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Paramagnetism in Nitrogen Implanted SnO2 by Low Energy Ion beam Irradiation

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The electron paramagnetic resonance (EPR) spectrum of nitrogen implanted SnO2 thin films have been study. An isotropic g (gyromagnetic ratio) tensor is observed and calculated for all Samples (viz. as deposited and for different concentration of nitrogen in SnO2). The different g values are attributed to the different concentration of paramagnetic species. With the increase in doping of nitrogen from 2% to 6%, the substitution of oxygen vacancies and interstitial atom in electronic structure is also observed. This is confirmed by absorption spectrum recorded by UV Visible.

Keywords: Electron paramagnetic resonance; Isotropic; SnO_2

1 Introduction

SnO_2 does belong to the class of materials which can be easily tuned to exhibit different properties because of their electronic structure. SnO_2 was studied extensively and found to be suitable for various applications. One of the prominent properties of Tin Oxide (SnO_2) is the ferromagnetism at room temperature after doping with Ni, Fe and Co etc. and hence has been used in the fabrication of dilute semiconductors (DMS)[1-5]. The origin of the observed ferromagnetism in undoped tin oxide is neutral cation vacancies in $SnO_{2[}$[ref6]. The most stable charge state of Sn in n- type SnO_2 is +4[ref6] and electron spin in case of SnO_2 are responsible to make SnO2 useful in spintronics[7]. As a typical wide-band gap semiconductor, SnO2 is a promising candidate for the probable applications in the field of spintronics, and many research work have been performed to investigate origin of the observed ferromagnetism in SnO_2[ref8]. SnO_2 has also been reported to be a promising material for photodetectors and ultraviolet Light Emitting Diodes (LED)[9]. It could also be prominent building block for junctions in opto-electronic devices provide if doped with a p-type dopant[10]. Pure SnO_2 have intrinsic n-type conduction due to natural oxygen vacancy defects. The p-type conduction has been proposed by doping nitrogen in SnO2. Nitrogen is a suitable dopant due to the high solubility and non-toxicity[11,12]. (SnO_2-N) is also characterized to show magnetism and proposed to use as dilute magnetic semiconductors. This different kind of magnetism (Paramagnetism and Ferromagnetism) arises by filling up the native oxygen vacancies by suitable dopant. The experimental evidences indicate that the oxygen vacancies are the key factor[13]. For instance, after annealing in air or oxygen, SnO_2 nanoparticles and films showed an obvious decrease in magnetization or a transition from ferromagnetic to diamagnetic[14]. Furthermore, the magnetization of SnO_2 nanoparticles increases significantly after vacuum annealing[15]. On the other hand, it was reported that the thinner SnO_2 film has a much larger magnetization than that of the thick films[16] and the magnetic moment of SnO_2 nanoparticles decrease with its size increasing[14], which suggest that if the observed ferromagnetism in SnO_2 nanoparticles and films comes from oxygen vacancies, these vacancies are just located mainly at the surface. The pure SnO_2 is an intrinsic n type semiconductor. The existence of conductivity is mainly due to the non-stoichiometry (oxygen vacancies)[13]. SnO_2 is also reported as the p-type semiconductors, the p-type conduction is originated in SnO_2 after doping with pentavalent dopant like nitrogen *etc*. Because of its high solubility and non-toxicity nitrogen is an excellent p-type dopant[17].

Nitrogen has the almost same ionic radius and electronegativity as of oxygen hence can replace the p-orbital electron of oxygen resulting in filling up the

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vacancies which might reduce the free electrons. High percentage of doping with pentavalent impurity in SnO_2 may create the holes and shifting of fermi level towards valence band minimum. This may induce p-type conductivity in SnO_2 leaving unpaired electrons in the metal oxides. These unpaired electrons act as a paramagnetic species. The Paramagnetism in Nitrogen doped SnO_2 is due to the 2p states of anionic nitrogen which makes SnO_2 a potential material for application in Dilute Magnetic Semiconductors[13]. Nitrogen is a group V element and acts as an accepter and substitute the oxygen lattice site. In this way it can affect the non-stoichiometry and hence optical band gap. This disturbance in native defects can be resulted in variation of carrier density near conduction band minimum and valence band maximum which further affects the absorptions of ultra violet and visible light. The Nitrogen doped SnO_2 show the substantial variation in band gap and absorption in visible range[18]. Hence to explore the possibility of magnetization and tuning the absorption spectra for various applications, we studied the mechanism of creating the holes in SnO_2 by implanting the nitrogen through low energy ion beam.

