Influence of the grain's morphology and their distribution on surface, electronic and magnetic properties of $Sn_{1-x}Co_xO_2$ nanocrystalline Diluted Magnetic Semiconductors.

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ABSTRACT

With a view to understand not only the nanosize dependent properties of microstructure and electronic properties, but also to study the correlations between the surface effects associated with the magnetic nano-particles, especially consequent changes in the electronic structure and associated phonon confinement effect on nanocrystalline $Sn_{1-x}Co_xO_2$ DMS system, a systematic investigations have been undertaken. Samples were prepared by modified tartaric acid assisted sol-gel route and annealed in air between 300 to 600 ˚C in order to vary the crystallite sizes.. From Reitveld refinement of XRD data, FTIR, SAD patterns, Raman and XPS studies, it has been confirmed that the synthesized samples are having single phase tetragonal rutile structure. The tetragonality 'c/a' value seems to change systematically with decreasing crystallite size. TEM studies revealed that the surface nanoparticles are aggregating with increasing particle size without forming any secondary phases within the limit of surface diffusion of dopant. The reduction of intensities of Raman peaks, shift in their positions, their shape and size distribution are found to be influenced predominantly by the nano size of the materials. The optical band gap of the materials clearly indicates a blue shift with decreasing particle sizes. From XPS data, it has been observed that the core level Co 2p binding energy values and FWHM values have been changed systematically with decreasing the nano size of the materials. However, the non-linear variation of FWHM of O1s core level XPS spectra has been observed. These results are attributed not only due to the random distribution of crystallites and local structural disorder but also due to the effect of nano size on electronic structural modifications. Moreover, surface defects are playing main role in controlling the surface bonds and associated surface properties with varying crystallite size. The Magnetization studies clearly indicated the presence of room temperature ferromagnetism in all the prepared samples. Further, the mechanism was analyzed in influencing the nano size effects on the behaviour of ferromagnetism of nano crystalline $Sn_{0.95}Co_{0.05}O_2$ powders, which may exploit for spintronic, magneto-optical, magnetic storage and ferrofluidic applications.

Keywords: Diluted magnetic semiconductors**,** nanocrystalline, electronic structure, ferromagnetism.

1 INTRODUCTION

In search of low cost high ferromagnetic Curie-temperature with good ohmic behaviour at the interfaces and a precise controllable spin properties, oxide based Diluted Magnetic Semiconductors (DMS) with wide band gap such as TiO_2 ZnO, SnO_2 and HfO_2 doped with transition metal ions (Co, Mn, Ni, Fe, Cr etc.,) have attracted considerable attention in recent years due to their unique magnetic, magneto-optical, and magneto-electrical effects thereby creating tremendous interest for various applications such as spintronics devices, biomedical applications, magnetic storage, ferrofluids, etc. However, it is of particular importance to understand not only the role of dimensionality but also surface driven effects in shaping the spin-polarized electronic structure of nanocrystalline oxide based DMSs, because due to quantum confinement in the lattice and the nanometric grain's morphology and their distributions may result in intriguing ferromagnetic properties. Apart from this, the synthesis of stable nanocrystalline DMSs with controllable grain size and surface morphology are of great fundamental and technological interest and has attracted much experimental efforts. The changes in surface bonds, crystallite's size, shape and their distributions might have also lead to the surface reconstruction. Thus this type of disorder might change the translation symmetry of the sample's surface. Therefore, the variation of the grain's structure is crucial in order to tailor the surface morphology and local disorder in the lattice during annealing process. In the present work, the beneficial surface and other associated properties of nanocrystalline Co doped SnO_2 samples are exploited to understand the correlations between the surface driven effects associated with the magnetic nano-particles. Further, the changes in the surface diffusion behaviour of dopant and the electronic structure as a function of the size of the nanocrystallites of $Sn_{1-x}Co_xO_2$ DMSs are analyzed and the results are reported.

2 EXPERIMENTAL

Nanocrystalline Co doped SnO_2 ($Sn_{0.95}Co_{0.05}O_2$) samples were prepared by the tartaric acid assisted sol-gel method [1]. In this method, starting precursors were converted to tartarates and P^H was adjusted to a value between, 5 - 6 by adding ammonia and tartaric acid. Later, ethylene glycol was added as a promoter of tartaric polymerization. The

tartaric acid is expected to increase the transformation of amorphous to rutile crystalline structure. Finally the powders were annealed at four different temperatures between 300 – 600°C for about 4 hrs. For comparison purposes, the prestine SnO_2 sample was also prepared in similar experimental conditions.

