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Abstract
Optical properties of spray pyrolysed $Sn_{1-x}Co_xO_{2-\delta}$ $(0 \leqslant x \leqslant 0.15)$ thin films exhibiting room temperature ferromagnetism have been investigated in the energy range 1–6 eV. The onset of optical absorption is blueshifted by as much as 220 meV for a cobalt concentration of $10a/o$ $(x = 0.10)$. Our detailed analysis indicates that the most probable cause of the blueshift is the Burstein–Moss effect. The optical conductivity calculations reveal that Co does not introduce any mid-gap states. Also the small change in the slope of α^2 versus $h\nu$ indicates that the O and Sn band edges are affected on Co addition. This band-edge shift also implies the presence of strong Coulomb interaction between Co, Sn and O sites, as a plausible cause of the observed ferromagnetism in these samples. The Burstein–Moss effect seems to be masking the effect of band structure modification introduced by Co addition. The high (∼75%) optical transparency of these films in the visible region remains practically unaffected on Co addition.

1. Introduction

Tin oxide is one of the rare forms of semiconductors exhibiting high transparency and high electrical conductivity simultaneously. Due to this, tin oxide thin films have been widely used as transparent electrodes in LEDs, electrochromic displays, liquid crystal displays, solar cells, CCDs [1] etc. A potential application in the emerging field of spintronics [2] becomes possible when transition metal doping (Co, Mn, Fe etc) is done in SnO_2, and room temperature ferromagnetism (RTFM) is induced [3]. We have recently reported carrier mediated RTFM in $Sn_{1-x}Co_xO_{2-\delta}$ thin films prepared by a spray pyrolysis technique [4]. In this paper, we report the optical properties of these well characterized ferromagnetic semiconducting thin

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films. The study helps us to understand the origin of the observed blueshift in thin films of transparent ferromagnetic $Sn_{1-x}Co_xO_{2-\delta}$ semiconductor and its relation with the observed ferromagnetism. Generally, the blueshift in the optical absorption of semiconductors is attributed to many reasons, such as a decrease in lattice constant [5] (due to internal strain), the quantum size effect [6], electronic modification of the band edges [7] and the Burstein–Moss shift [8]. The present study of various physical parameters (aspects) of $Sn_{1-x}Co_xO_{2-\delta}$ thin films indicates that the observed blueshift may be attributed to the Burstein–Moss effect and electronic structural changes. The Burstein–Moss effect is due to the partial filling of the lowest states of the conduction band, which leads to a blocking of the lowest states, and hence an electronic transition from the valence band to the conduction band has to occur at higher energies, which result in the widening of the optically observed band gap.

2. Experimental details

Thin films of $Sn_{1-x}Co_xO_{2-\delta}$ with $x = 0, 0.05, 0.10$ and 0.15 were grown on quartz substrates at a temperature of $450\,°C$ by spray pyrolysing a mixture of 1 M aqueous solutions of $SnCl_4 \cdot 5H_2O$ and $(CH_3COO)_2Co \cdot 4H_2O$ in appropriate proportions. Spray depositions were carried out for 20–25 s in the ambient atmosphere using nitrogen as a carrier gas at a pressure of $\sim 4.0 \times 10^4$ N m^{-2}. The resultant films were annealed in air at $500\,°C$ for 30 min to obtain a homogeneous and stable material. The homogeneity and stability of the films was confirmed by carrying out the deposition a number of times under identical conditions and observing the same physical parameters. The structural characterization of the films was made by using Philips X'Pert PRO (model PW 3040) diffractometer in the glancing angle (GA) mode with GA = 2°. The goniometric resolution of the instrument is 0.001°. Hall measurements were carried out in the van der Pauw geometry at room temperature. Room temperature normal transmittance (T) and near-normal reflectance (R) measurements as a function of incident energy varying from 1 to 6 eV were carried out using a double beam spectrophotometer (Perkin Elmer, model Lamda 900) having a spectral resolution of 0.05 and 0.2 nm in the UV–VIS and NIR ranges, respectively. The complex refractive index $\tilde{n}(h\nu) = n + ik$ has been calculated numerically, by solving the Tomlin equations [9] for T and R. From the $\tilde{n}(h\nu)$ values thus obtained, it was possible to evaluate other optical constants, like the optical absorption coefficient $\alpha(h\nu)$ and the complex optical conductivity $\tilde{\sigma}(h\nu)$. The thickness of various films was measured to be ($\sim$350–460 nm) using a stylus profilometer (model XP-II, Ambios Technologies); this was then verified by calculating the thickness using the approximation of 'weakly absorbing films' [10].

