AIP | Journal of Applied Physics

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Citation: J. Appl. Phys. **97**, 10A925 (2005); doi: 10.1063/1.1855707
View online: http://dx.doi.org/10.1063/1.1855707
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v97/i10
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Magnetic and optical properties of rare earth doped $Sn_{0.95}RE_{0.05}O_{2-\delta}$ (RE=Gd, Dy, Er)

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(Presented on 8 November 2004; published online 2 May 2005)

The magnetic and optical properties of rare earth (Gd, Dy, and Er) ion doped SnO_2 bulk and optical properties of thin films are investigated. The bulk samples were found to show an upturn in ac magnetic susceptibility at low temperatures T_U and exhibited a paramagnetic moment at room temperature. The band gap of the bulk samples was found to be independent of the rare earth (RE) ions while for the thin films it varied from 3.48 eV to 3.58 eV. The observed low temperature upturn suggests an interesting magnetic property in SnO_2 with RE doping. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1855707]

I. INTRODUCTION

The quest for dilute magnetic semiconductors (DMS), which exhibit magnetism at temperatures below and above room temperature spans over several classes of materials. Such materials are important in the development of spintronic applications like spin injectors for semiconductor heterostructures that can operate preferably without cryogenic cooling. Group III-V and II-VI DMS materials typically exhibit Curie temperatures T_c well below ambient temperature due to weak interaction of the magnetic impurities. Calculations based on the Zener's model of magnetism suggested that the strongest interaction is that mediated by holes, and experimental studies carried out to date have borne out this prediction.[1] One notable exception is that of Mn-doped GaN, which grows *n*-type by gas-source molecular beam epitaxy under certain conditions and appears to be ferromagnetic at room temperature.[2] In addition, it has recently been shown that wide band-gap oxide semiconductors exhibit DMS property with 3*d*-transition metal dopants. Co-doped TiO_2 anatase and Co-doped SnO_2 are ferromagnetic well above room temperature, however, the mechanism of magnetism remains unknown.[3–6]

Most of the conventional III-V based DMS materials exhibit Curie temperatures of about 150 K or less and are *p*-type, which means that the exchange interaction leading to ferromagnetic behavior is hole mediated. Much of the effort expended to date to understand the properties of thin-film DMS materials has focused on Mn-doped II-VI, III-V, and Group IV semiconductors. Relatively little effort has gone into the investigation of oxide-based semiconductors to find out whether they are magnetically more robust. Such a study is important as oxides have a wider base in terms of band-gap tenability and electrical property variations. Co-doped TiO_2 has recently been discovered to be the most magnetically robust DMS with regard to magnetic moment at saturation, coercivity field, and Curie temperature. Indeed, it is one of the very few DMS materials to exhibit ferromagnetic behavior above 300 K. In addition, it has been shown that TiO_2 can be grown epitaxially by both pulsed laser deposition (PLD) and oxygen plasma assisted molecular beam epitaxy. However, the resulting magnetic properties differed considerably for the two growth methods.

Wide and direct band-gap semiconductors are of great interest in ultraviolet (UV) optical devices, such as light emitting diodes and laser diodes.[7] Tin oxide (SnO_2) is an important *n*-type semiconductor with a wide band gap (E_g =3.6 eV at 300 K). Furthermore, recently applications of SnO_2 have been extended to solar cells because of the optical conduction of SnO_2. In recent years, considerable efforts have been focused on the synthesis of magnetic impurity doped SnO_2 thin films in order to explore DMS properties. A variety of methods such as sol-gel,[8] chemical vapor deposition,[9] magnetron sputtering,[10] and thermal evaporation[11] have been used to prepare SnO_2 thin films or nanoparticles.

Rare earth (RE) metal ion doping in various hosts, on the

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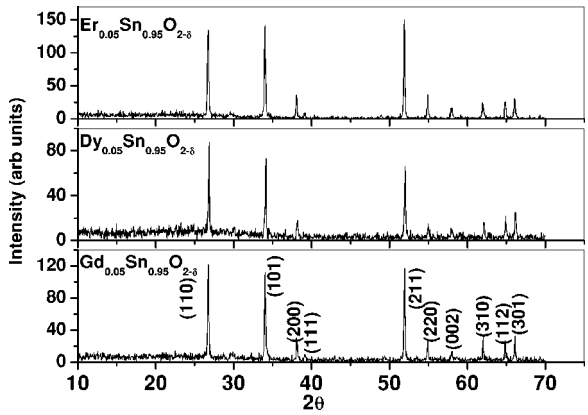

FIG. 1. X-ray diffractograms of polycrystalline $Gd_{0.05}Sn_{0.95}O_{2-\delta}$, $Dy_{0.05}Sn_{0.95}O_{2-\delta}$, and $Er_{0.05}Sn_{0.95}O_{2-\delta}$.