To understand the heat treatment profile of the calcined precursor TGA-DTA measurements were undertaken. To explain the structural and morphological behaviour XRD, TEM, FT-IR and Laser Raman studies were also undertaken. The electronic properties were investigated using the optical absorption, PL, resistivity and XPS measurements. Finally, the room temperature magnetization measurements were undertaken using a Vibrating Sample Magnetometer (Model: DMSADE-1660 MRS) upto a magnetic field of 15 kOe.

3 RESULTS AND DISCUSSION

3.1Structural properties

The XRD patterns of $Sn_{1-x}Co_xO$ (x=0.05) powder samples annealed at different temperature are shown in Fig.1. (pristine SnO_2 annealed at 600 °C is also included).

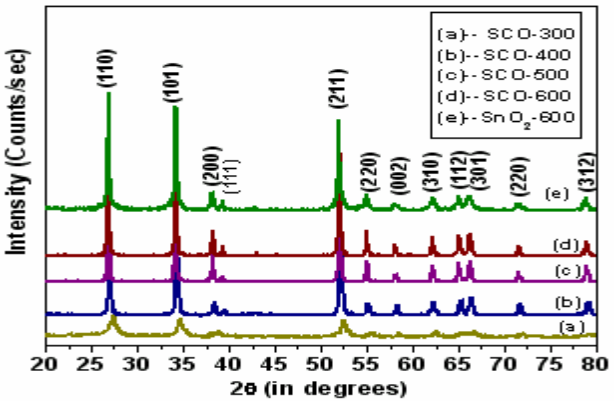

Figure1. XRD patterns of $Sn_{0.95}Co_{0.05}O_2$ samples

It can be seen from these patterns that all the samples are found to exhibit tetragonal Rutile structure and are comparable with JCPDS data [Card No: 41-1445]. The average lattice parameters *a* and *c* were obtained from Rietveld refinement analysis and are presented in Table-1. From the changes in c/a values, one may conclude that the local disorder or tetragonal deviation with varying annealing temperature might be playing crucial role leading to population of surface or bulk oxygen vacancies due to the substitution of Co^{2+} in the place of Sn^{4+}. Moreover, with increasing crystallite size the strain decreases resulting in the relaxation of local vibration modes, which in turn affects the lattice parameters. The average crystallite size of the powders (*D*) was determined by considering the instrumental broadening and sample broadening using Rietveld refinement analysis and are found to be in the range 15 – 46 nm.

Table: 1. XRD data of $Sn_{1-x}Co_xO_2$ (X = 0, 0.05) samples.

Sample Name	Annea-ling Temp (°C)	Average crystallit Size (nm) XRD	Averag Particl Size (nm) TEM	<a> (˚A)	<c> (˚A)	*c/a*
SCO-300	300	15	18	4.741	3.155	0.6655
SCO-400	400	24	25	4.726	3.177	0.6722
SCO-500	500	32	35	4.711	3.163	0.6714
SCO-600	600	40	45	4.719	3.173	0.6724
SO-600	600	46	50	4.683	3.155	0.6737

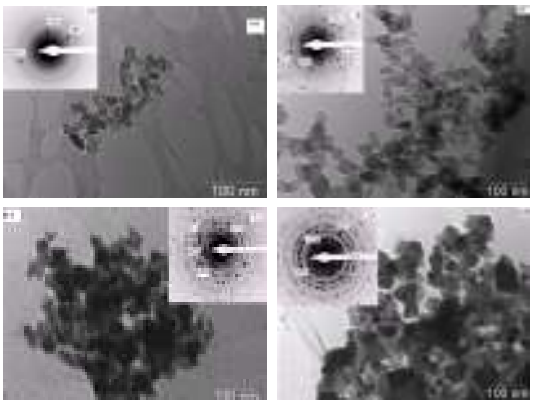

Figure 2. TEM morphology and SAD patterns (shown inset) of Co doped SnO_2 samples.

Fig. 2 illustrates the morphology and the electron diffraction patterns (shown inset) of the samples. It has been observed that the average particle sizes obtained from TEM are found to be in the range 18- 50 nm. A close observation of TEM morphological images with increasing annealing temperature clearly indicate that the nano-particles might have aggregated and the observed behavior may be attributed to the redistribution of surface atoms due to change in particle's size, and shape along with the increase of surface defects. The results indicate that the particle size may influence the surface morphology of the samples of present investigation. Moreover, the TEM images clearly indicate the presence of nanoparticle aggregates with increasing annealing temperature. Thus the studies of present investigation provide strong evidence for the close connection between the grain structure, interfacial or grain boundary defects and the occurrence of room temperature ferromagnetism.