3. Results and discussion

Figure 1 shows the transmittance curves of various $Sn_{1-x}Co_xO_{2-\delta}$ ($0 \leqslant x \leqslant 0.15$) thin films recorded under normal incidence at room temperature (RT). It may be noted that the transmittance in the visible region is not much affected on Co incorporation, which is technologically quite promising. The transmittance edge shows a blueshift with increase in the Co concentration up to $x = 0.10$ in the films. The blueshift can be quantified in many ways including extrapolation towards zero either in the plots of α versus $h\nu$ [11] or α^2 versus $h\nu$ [9], determination of the energy corresponding to 10% [12] or 50% [13, 14] transmittance through the samples or energy corresponding to a high value of α (10^5 cm^{-1}) [15]. In the present case, the observed blueshift has been quantified in terms of shift in the energy of incident radiation corresponding to 20% transmittance. This value has been chosen as it corresponds to the nearly linear rapid fall of the film transmittance and thus can be determined with fair precision. It may be noted from figure 1 that this energy value is maximum for $x = 0.10$, i.e. a shift of about
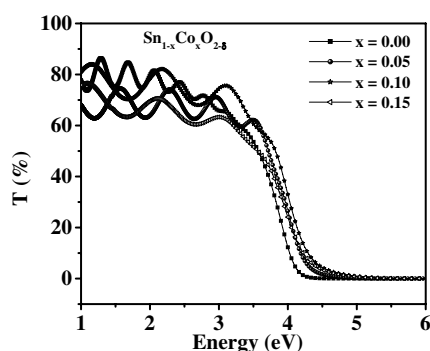
Figure 1. Normal transmittance $T(\%)$ versus incident photon energy $(h\nu)$ of $Sn_{1-x}Co_xO_{2-\delta}$ films with $(0 \leqslant x \leqslant 0.15)$ deposited at $450\,°C$ showing a blueshift with increase in Co concentration, x. Visible transmittance is not much affected on Co addition.
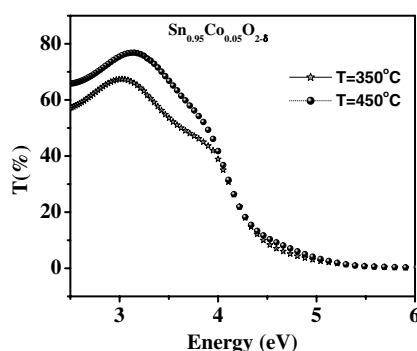

Figure 2. Normal transmittance $T(\%)$ as a function of incident photon energy $(h\nu)$ of the $Sn_{0.95}Co_{0.05}O_{2-\delta}$ films prepared at 450 and $350\,°C$, indicating that there is no blueshift on varying the crystallite size.

200 meV (which was later found to be a good estimation as shown in figure 3). At $x = 0.15$, the blueshift drops back to a lower value from its maximum value at $x = 0.10$. This can be understood as at $x = 0.15$ the film was found to contain not only SnO_2 but also the Co_3O_4 phase [4]. This indicates that in this film only a fraction of the Co ions is incorporated in the SnO_2 matrix and the rest are used in the formation of the segregated Co_3O_4 phase.