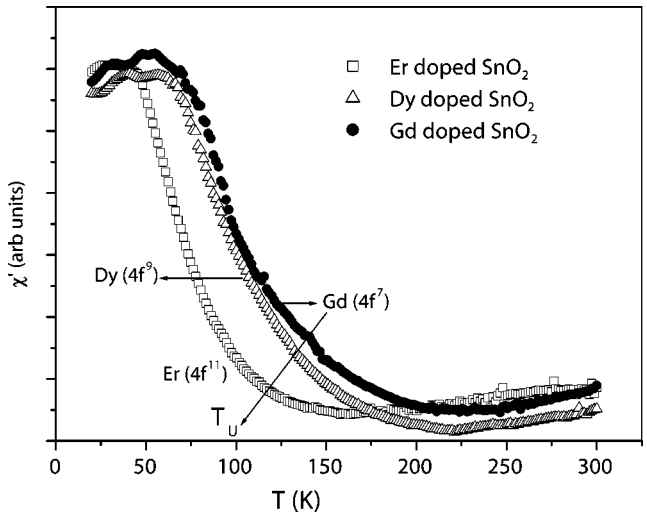

FIG. 2. Temperature variation of ac magnetic susceptibility of bulk RE-doped SnO_2.

other hand, has been investigated most frequently due to their unique fluorescence properties, stability, and high emission quantum yields. It is also important to note that rare earth ions can be doped into oxide hosts with relative ease. It was envisaged that if rare earth ions can be doped into oxide based semiconductors, then band-gap excitations may result in efficient energy transfer that would result in interesting optical as well as magnetic properties. It is therefore interesting from a technological point of view to dope oxide semiconductors with rare earth ions to see the possibility of coexistence of optical and magnetic properties. If found, such a coexistence will be of great importance for magneto-optical device applications.

II. EXPERIMENT

Polycrystalline $Gd_{0.05}Sn_{0.95}O_{2-\delta}$, $Dy_{0.05}Sn_{0.95}O_{2-\delta}$, and $Er_{0.05}Sn_{0.95}O_{2-\delta}$ samples were prepared using conventional solid-state method. High pure (>99.9%) oxides of rare earth, Gd_2O_3, Dy_2O_3, and Er_2O_3 were weighed stoichiometrically with SnO_2, mixed thoroughly and calcined at 1200 °C for 24 h. This procedure was repeated thrice and the resultant powder was pressed into pellets and sintered at 1350 °C for 24 h. The phase formation was confirmed by x-ray, diffraction. These pellets were used as targets to grow thin films by PLD technique using Nd:YAG (YAG—yttrium aluminum garnet) pulsed laser (wavelength 355 nm, pulse width 19 ns, repetition rate 10 Hz, and laser fluence 2 J cm^{-2}). The following discussion is based on films grown at an oxygen partial pressure of 1×10^{-4} Torr and a substrate temperature of 700 °C as these growth parameters yielded the best results. The diffuse absorption spectroscopy for the samples was found using a Carey UV-Vis spectrometer. The room temperature magnetic moment up to a field of 1 T was measured using a Varian vibrating sample magnetometer, and ac magnetic susceptibility studies in the temperature range of 300 K–14 K were carried using a commercial ac susceptometer.

TABLE I. Paramagnetic moment of the bulk sample obtained from VSM of 1 T at room temperature, optical band gap of the thin films and lattice constants of bulk sample.

Compound	Paramagnetic moment (μ_B/RE ion)	Band gap (eV)	Lattice constants (Å)
$Gd_{0.05}Sn_{0.95}O_{2-\delta}$	0.018	3.58	a=4.719, c=3.177
$Dy_{0.05}Sn_{0.95}O_{2-\delta}$	0.021	3.50	a=4.717, c=3.175
$Er_{0.05}Sn_{0.95}O_{2-\delta}$	0.017	3.48	a=4.703, c=3.173

III. RESULTS AND DISCUSSION

The X-ray diffractograms of $Gd_{0.05}Sn_{0.95}O_{2-\delta}$, $Dy_{0.05}Sn_{0.95}O_{2-\delta}$, and $Er_{0.05}Sn_{0.95}O_{2-\delta}$ are shown in Fig. 1. The samples could be indexed to a tetragonal structure with lattice parameters listed in Table I.

