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EFFECT OF ANNEALING TEMPERATURE ON THE MAGNETIC PROPERTIES OF CO-DOPED SNO_2

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ABSTRACT

Annealing temperature plays a very crucial role in the surface morphology and magnetic properties of Co doped SnO_2. In this paper, we present a systematic investigation of the effect of annealing temperature on the magnetic properties of Co doped SnO_2. $Sn_{1-x}Co_xO_2$ samples have been chemically synthesized with low Co concentration (≤ 1%). The X-ray diffraction (XRD), and scanning electron microscopy (SEM), are used to characterize these samples. The XRD pattern shows the tetragonal rutile structure. The crystallite size and the average particle size increases with increase in annealing temperature. The samples sintered at 350°C, 450°C and 550°c show ferromagnetism at room temperature while those sintered at ≥ 600°C show paramagnetism. With the increase of annealing temperature, the ferromagnetism observed at room temperature in the low temperature sintered samples is gradually suppressed and finally completely removed. This destruction of ferromagnetism at higher annealing temperatures can be understood by considering a metastable ferromagnetic phase and its stability under varying temperature and atmosphere. Also the ferromagnetic properties depend not only on the surface diffusion of Co ions and the distribution of defects such as oxygen vacancies or vacancy clusters but also on the nanometric size of the materials and their surface conditions.

Keywords:- Co-doped SnO_2, Diluted Magnetic Semiconductor, Sol-Gel method, Room temperature ferromagnetism.

1 Introduction:-

Diluted magnetic semiconductors (DMSs) have recently attracted broad interest for their promise in generating and manipulating spin polarized currents [***Punnoose et al. (2004), Coey et al. (2004), Ogale et al. (2003), Batzil et al. (2005)***]. Recently many investigations have been extensively focussed on transition metal (TM) doped wide band gap

semiconductors such as zinc oxide (ZnO), titanium dioxide (TiO_2) and tin dioxide (SnO_2) owing to room temperature ferromagnetism (RTFM). In particular, Tin Oxide (SnO_2) is a very interesting oxide semiconductor with a wide band gap of 3.6 ev. Its optical transparency, electrical conductivity and chemical sensitivity make it a very attractive material for solar cells, heat mirrors, catalysis and gas sensing applications [***Bahra et al. (2008), Godinho et al. (2009), Nomura et al. (2011), Zhou et al. (2012), Li et al. (2010), Wu et al. (2012), Okabayashi et al. (2012)*]**. The ferromagnetic property is intrinsic to the SnO_2 system. The search for room-temperature ferromagnetism (RTFM) in SnO_2 is one of the most intensively studied topic nowadays [***Nomura et al. (2011), Zhou et al. (2012), Li et al. (2010), Wu et al. (2012), Okabayashi et al. (2012)***]. ***Bouaine et al. (2007)*** studied that with low TM doped concentration, the SnO_2 lattice contracts, band gap decreases and a ferromagnetic behaviour is developed. By increasing the doping level leads to rapid expansion of the lattice and hence with higher doping concentration ferromagnetism is destroyed and a paramagnetic behaviour is observed. Sometimes magnetic measurements reveal a mixture of paramagnetic and antiferromagnetic behaviour at this stage [***Hays et al. (2005), Wang et al. (2009), Wang et al. (2009), Li et al. (2010)***]. It has been also been concluded that, when the crystallite size of some of the DMS materials is reduced to below 20 nm, they are found to exhibit better ferromagnetic properties when compared with those having microcrystalline particles (>100 nm). Therefore, it is important to study the influence of nanometric size on various physical properties of oxide based diluted magnetic semiconductors [***Liu et al. (2007), Aragon et al. (2010)***].The TM doping is an effective route to optimize the physical properties by introducing magnetic functionality in this conventional oxide semiconductor. The large sp-d exchange interaction between magnetic ions and the SnO_2 electron bands lead to a number of unusual properties such as electronic structure changes, magneto-optical and opto-electronic effects.