3.2. Electronic properties

The electronic properties were studied using XPS, optical absorption and resistivity measurements. The core level binding energy values of Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks are shown in Fig.3.The oxidation state of Co in

$Sn_{0.95}Co_{0.05}O_2$ samples is confirmed as +2 and there is no possibility of forming Co clusters and other cobalt oxide binaries. Further, in the present investigation, surface was etched with Ar^+ sputtering and the binding energy values are given in Table-2. It can be seen that with increasing particle size, the binding energy values are found to decrease continuously.

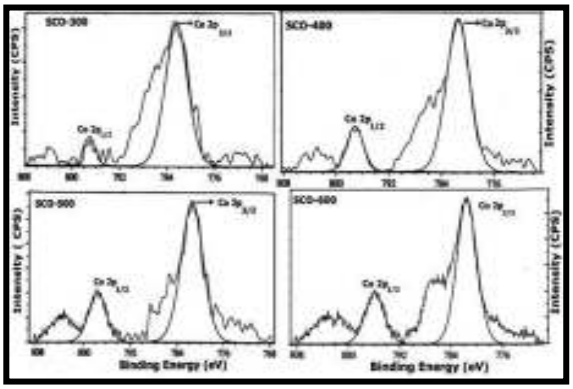

Figure 3. XPS core level deconvoluted spectra of Co 2p of different samples

The room temperature absorption spectra of all the samples of the present investigation are shown in Fig.4. The energy band gap values were estimated using second derivative approach and are given in Table-2.. It is interesting to note from the table that upon Co doping, the band gap values are found to decrease indicating red shift, while as the band gap values are increasing with decreasing particle size indicating blue shift in the

Table 2: XPS data of core level Co 2p element and optical band gaps.

Sample Code	Binding Energy (e.V)		$\Delta B.E$ (eV)	E_g (eV)
	Co $2p_{3/2}$	Co $2p_{1/2}$		
SCO300	782.02	797.82	15.80	3.51
SCO400	781.55	797.25	15.70	3.43
SCO500	781.14	796.63	15.49	3.39
SCO600	780.61	795.90	15.29	3.32
SO-600	-	-	-	4.12

bandgap values. Further, it can also be seen from the optical absorption spectra that a shoulder is observed right above the direct photon energy i.e.~3.6–3.9 eV and its width is found to decrease with increasing annealing temperature. This appearance of shoulder may be due to transitions from O(p)—states in the valence band to Sn(s)—states in the conduction band.

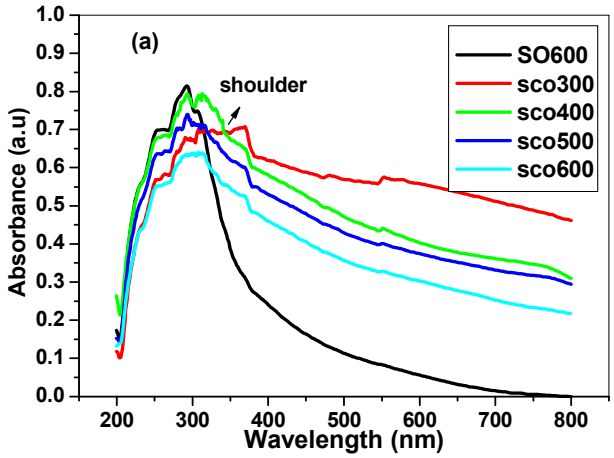

Figure 4. Optical absorbance DR spectra of $Sn_{1-x}Co_xO_2$ (X = 0.05, 0).

In order to understand the surface nature of nanograins, the electrical measurements were also carried out in air, over a temperature range 35 – 300 ^{0}C. Plots of resistivity versus temperature are shown in Fig. 5. It can be seen from the figure that the resistivity of the samples is found to decrease with increasing annealing temperature and grain size. It is also interesting to note that, an abnormal resistivity peaks appeared in the temperature range 70-180^{o}C and that the peak width is found to increase gradually with increasing grain size. As SnO_2 is a well known gas sensor material, these resistivity peaks might be attributed to the chemisorption behaviour of the nanocrystalline samples. The chemisorption behaviour might have arisen due to surface oxygen vacancies of the nanocrystalline materials. This chemisorption behaviour is increasing with decreasing the crystallite size. Thus these results indicate that the influence of nanometric size and surface nature of these materials on the surface oxygen vacancies.. From these results one may conclude that the grain boundary effects might be influencing the electrical transport properties.