In order to look into the possible causes for the observed blueshift, we consider first the role of variation of the lattice parameters of SnO_2 with Co concentration. The x-ray diffraction (XRD) patterns of films with $0 \leqslant x \leqslant 0.10$ showed [4] peaks corresponding to the SnO_2 phase only. From the detailed XRD studies the lattice parameters a and c of the films having different concentration of Co have been calculated from the Bragg peaks after correcting for instrumental broadening (as shown in table 1). The data show that there is not much change in the lattice parameters for x varying up to 0.10. However, a tendency for a slight increase in c parameter is revealed. It suggests, if at all, a decrease in the optical band gap leading to a redshift. The small decrease of lattice parameter a in the case of films with $x = 0.15$ can be attributed to the presence of a Co_3O_4 phase in this film. The presence of Co_3O_4 is likely to introduce compressive strain in the SnO_2 crystallites thereby causing a reduction in lattice parameters. It can thus be concluded that the continuously increasing blueshift up to $x = 0.10$ is not due to the change in the size of the lattice.

Table 1. Variation of lattice parameters and crystallite size of $Sn_{1-x}Co_xO_{2-\delta}$ thin films with Co concentration for films deposited at 350 and 450 °C.

Co concentration (x)	Lattice constants (Å)		Crystallite size (nm)
	a	c	
0 (JCPDS data)	4.737	3.186	—
0 (T_s = 450 °C)	4.737	3.184	26.7
0.05 (T_s = 450 °C)	4.738	3.187	13.6
0.10 (T_s = 450 °C)	4.737	3.186	12.3
0.15 (SnO_2) (T_s = 450 °C)	4.733	3.185	9.1
Pure Co_3O_4 film	—	—	16.2
0.05 (T_s = 350 °C)	4.711	3.168	10.1

To explore the possibility of a quantum size effect, a detailed analysis of the crystallite size from x-ray patterns has been carried out. As given in table 1, the crystallite size is seen to reduce continuously from 26.7 to 9.1 nm on increasing the Co concentration from $x = 0$ to 0.15. To see if the quantum size effect can account for the observed blueshift, we prepared samples of $Sn_{0.95}Co_{0.05}O_{2-\delta}$ at two different temperatures—450 and 350 °C—with a view to obtaining different crystallite sizes at fixed concentration. The crystallite size calculation now reveals the sizes to be 13.6 and 10.1 nm, respectively. The normal transmittance behaviour (figure 2) of these films grown at 450 and 350 °C shows that there is no appreciable change in the transmittance edge. This indicates that the origin of the blueshift due to cobalt incorporation is not associated with the quantum-size effect. Our data thus suggest that the Bohr excitonic radius for SnO_2 is smaller than 9.1 nm. Also, theoretically the expected Bohr exciton radius, given approximately by $a_{ex} = a_0\varepsilon/m^*$, where a_0 is the Bohr radius, $\varepsilon \cong 13$ is the static dielectric constant and m^* is the exciton reduced mass that may be replaced by the electron effective mass (since the holes are very heavy $m_h \cong 3m_0$ in SnO_2 semiconductor and $m_e^* = 0.20m_0$ (present work)), is about 3.24 nm [16].

The optical band gap has been determined from the spectral dependence of the absorption coefficient $\alpha(h\nu)$, where $\alpha = \frac{4\pi\kappa}{\lambda}$, λ is the wavelength of the incident radiation and κ is the imaginary part of the complex refractive index (extinction coefficient). At photon energies exceeding the band gap (E_g), the absorption coefficient α varies linearly with $(h\nu - E_g)^{1/2}$ for a direct gap semiconductor and with $(h\nu - E_g)^2$ for an indirect gap semiconductor. Band structure calculations [17] have revealed a direct band gap for SnO_2 just below the onset of indirect transitions. The plots of α^2 versus $h\nu$ for our films (shown in figure 3) reveal that all the films ($0 \leqslant x \leqslant 0.15$) have a direct band gap. The linear extrapolation to zero absorption gives a band gap value of 4.0 eV for undoped SnO_2 thin film. On increasing the Co concentration x, the band gap shifts to higher energies, showing a maximum blueshift of 220 meV for $x = 0.10$. In addition, there is no evidence for strong absorption at energies below the gap.