Many works reported ferromagnetic properties of TM doped SnO_2 thin films. ***Ogale et al. (2003)*** reported room-temperature ferromagnetism in pulsed laser deposited SnO_2 : Co (5% and 27%) thin films. Fitzgerald et al. found ferromagnetism in Co-doped SnO_2 thin films for cobalt contents ranging from 0.1 to 15% [***Coey et al. (2004)***]. But, ferromagnetism is much more difficult to find in polycrystalline samples and hence give some conflicting results. For example, ***Punnoose et al. (2004)*** detected room temperature ferromagnetism in Co doped SnO_2 powders synthesized by wet chemical method for Co concentration $\leq$ 1%,

while the same method failed to exhibit RTFM for higher concentrations. Similarly, $Sn_{1-x}Co_xO_2$ for x = 0, 0.5 and 2% samples prepared by co-precipitation technique [***Bouaine et al. (2007)***], $Sn_{1-x}Co_xO_2$ (x = 0.005,0.02 and 0.1) samples synthesized by wet chemical method [***Liu et al. (2006)***] and $Sn_{1-x}Co_xO_2$ (x = 0.05) samples prepared by solid state reaction method also failed to exhibit room temperature ferromagnetism [***Fitzgerald et al. (2004)***]. Whereas RTFM is possible among 5% Co doped SnO_2 DMS materials having single phase and prepared by tartaric gel route [***Srinivas et al. (2009)***]. In view of this, it is clear that applying appropriate growth conditions is a crucial factor in order to obtain room temperature ferromagnetism. These controversial observations raise questions about the intrinsic nature of ferromagnetism in the Co –doped SnO_2 system. This is of particular importance since recent studies on thin films DMS suggested that ferromagnetism could have an extrinsic origin.

In this work, we have chemically synthesized undoped and Co –doped SnO_2 powders with low Co concentration (≤ 1%) and studied the effect of annealing temperature on room temperature ferromagnetism of Co –doped SnO_2 samples. A systematic investigation of magnetic properties of these samples sintered at different annealing temperatures has been done to understand the origin of ferromagnetism in accordance with appropriate growth conditions.

2. Experimental Method:-

Undoped and Co –doped SnO_2 powders were synthesized by reacting appropriate amounts of $SnCl_2.2H_2O$ and $CoCl_2.6H_2O$ in proportion 50:1, dissolved in 100ml of deoxygenated distilled water. The salts were then precipitated at 80^oC using 50 ml of NH_4OH and kept at this temperature for several hours. The precipitate was then filtered, thoroughly washed and dried in air for several hours. The dried precipitates were then prepared by annealing for 2 hrs at different temperatures between 350^oC to 650^oC to obtain the final Co –doped SnO_2 powder. Characterization of the samples by x-ray diffraction (XRD) and SEM showed the formation of $Sn_{1-x}Co_xO_2$, when prepared by annealing the precipitates in the 350^oC to 650^oC range. The crystalline quality and the grain size of the samples were evaluated using XRD measurements. The magnetic properties of the Co-doped SnO_2 powders were carried out with Vibrating Sample Magnetometer (VSM).

3. Results and Discussion:-

3.1 Structural Investigations: Fig.1 shows the room temperature X-ray diffraction spectra for SnO_2:Co (≤ 1%) prepared at 350°C to 650°C for 2 hrs. The XRD patterns of $Sn_{1-x}Co_xO2$ samples have tetragonal rutile structure and comparable with the standard data**.** No additional phases such as the SnO_2 orthorhombic phase, metallic Co or other SnO or CoO based phases are observed. With increase in annealing temperature the cassiterite SnO_2 phase decreases while the relative concentration of the orthorohombic phase gradually increased. The average crystallite size (D) has been determined using the diffraction peaks (110) and (101) using Scherer's formula

$$D = \frac{k\lambda}{\beta\cos\theta}$$

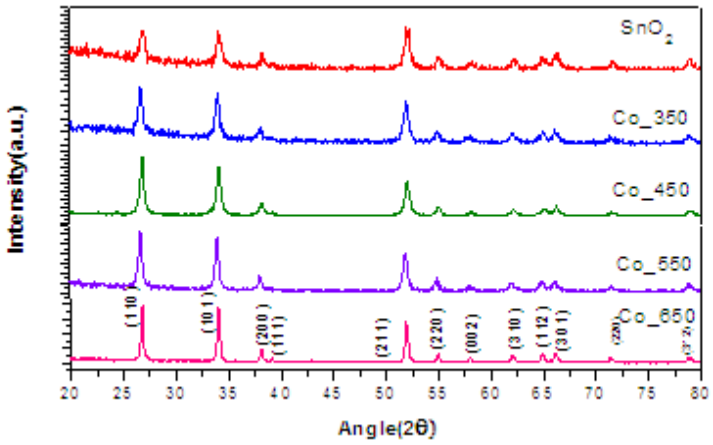

Fig:1 XRD patterns of Co doped SnO_2 (x=0.005) annealed between 350°C to 650°C and pristine SnO_2 annealed at 450°C

