Chapter- IV

Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO₂ and codoped SnO₂

Introduction

Considerable research has been concentrated on the development and synthesis of Mn-doped Tin oxide, Ni-doped Tin oxide phases that would exhibit room temperature ferromagnetism (RTFM). After the theoretical predictions [37-39], [42-43], the transition metals, Mn and Ni are the dopants that are most widely explored. Several groups have reported on the magnetic properties of Mn- doped thin films [40-41] and on SnO₂ nanocrystals [44], which show room temperature ferromagnetism. However, it is important to note that there is still a lot of controversy to be found in the published results. Some groups have claimed that the observed ferromagnetism is caused by the formation of impurity phases or clustering of magnetic metals in the synthesized materials [40-41]. Furthermore, nanocrystalline sample of Mn, Ni doped tin oxide have been reported to be paramagnetic, some have been reported to be ferromagnetic [38, 41]. Nanocrystalline samples are important subjects for investigation, as they are prepared under equilibrium conditions. Success in preparing such samples can provide valuable information on whether the observed magnetic properties in nanocrystalline samples are indeed intrinsic properties of the materials. In this chapter, the experimental results obtained from Mn-doped SnO₂ nanocrystalline samples, Ni-doped nanocrystalline samples are presented. First, a series of Mn-doped, Ni-doped SnO₂ samples were prepared and characterized. This group of samples can be described by the formula, Sn₁₋ₓMnₓO₂, where [x=0.04 to0.10]. Secondly, in order to improve the magnetic property in SnO₂, Ni and Mn, were introduced into the system. The following various samples were prepared: Sn₁.₉Ni₀.₀₃Mn₀.₀₇O₂ and Sn₁.₈Ni₀.₁₀Mn₀.₁₀O₂. (Mn, Ni)-codoped has not yet been reported. The purpose of the introduction of Ni was to induce the room temperature ferromagnetism and increase the magnetic moment of SnO₂, which is important for the
spin lifetime and thus crucial for spin transport in possible spintronic devices. When Ni ions are introduced into the SnO$_2$ along with Mn, incorporation of Ni in the system could increase the carrier concentration of the samples. It causes an imbalance in the total valence state of the system and thus may induce ferromagnetism in the samples.

![Flow chart showing the Preparation of (Mn, Ni) codoped Nanostructured DMS](image)

Figure 4.1 Flow chart showing the Preparation of (Mn, Ni) codoped Nanostructured DMS

### 4.1 Experimental Technique

All the samples were prepared by simple and low cost soft chemical route. The Sn$_{1-x}$Mn$_x$O$_2$ [x=0.04 to 0.10] was prepared by using SnCl$_4$.5H$_2$O and Mn (CH$_3$COO)$_2$.4H$_2$O as the sources of Sn, Mn respectively. The salts were added in de-ionized water and stirred at 80°C for four hours under air atmosphere. For each doping concentration(x), a separate solution was made.
The solutions were kept 10 days undisturbed (optimized) for aging. Pale pink Colored sol was obtained at the end of 10 days and with the heat treatment at 500°C for one hour in oven, Mn doped SnO₂ DMS nano powders were harvested.

Similar method is used for the preparation of (Mn, Ni)-codoped SnO₂ nanopowders. Separate solutions of Sn₁₋ₓMnₓO₂ [x=0.07, x=0.10], and Sn₁₋ₓNiₓO₂ [y=0.03, y=0.10] were prepared and aging for ten days. Separate Sn₁₋ₓMnₓO₂, (x=0.10) solution and similar Sn₁₋ₓNiₓO₂ solution were combined together and stirred at 80°C for four hours, aging for ten days and finally the sols were under heat treatment for one hour at 500°C, finally Sn₂₋ₓ₋yMnₓNiₓO₂ {x=0.07, y=0.03 and x=0.10, y=0.10} nanopowder were harvested. Crystal structures and phase purity of the samples were analyzed by means of the powder X-ray diffraction technique (Shimadu XRD-6000) and Cu₅₀₄₁ radiation. The morphological features of the sample were observed using the scanning electron microscope (SEM: JEOL JSM6390). The chemical composition of the samples was determined by oxford instrument –INCAPENTAFET-X3 Elemental dispersive x-ray analyzer. The magnetic properties of the samples were analyzed by vibrating sample magnetometer using LAKE SHORE -7410(US). The photoluminescence measurements were performed by HORIBA JOBINYVON-FLUVROLOG 3 with an applied wavelength of 365 nm. The electrical properties were done by Hall (ECOPIA HMS-3000) measurement system.