Though the absorption coefficient studies gives the onset of band transitions, study of the optical conductivity (in particular, the real part of the optical conductivity $\sigma_1 \propto 4\pi n\kappa/\lambda$, where n and κ are the real and imaginary parts of refractive index, respectively) is a better tool for comparing the predictions of band theory. Figure 4 shows the plots for the variation of the real part of the optical conductivity with incident photon energy. It may be noted that below the band edge the optical conductivity is almost invariant until the incident energy of radiation exceeds the optical band gap. The absence of in-gap conductivity indicates that the on-site Coulomb energy on adding another electron to the Co is very large [7].

To investigate further if any modifications of the electronic structure are introduced by the addition of Co, we determined the slope of the linear part of α^2 versus $h\nu$ (figure 4) and

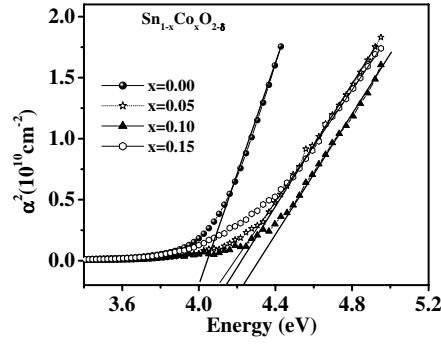**Figure 3.** α^2 versus $h\nu$ plots computed for Co concentrations $x = 0$, 0.05, 0.10 and 0.15. This gives a direct band gap value of 4.0 eV for a degenerate SnO$_2$ semiconductor.
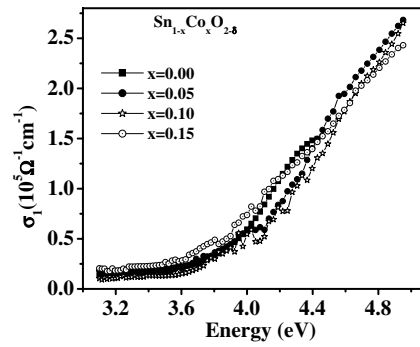

Figure 4. The real part of the optical conductivity (σ_1) plotted as a function of photon energy ($h\nu$) of Sn$_{1-x}$Co$_x$O$_{2-\delta}$ with ($0 \leqslant x \leqslant 0.15$) showing that Co does not introduce any mid-gap states.

obtained its variation with Co concentration. The small change in the slope of α^2 versus $h\nu$ indicates that the conduction band edge (which is a result of 90% of Sn s content [18]) and the valence band edge (which is a result of O p content) are affected by addition of Co. The Coulomb interaction between Co, Sn and O sites provides a strong interaction, which could also partially account for the observed ferromagnetism as proposed in [7], in addition to the predominant contribution from the polarization of the free charge carriers. Also it seems that the large Burstein–Moss effect is just masking the effect of the small band structure modification introduced by addition of Co. If the O and Sn band edges are not affected by the substitution of Co, this blueshift should be understood in terms of the reduction of the interband oscillation strength upon dilution of Sn by Co. However, this scenario leads not to a shift in the band edges but a change in the slope of the α^2 versus $h\nu$ plot, contrary to our observation. Further, as evidenced from the x-ray analysis, at the extreme solubility limits the phases are SnO$_2$ and Co$_3$O$_4$. If SnO$_2$ ($E_g = 3.92$ eV) and Co$_3$O$_4$ ($E_g = 1.5$ eV [19]) form a solid solution, then, using Vegard's law, there should have been a redshift of $\sim$200 meV instead of a blueshift. Hall measurements indicate that the majority carriers are electrons and their concentration increases monotonically with Co concentration up to $x = 0.10$, i.e. from 0.82×10^{19} cm^{-3} at $x = 0.0$ to 6.09×10^{19} cm^{-3} at $x = 0.10$. The origin of conduction electrons upon Co doping is understood [20] on the basis of charge balance formulae for Co replacing Sn in the SnO$_2$ matrix, given as $(Sn^{4+})_{1-x}(Co^{2+})_x O^{2-}_{2-x}$ and/or $(Sn^{4+})_{1-x}(Co^{3+})_x O^{2-}_{2-x/2}$.
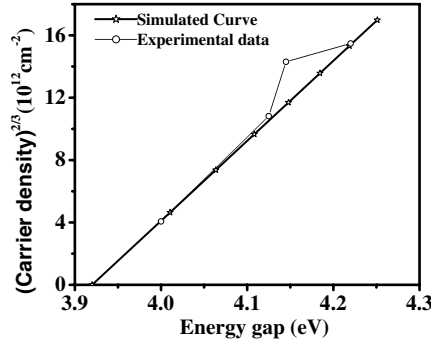
Figure 5. Straight line behaviour of the E_g versus $n_e^{2/3}$ plot for $Sn_{1-x}Co_xO_{2-\delta}$ thin films indicating a Burstein–Moss optical blueshift.