2 Preparation of Samples and parameters for ion implantation

The thin films of SnO_2 have been deposited by rf-sputtering technique using target prepared by SnO_2 powder (99.99% Alpha Aesar). The Base pressure of chamber was 6×10^{-6} torr while depositing the thin films at 150 volts for 40 minutes. The distance between substrate (Silicon) and target was 20 cm. The prepared samples were annealed at 400 degree Celsius. The annealed samples were crystalline. In the crystalline SnO_2 thin films, we implanted Nitrogen using low energy ion beam at IUAC (Inter University Accelerator Centre, New Delhi). The energy of beam was 70 keV with the ion fluences (D) of 1×10^{16} ions/cm^2, 2×10^{16} ions/cm^2 and 3×10^{16} ions/cm^2.

Time of beam was calculated by the below equation,

$$T = \frac{DqeA}{I} \qquad \ldots (1)$$

Here D: Fluence in ions/cm^{2,} q-Charge state e-Electronic charge A-Area in cm^2, I–current in Ampere

Table 1 — Parameters for Implantation

Ion beam Current (I)	1 μA
Area of sample (A)	1 cm^2
Charge State of implanting species	+1

Using the above-mentioned values listed in Table 1, the time for exposing the samples to irradiation were calculated corresponding to three fluences (D). The low energy ion beam was allowed to fall on the sample for different duration in order to have 2%, 4% and 6 % nitrogen in SnO_2. These samples are named as a, b, c and d for as deposited, doping with 2%, 4% and 6% respectively. The implanting species supposed to occupy the different depth and distribution profile. The depth of implantation was calculated by SRIM (Stopping and Ranging in Matter) software. The X-band (10 GHz) EPR of N-SnO_2 was recorded at room temperature with magnetic field as a variable.

3 Electron Paramagnetic Resonance

EPR spectroscopy is an efficient experimental technique to investigate the paramagnetic species and the different kind of defects present in the material. The as-deposited and nitrogen implanted SnO_2 (N-SnO_2) thin films by low energy ion beam were investigated by EPR spectroscopy (Fig. 1). The spectrum shows the absence of interaction of electron with nucleus as there is only one peak. Also, the gyromagnetic ratio (g) is isotropic and calculated from the below equation,

$$g = \frac{\gamma h}{\mu b H} \qquad \ldots (2)$$

Where, H is the magnetic field (gauss), γ is the frequency (Hz), μ_b is the Bohr magnetron equal to 9.274×10^{-21} erg/gauss and h is Planck's constant, 6.626×10^{-27} erg-s/cycle.

From the above equation g value in as-deposited is higher in comparison of SnO_2: N. The computed value of the g for the samples doped (or implanted) with nitrogen with various concentration confirms the paramagnetic nature of SnO_2. The g value in the present case is in

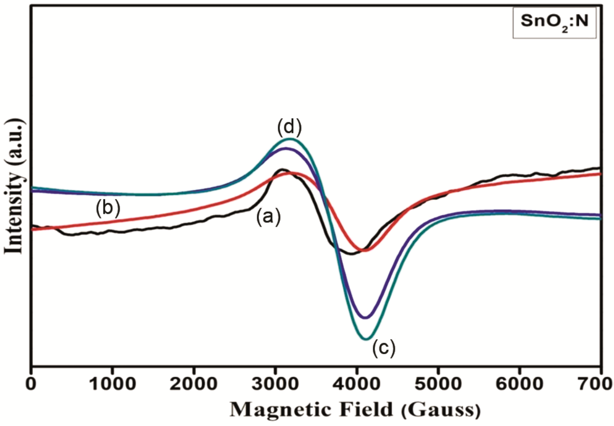

Fig. 1 — EPR of pure and nitrogen implanted SnO2 thin films

agreement with the theoretical and experimental value to within the experimental error[19]. The gyromagnetic ratio (g) values computed (1.88, 1.91, 2.02 for the samples b, d, and c respectively) at X-band almost equal to the reported results. The excellent fit to the data at the frequency (9 GHz) confirms that this is the correct spin Hamiltonian.

This indicates the interaction takes place only with Sn atom, in as deposited sample the blurred signal is due to oxygen deficiency. Whereas in doped samples the peaks were sharpen due to replacement of oxygen vacancies by nitrogen. The hyperfine structure was found in SnO_2 doped with high percentage of nitrogen[19].