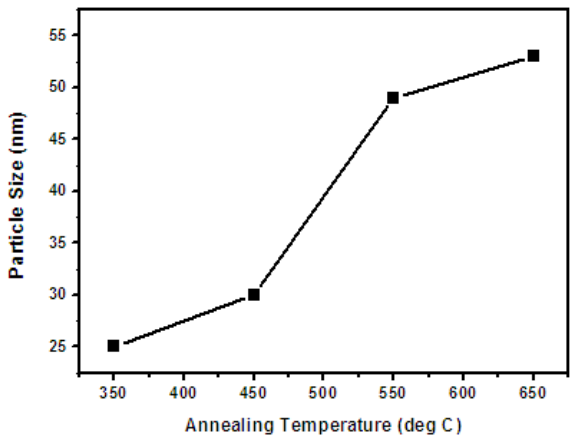

Fig.2 Variation of particle size of Co-doped SnO_2(≤ 1%) with change in annealing temperature

where K is a constant whose value is taken as 0.89, λ is the wavelength of CuK radiation and β is the corrected full width at half maximum (fwhm) of the diffraction peak. Fig.2 shows the **v**ariation of particle size of Co-doped SnO_2(≤ 1%) with change in annealing temperature. The figure shows that the average particle size increases with increase in annealing temperature. In Table 1, the crystallite size vary from 22-49 nm while the average particle size vary from 25 -53 nm. It can be seen that crystallite size of the SCO-450 sample is less when compared with that of the SnO_2-450 sample. The variation of both the lattice parameters (Table 1) is not systematic. At higher annealing temperatures there might be diffusion of randomly distributed Co ions toward the surface leading to grain growth during the annealing process. Diffusion of Co^{2+} ions might cause significant changes and disorder in SnO_2 structures as

TABLE 1: XRD Data of Co (x=0.005) Doped SnO_2 Samples and Pristine SnO_2 Sample.

Sample Name	Annealing Temp (^oC)	Crystallite Size (nm)	Average Particle Size (nm)	a (^oA)	c (^oA)
SCO-350	350	22	25	4.743	3.156
SCO-450	450	28	29	4.740	3.178
SCO-550	550	43	47	4.709	3.163
SCO-650	650	49	53	4.711	3.175
SnO_2-450	450	35	40	4.683	3.157

well as many dramatic changes in the properties of the material. The large difference in the charges and coordination number of Sn^{4+} and Co^{2+} ions will also contribute to structural disorder in SnO_2 due to removal of some oxygen ions that were attracted to the octahedral coordinated Sn^{4+}. Hence the non-systematic variation in the lattice parameters may be attributed to the microstructural changes due to either to non-uniform stress or strain during the grain growth or to the existence of local structural disorder in the materials at the time of formation.

3.2 Sccaning Electron Microscopy (SEM) investigations :- Fig. 3 illustrates the surface morphology of nanocrystalline Co doped SnO_2 powders prepared by annealing at 350^{o}C ,

450 ^{o}C , 550 ^{o}C , and 650 ^{o}C. It can be seen from the morphological images that the particles are found to aggregate with increasing annealing temperature and may be attributed to a lesser number of nucleation centres leading to surface redistribution of grains. With increasing annealing temperature, number of surface defects during annealing process also increases which may be attributed to the diffusion of randomly distributed Co ions toward the surface with increasing grain growth. A similar surface diffusion of dopants with increasing annealing temperature was reported earlier. Average particle sizes are in the range 25-53nm and are in agreement with those obtained from the XRD data.