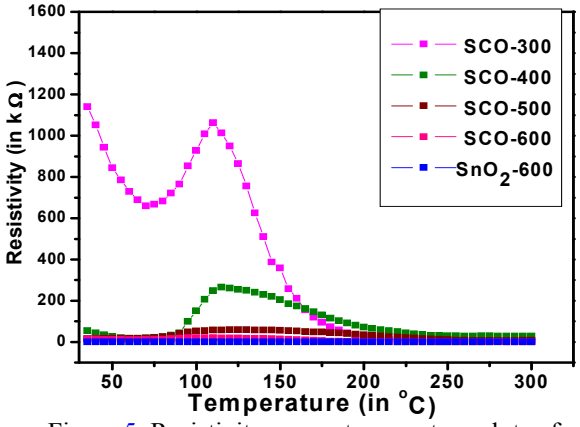

Figure 5. Resistivity verses temperature plots of $Sn_{1-x}Co_xO_2$ (X = 0.05, 0).

It is known that the surface bond contraction model [2-4] can explain both the band gap expansion and

increase in the binding energy of core-level electrons of nanoparticles with decreasing particle size. Thus modification of valence band observed in the samples of the present investigation may be attributed to the size effects and surface oxygen vacancies, which in turn results in changes in the electronic structure.

3.2. Magnetic properties

The magnetization measurements were performed using a vibrating sample magnetometer (VSM) at 300K. From the hysteresis curves of the samples (Fig. 6), it has been concluded that all the samples of present investigation are ferromagnetic at room temperature. The observed ferromagnetism in the samples of the present investigation is attributed to the Bound Magnetic Polarons (BMPs). The magnetization values are given in the Table. 3. The low values of M_s obtained in the samples of present investigation may be attributed to the fact that only a small portion of Co spins might have coupled ferromagnetically. The specific saturation magnetization values are found to increase with increasing annealing temperature (except in the case of SCO- 500) and grain size. In fact, this might be due to the surface diffusion of Co^{2+} ions with increasing annealing temperature and the behavior is in conformity with that of surface bond contraction and surface morphological changes observed in XPS and TEM studies. From all these results one may conclude that the precise control of dopant distributions in the lattice and the particle size and the surface condition of the samples enormously influence the local structure and hence the magnetic properties.

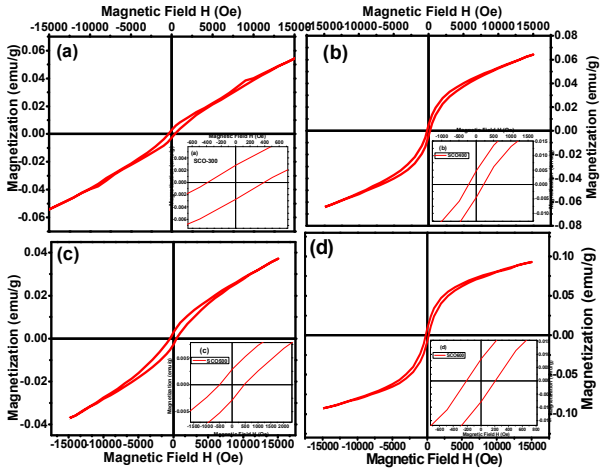

Figure 6: M-H Magnetization Curves for the $Sn_{0.95}Co_{0.05}O_2$ samples annealed at different temperatures.

Table: 3. Magnetization values for the $Sn_{1-x}Co_xO_2$ (X=0.05) samples annealed at different temperatures

Sample Code	Ms (emu/g)	Hc (Oe)	*Average Particle size (nm)*
SCO300	0.0543	389.295	18
SCO400	0.0643	215.170	25
SCO500	0.0371	478.047	35
SCO600	0.0929	209.232	45

4 CONCLUSIONS

It has been concluded that the nanometric size, oxygen defects, grain's morphology and their distribution along with the changes in surface bonds influence the electronic structure.

The magnetic properties of the samples are found to critically depend on surface chemistry influenced by the surface oxygen vacancies, nanometric size, shape of the grains and their distributions along with the grain's interface interactions with the surrounding particles.

It has also been concluded that the changes in the electronic structure increases the ferromagnetic coupling which is crucial for the enhancement of magnetization of the samples.

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