4 Optical Absorbance

The reported optical band gap value for tin oxide is 3.6 eV, corresponding to the absorption threshold in the UV region (l to 340 nm). However, in the present work, the SnO_2 was implanted with various percentage of nitrogen. N-SnO_2 has complicity in absorption spectra in ultraviolet and visible range. In Fig. 2 the UV-Visible spectra were recorded in 200-900 nm range of wavelengths and shown for both pure SnO_2 and N-SnO_2. Looking at the complete range of 200 nm to 900 nm, the absorbance spectra of all the samples appear to be relatively similar. According to Fig. 3 the tauc plot reveals the change in the values of band gaps. The band gap found to be decreased significantly in case of implanted samples. This lowering of band gap is attributed to the shifting of fermi level toward valence band. Shifting of fermi level towards valence band is quite obvious because of doping with group V element (implanted species). The shifting of fermi level is a sign of the conversion of host material from n-type to p-type semiconductor. Even the spectrum of pure SnO_2 was quite different from usual reported behavior. The calcination temperature and ambient air atmosphere may be the reason for this behavior. This anomalous behavior in optical properties has been already observed in the materials having rutile structure like SnO_2 and TiO_2[Ref15] which is further explained and ascribed to the Burstein– Moss effect. This effect is the consequence of the oxygen vacancies, resulting from various reasons[8,20]

$$O^{2-} = (1/2)\, O_2 + V_o \qquad \text{... (3)}$$

The above Kroger–Vink equation described the formation of an oxygen vacancy filled by two electrons through O_2 from the materials. The abnormal absorption in the present case is mainly due to the above-mentioned reasons. Remarkably, such kind of absorption is systematically higher in the case of N-doped materials[21]. Finally, the doping or implantation with nitrogen leads to the formation of free electrons which could not be trapped by vacancies.

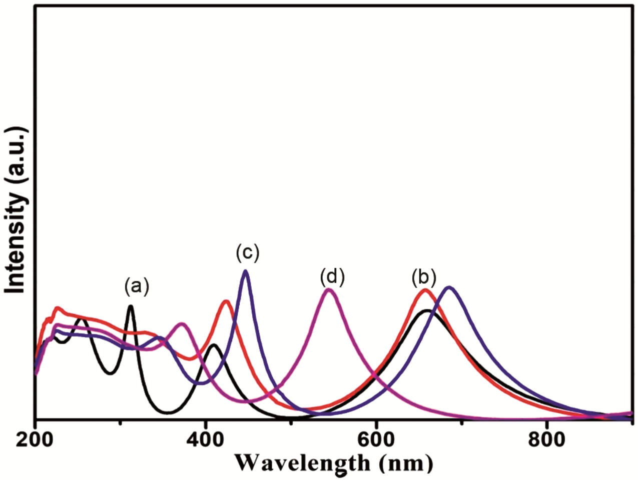

Fig. 2 — Absorption spectrum of pure and nitrogen implanted SnO_2 thin films

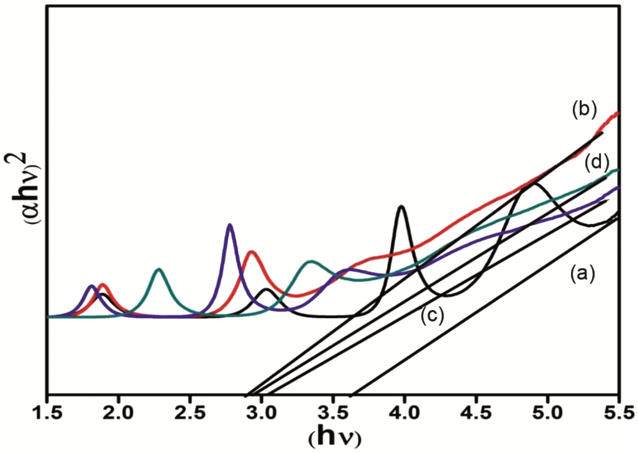

Fig. 3 — Tauc plot of pure and nitrogen implanted SnO_2 thin films

5 Conclusion

The electron paramagnetic resonance (EPR) spectrum of nitrogen implanted SnO_2 thin films have been study. An isotropic g tensor is observed and calculated for all samples (viz. as-deposited and for different concentration of nitrogen in SnO_2). The different g values are attributed to the different concentration of paramagnetic species. With the increase in doping of nitrogen from 2% to 6%, the substitution of oxygen vacancies and interstitial atom in electronic structure is also observed. This fact also confirmed by absorption spectrum recorded by UV-Visible spectroscopy. The nitrogen act as a substitute for oxygen atom in SnO_2 and thus a hole is created in 2p-state of nitrogen. These vacancies in 2p-state of nitrogen have a magnetic moment and respond to the applied external magnetic field. This can be treated as a paramagnetic center.

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