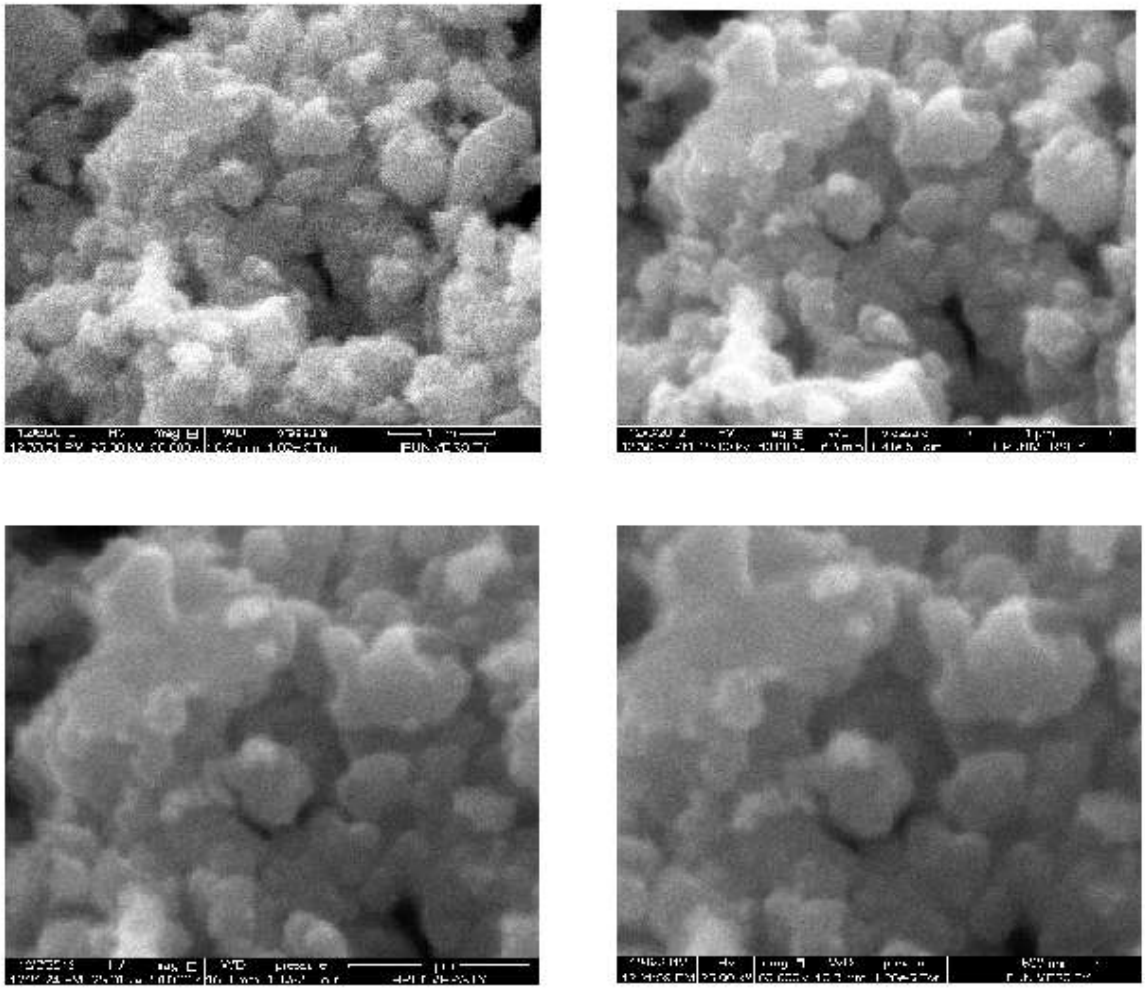

Fig.3 SEM morphology images for nanocrystalline Co doped SnO_2 powders annealed at (a) 350^{o}C (b) 450 ^{o}C (c) 550 ^{o}C , and (d) 650 ^{o}C

3.3 Magnetic Property Investigations: Fig.4 shows magnetization versus magnetic field (M-H) curves of Co doped SnO_2 samples prepared by annealing between 350^{o}C to 650^{c}C upto a maximum of 5000 Oe magnetic field. It is interesting to note that the samples prepared at 350^{o}C and 450^{o}C exhibit strong ferromagnetism. While the sample prepared at 550^{o}C show weak ferromagnetism with some paramagnetic contribution. But for the sample prepared at 650^{o}C, ferromagnetic behaviour is completely destroyed and the sample demonstrates paramagnetic behaviour. Hence, it can be seen from the M-H curve that the annealing temperature has crucial influence on the ferromagnetism of Co-doped $SnO_2$with Co concentration $\leq$ 1%. In fact, the room temperature ferromagnetism was reported earlier in some nanocrystaline SnO_2 samples doped with $\leq$ 1% cobalt, prepared by annealing between 350^{c}C and 600^{c}C. It has been reported that even nanocrystalline pristine SnO_2 also exhibits weak room temperature ferromagnetism. But in the present investigation, the pristine SnO_2sample annealed at 450^{o}C does not have a proper shape of the M-H curve so it has not