4.2 Results and discussion

4.2.1 Structural Properties by X-diffraction

The X-ray diffraction technique was applied to determine the crystal structure and phase purity of the samples. All the samples were found to be polycrystalline. Fig.4.1.a shows the XRD pattern for Mn-only doped SnO₂ samples. Sn₁₋ₓMnₓO₂ [x=0.04 to 0.10] samples are of the rutile tetragonal structure and all peaks indexed according to the JCPDS for SnO₂. Characteristic peaks with intensities corresponding to (110), (101), (211) and (310) planes were observed and no evidence of any other secondary phases and impurities was detected in the XRD pattern. It is clear that there are no extra peaks due to manganese
metal oxides implying that the transition metal ions get substituted at Sn site without changing the tetragonal rutile structure.

Furthermore, the crystallite size was calculated using the scherrer formula, \( D = \frac{K \lambda}{\beta \cos \theta} \), where \( \theta \) is the Bragg angle, \( \beta \) is the full width at half maxima, \( \lambda = 1.5405 \) Å in the CuK\textsubscript{α1} radiation.

Table 4.1 Structural parameters of Sn\(_{1-x}\)Mn\(_x\)O\(_2\) as a function of Mn concentration.

<table>
<thead>
<tr>
<th>parameter</th>
<th>Different amount of Mn in SnO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X=0.04</td>
</tr>
<tr>
<td>Lattice Constant a(Å(^o))</td>
<td>4.751</td>
</tr>
<tr>
<td>Lattice Constant c(Å(^o))</td>
<td>3.194</td>
</tr>
<tr>
<td>Cell Volume(Å(^3))</td>
<td>72.12</td>
</tr>
<tr>
<td>Grain Size (D) nm</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 4.1 gives the information about the lattice constants calculated from XRD data of Mn-doped SnO\(_2\) with different amounts of dopant ions. The determination of lattice constants of Mn doped SnO\(_2\) nanopowder shows that an increasing the Mn concentration from x=0.04 to x=0.10, the unit cell volume continuously reduces from its value. The observed contraction of the lattice revealed by the shifting of the XRD peaks on Mn doping is understandable as the radius of Mn\(^{3+}\) ion is 0.58Å as against 0.69 Å for the Sn\(^{4+}\) ion for a coordination number of 6. This conjecture also finds supports from the studies performed on oxides of manganese showing that in its oxides, Mn\(^{3+}\) prefers to be in an octahedral coordination, just like Sn\(^{4+}\) in the rutile tetragonal structure of SnO\(_2\) lattice. The magnitude of the lattice volume change indicates that the valence of the Mn ion is most probably +3. The small decrease in unit cell volume points towards Mn\(^{3+}\) as the most probable form of Mn ion in the present case. The decrease in the lattice parameters a and c, on increasing the Mn concentration up to x=0.08 is not in agreement with Vegard’s Law [24].
Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO$_2$ and codoped SnO$_2$

Figure 4.1a XRD patterns of Sn$_{1-x}$Mn$_x$O$_2$ with $x=0.04$, $x=0.06$, $x=0.08$ and $x=0.10$

Figure 4.1b Lattice volume of Sn$_{1-x}$Mn$_x$O$_2$, $0.04 \leq x \leq 0.10$ as a function of Mn concentration
Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO₂ and codoped SnO₂

Figure 4.1c Grain size of Sn₁₋ₓMnₓO₂, 0.04≤x≤0.10 as a function of Mn concentration

Fig.4.2.a. shows X-ray diffraction patterns for Ni-doped SnO₂. The samples are polycrystalline, and a preferred orientation could not be detected. The X-ray diffraction patterns characteristic of rutile type tetragonal structure. The Full Width half maximum of (110) peak decrease with Ni concentration, indicating the decrease of the crystallite size. The obtained lattice constants were tabulated in Table 4.2. The a and c value decrease up to x=0.08, which could be attributed to the different between the effective ionic radius of Ni while it is smaller than that of Sn (69 pm). The little change in the lattice constant indicates that there is a small change in lattice volume. The intensity ratio of I (101) to I (110) decrease from 1.017 to 0.840 when the Ni concentration in the SnO₂ lattice. The observed decrease in the intensity ratio is ascribed to the substitution of Sn by Ni in the lattice of SnO₂. We can conclude that the solubility limit of Ni in SnO₂ is in the vicinity of x=0.10.
Chapter IV  
Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO$_2$ and codoped SnO$_2$