Assuming that each Co substitution generates, on average, one electron, E_g should have been redshifted by an amount of approximately 242 meV from the value of SnO_2. Therefore, the rigid alloy (solid solution) concept does not explain the observed blueshift. Shinde *et al* also reported an increase in carrier concentration with Co doping in TiO_2 [21].

On the other hand, the effective energy gap for direct transitions in the doped material in the case of unperturbed conduction and valence band edges is given by

$$E_g^0 = E_{g0} + \Delta E_g^{BM},$$

where the Burstein–Moss shift is given by

$$\Delta E_g^{BM} = \frac{\hbar^2}{2m_{vc}^*}(3\pi^2 n_e)^{2/3}, \tag{1}$$

where E_{g0} is the direct band gap and n_e is the free electron density, with the effective reduced mass

$$\frac{1}{m_{vc}^*} = \frac{1}{m_v^*} + \frac{1}{m_c^*},$$

where m_v^* and m_c^* represents the effective mass for the hole and electron, respectively.

Equation (1) predicts a shift in the energy gap proportional to $n_e^{2/3}$. A plot of $n_e^{2/3}$ versus E_g (figure 5) shows a linear relationship, indicating that the blueshift in our case is a result of the Burstein–Moss effect. The intercept of linear extrapolation of $n_e^{2/3}$ versus E_g plot on the energy axis yields a value of 3.92 eV for the band gap of a non-degenerate SnO_2 semiconductor, which is in agreement with the reported value [22]. Also, the simulated data using equation (1) show that the best-fit results yield a value of $0.2m_0$ for m_c^*, $3m_0$ for m_v^*, where m_0 is the rest mass of the electron. These values are in agreement with the earlier reported results [1, 18]. Here, it is worthwhile mentioning that we neglected the role of electron–electron and electron–impurity scattering, which may not be realistic. However, it does not affect the conclusions of the present study. It is worth mentioning that the Burstein–Moss shift has been reported in a SnO_2 degenerate semiconductor [23] whereas it was observed for the first time in $Sn_{1-x}Co_xO_{2-\delta}$ thin films.

4. Conclusions

Thin films of $Sn_{1-x}Co_xO_{2-\delta}$ transparent ferromagnetic semiconductor prepared by spray pyrolysis show a blueshift in the optical gap with increase in Co concentration. A maximum

blueshift of 220 meV is seen for $x = 0.10$. The linear behaviour of α^2 versus $h\nu$ and the relationship of the direct band gap with carrier concentration indicate the Burstein–Moss shift to be the most probable cause of this blueshift. The best fit results of the (carrier concentration)$^{2/3}$ versus optical energy gap relation yield a value of $0.2m_0$ for the electron effective mass and $3m_0$ for the hole effective mass. The optical conductivity calculations show that the Co ions do not introduce any mid-gap states. Also the small change in the slope of the α^2 versus $h\nu$ plot indicates that the band edges are significantly affected by Co substitution. This band-edge shift implies strong Coulomb interaction, which may be partially responsible for the observed ferromagnetism in these films. Also the Moss–Burstein effect seems to be just masking the effect of band structure modification introduced by the addition of Co. Significantly, the optical transparency in the visible region is not affected upon addition of Co.

Acknowledgments

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