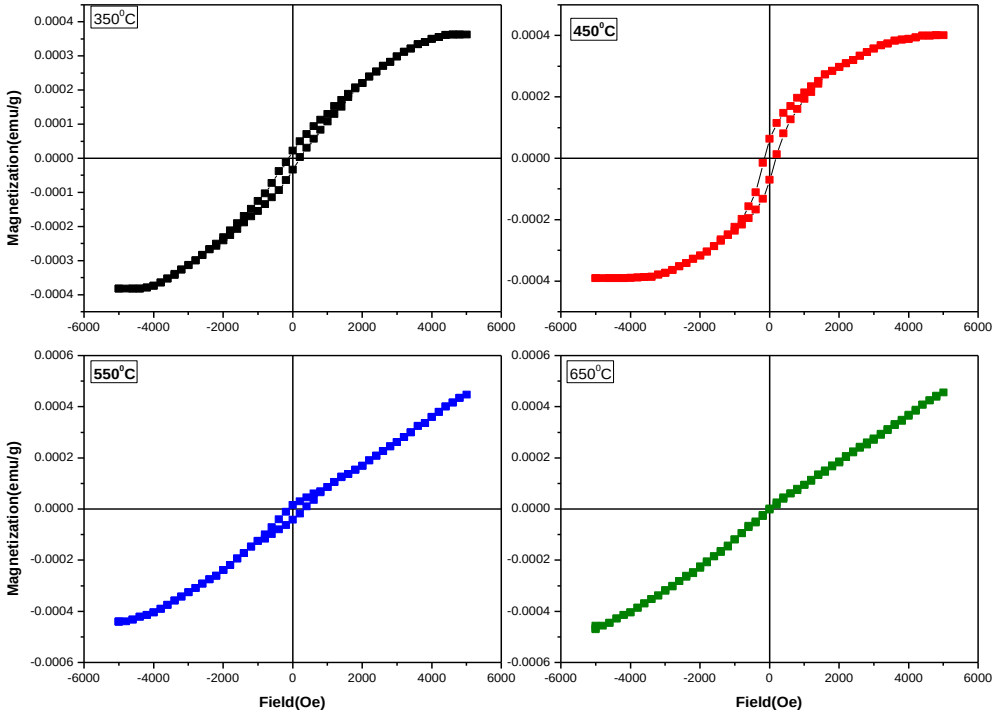

Fig.4 M-H magnetization curves for nanocrystalline $Sn_{1-x}Co_xO_2$ (x=0.005) samples annealed at a)350^{o}C, b) 450^{o}C, c) 550^{o}C and d) 650^{o}C

been presented. The irregular behaviour might be due to non-uniform nature of the grain's structure, random distribution of oxygen vacancies and strong anisotropy. The slight appearance of ferromagnetism in the pristine SnO_2 may be attributed to effective exchange interactions between the unpaired electron spins originating from the surface defects such as oxygen vacancy clusters instead of single neutral oxygen vacancies associated with the nanometric size. The appearance of ferromagnetism in $Sn_{1-x}Co_xO_2$ samples with $x \leq 0.01$ annealed is very complex phenomenon. Here, the origin of ferromagnetism has been made to explain by the phenomenon using the bound magnetic polarons (BMPs) model [***Fitzgerald et al. (2006), Coey et al. (2005), Wang et al . (2006)***]. According to this model, the localized spins of the dopant ion interact with the charge carriers which are bound to a small number of defects such as oxygen vacancies, resulting in a magnetic polarization of the surrounding local moments. In the samples of present investigation, due to the substitution of Co^{2+} for Sn^{4+}, a number of free charge carriers and oxygen vacancies might have been introduced to maintain the charge neutrality leading to the formation of BMPs. The exchange interactions between these BMPs, which are coupled with the available small quantity of randomly distributed neighboring Co^{2+}, might be responsible for the observed ferromagnetism [***Liu et al. (2007)***]. Also for $x \leq 0.01$ the SnO_2 lattice contracts resulting in the reduction of the distance between nearby Co^{2+} spins and possibly triggering a ferromagnetic coupling. Increasing the Co concentration and annealing temperature leads to enormous structural changes due to surface diffusion of Co ions . Hence this might destroy the ferromagnetic ordering since the magnetic exchange interaction is extremely sensitive to the distance between the interacting spins.

4. Conclusions:-

In the present investigations, Co doped SnO_2 (x=0.005) powder samples have been synthesized successfully by co-precipitation technique to study their structural and magnetic properties with varying annealing temperatures. It has been concluded that the structural properties are affected by the local disorder and grain structure. From the morphological images it is seen that the particles aggregate more with increasing annealing temperature and may be attributed to a lesser number of nucleation centres leading to surface redistribution of grains. Increasing the Co concentration and annealing temperature leads to enormous structural changes due to surface diffusion of Co ions. Hence this might destroy the ferromagnetic ordering since the magnetic exchange interaction is extremely sensitive to the

distance between the interacting spins. Finally the experimental results may be useful for tunning the magnetic properties of Co doped SnO_2 based DMS materials.

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