ZnO films at 300 keV with doses ranging from 3×10^{15} to 1×10^{17}. Optical transmittance spectra were measured using Shimadzu spectrophotometer (UV-2401 PC). The Raman measurements in backscattering geometry were carried out at room temperature by a Horiba HR 800 micro-Raman system using Ar laser (488 nm) as the excitation source with spectral resolution 0.21 cm^{-1}/pixel. Photoluminescence (PL) spectra of our samples were taken by Perkin Elmer, LS-55 luminescence spectrometer. The PL emission spectra of the unimplanted and implanted ZnO films were measured with an excitation wavelength of 325 nm at room temperature. DC electrical resistivity and magnetoresistance (MR) as a function of temperature were measured using the Vander–Pauw [VDP] method [17]. For the measurements of MR as well as Hall effect, the required magnetic field was created using a 15 T cryogen-free superconducting magnet (Cryogenic Limited make). All these measurements were carried at different cryogenic temperatures.

3. Results and discussion

3.1. SRIM analysis for implantation profile

The implantation profile of Fe^{10+} ions in the ZnO film was simulated using SRIM-2008 program [14,18]. Fig. 1(a) shows the result of Monte Carlo simulation of Fe^{10+} implantation in ZnO, whereas Fig. 1(b) shows the implantation profile of 300 keV ions implanted in it. The mean projected range of 300 keV Fe^{10+} ions in ZnO film is ~700 Å and the longitudinal straggling σ is ~320 Å. Due to the straggling, the projected range with Gaussian distribution lies nearby the mean projected range ~700 Å. Thus about 99% Fe^{10+} ions exist in the region from surface to 1250 Å (=125 nm) depth of ZnO.

3.2. Morphological and structural behaviour

Fig. 2 shows the X-ray diffraction patterns of our films, the patterns consist of three major peaks at 31.87°, 34.56° and 36.41° corresponding to ZnO (0 1 0), (0 0 2) and (0 1 1) respectively. The samples are of polycrystalline behaviour, the (0 1 1) peak is most intense for the samples except that with 3×10^{15} fluence. The

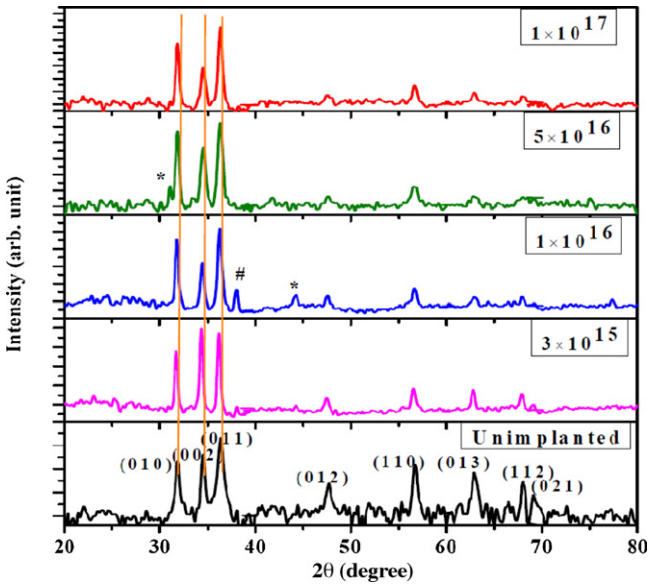

Fig. 2. The X-ray diffraction pattern of unimplanted and implanted ZnO films with different Fe^{10+} fluencies. The mark (*) represents impurity phase in the samples and (#) represents $ZnFe_2O_4$ position in diffraction pattern.