The lattice constants were found to be the same for all the three samples possibly due to the very low concentration of the rare earth ion present in the host lattice. The temperature variation of susceptibility for the bulk samples is shown in Fig. 2. It is seen that all the three samples exhibit a paramagnetic behavior at room temperature with an upturn (~150 K) followed by saturation at low temperatures. The temperature of the upturn is found to be the highest for the Gd doped compound (175 K), lowest for the Er doped compound (~110 K), and the Dy doped compound exhibiting it at around 150 K. It is interesting to see if these upturn temperatures correspond to the ordering temperatures of the RE ions used for doping in this study. Table II lists the ordering temperatures [Curie (T_C) and Neel (T_N)] of the RE ions. We found that SnO_2 doped with Gd and Er showed T_U's that do not correspond to the elemental ordering temperatures of the respective RE ions, thus ruling out the observed upturn due

TABLE II. Curie temperature T_C and Neel temperature T_N of the RE ions.

	T_C (K)	T_N (K)
Er	20	84
Dy	85	179
Gd	293	···

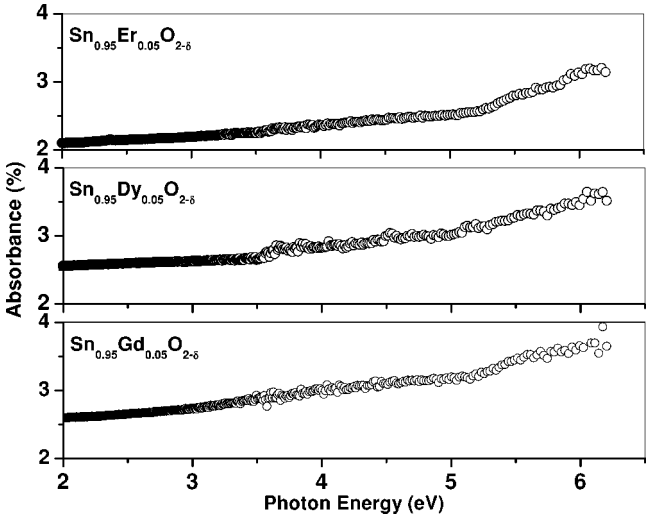

FIG. 3. Absorption spectra of rare earth doped thin films.

to cluster formation. On the other hand, in Dy doped SnO_2, the observed upturn (T_U) may be due to cluster formation as the magnetic ordering temperature of Dy matches with that of T_U obtained from χ' vs T curves.

In general, bulk SnO_2 system is devoid of charge carriers due to the stoichiometric oxygen concentration. Since the dopants are randomly spread out in the lattice, the probability of a rare earth ion placed next to each other is high. This leads to the low paramagnetic moment per RE ion as listed in Table I. The observed magnetic moments ($0.018-0.021\ \mu_B$/RE-ion) are much lower than the theoretical spin only moment of the RE ions. It is also possible that higher magnetic fields are required to saturate the moment as seen in the case of other systems like manganites where a field of 15 T was needed to saturate the moments.[12] Moreover, in order to affirm any ferromagnetic behavior in these systems, detailed low field (<10 Oe) SQUID magnetometry measurements are essential. Studies on thin film samples are underway to see if the RE doped SnO_2 samples could realize intrinsic DMS effect due to the fact that oxygen partial pressure variation during the film growth induce charge carriers in to the system by varying the oxygen partial pressure. Figure 3 shows the band gap of the bulk samples. Band gap is found to be independent of the rare earth ions while for the thin films it varied from 3.48 eV to 3.58 eV. Structural and magnetic studies on thin films are underway and will be reported elsewhere. In summary, RE-doped bulk SnO_2 showed intrinsic DMS behavior at low temperature.

IV. CONCLUSIONS

We observed intrinsic ferromagnetism at low temperatures in RE (Gd, Dy, and Er)-doped SnO_2. All the bulk RE doped SnO samples were found to show an upturn T_U around 150 K by ac-susceptibility measurements. The samples showed paramagnetic moments ($\sim 0.02\ \mu_B$/RE-ion) smaller than the theoretical spin-only moments of the respective RE ions. The band gap of the bulk sample was found to be independent of the rare earth ions while for the thin films it varied from 3.48 eV to 3.58 eV. The absence of carriers in the bulk RE doped SnO_2 samples may be responsible for the low not realizing intrinsic DMS behavior. RE-doped SnO_2 system can offer a great deal of interest in understanding the physics if obtained as intrinsic DMS systems in the bulk or thin film form.

ACKNOWLEDGMENTS

The authors thank Bhavani Kumar, SAIF IIT-Madras for the band-gap measurements, N. Rama and Dr. M. Kottaisamy, IIT-Madras, and R. Nirmala, TIFR, Mumbai for useful discussions.

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