Figure 4.2a XRD patterns of Sn$_{1-x}$Ni$_x$O$_2$ with $x=0.04$, $x=0.06$, $x=0.08$ and $x=0.10$

Figure 4.2b Lattice volume of Sn$_{1-x}$Ni$_x$O$_2$, $0.04 \leq x \leq 0.10$ as a function of Ni concentration
Figure 4.2c Grain size of Sn$_{1-x}$Ni$_x$O$_2$, 0.04≤x≤0.10 as a function of Mn concentration

Table 4.2 Structural parameters of Sn$_{1-x}$Ni$_x$O$_2$ as a function of Ni concentration.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Different amount of Ni in SnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X=0.04</td>
</tr>
<tr>
<td>Lattice Constant a(A°)</td>
<td>4.737</td>
</tr>
<tr>
<td>Lattice Constant c(A°)</td>
<td>3.211</td>
</tr>
<tr>
<td>Cell Volume(A°$^3$)</td>
<td>72.2</td>
</tr>
<tr>
<td>Grain Size (D) nm</td>
<td>7</td>
</tr>
</tbody>
</table>

Fig.4.3a and 4.3b show X-ray diffraction patterns and the doping-level dependences of lattice parameters a and c for two samples of Sn$_{2-x-y}$Mn$_x$Ni$_y$O$_2$ prepared by soft chemical technique. We have already mentioned that in the preparation of ferromagnetic samples S.J.Liu et al. [13] used a double doping approach. They used Zn and Mn ions as dopants.
to induce ferromagnetic states in the system. Similarly, we have prepared a few samples containing two magnetic ions. Our motivation for “double doping” was very simple: an introduction of two different species of magnetic ions in the system might favor enhancement of the ferromagnetic properties of the samples. Both ions, Mn and Ni, have high magnetic moments and thus an enhancement of ferromagnetism. Although Mn and Ni single doped samples showed totally different magnetic properties, the double doped samples were room temperature ferromagnets. The nominal formula for this few samples was Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ and Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$. Fig.4.3a shows the X-ray diffraction patterns of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ and Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$. The X-ray diffraction patterns for all the samples can be indexed based on the unit cell of rutile tetragonal SnO$_2$. It can be seen that two compounds with x=0.07, y=0.03 and x=0.10, y=0.10 obviously are of polycrystalline and no other visible peaks are present in these samples, with increasing Ni content, lattice parameter a increased almost linearly from a=4.695 Å to a=4.697 Å, when y rose from 0.03 to 0.10, respectively. The obtained dependence of lattice parameter a on the Ni content is in good agreement with data published by S.J.Liu et al. [13], where they showed a decrease with introduction of codoping. This result is reasonable and is very comparable with the data presented for single –doped sample (Fig.4.1a, Fig.4.2a). If the ionic radii of Mn and Ni are compared, and it may be due to the magnetic ions, (i.e.) Mn and Ni are present in oxidation states of 2+ and 2+, respectively[61]. This indicates that the expansion of lattice parameter “a” is bigger ionic size of the Mn$^{2+}$ ions. The change in lattice parameter “a” suggests that magnetic ions were successfully introduced into the crystal structure of SnO$_2$. 
Figure 4.3a XRD patterns of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ and Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$.

From the XRD pattern, the full width at half maxima (FWHM) of diffraction peak (110) becomes broader, peaks position shift toward lower angle, indicates the possible change of crystallite size.

Table 4.3 lattice parameters of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ and Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ as a function of Mn, Ni concentration.

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>Sn$<em>{1.9}$Mn$</em>{0.07}$Ni$_{0.03}$O$_2$</th>
<th>Sn$<em>{1.8}$Mn$</em>{0.1}$Ni$_{0.1}$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>4.695</td>
<td>4.697</td>
</tr>
<tr>
<td>c (Å)</td>
<td>3.169</td>
<td>3.191</td>
</tr>
</tbody>
</table>
Table 4.3a Grain size of Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ and Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ sample for different planes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain size (nm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plane (110)</td>
<td>Plane (101)</td>
<td>Plane (211)</td>
</tr>
<tr>
<td>Sn$<em>{1.9}$Mn$</em>{0.07}$Ni$_{0.03}$O$_2$</td>
<td>4.5</td>
<td>6.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Sn$<em>{1.8}$Mn$</em>{0.1}$Ni$_{0.1}$O$_2$</td>
<td>3.7</td>
<td>5.1</td>
<td>3.6</td>
</tr>
</tbody>
</table>

The crystal size estimated was 6.0 nm and 5.1 nm respectively of the diffraction peak (101). This result proves that (Mn, Ni) –codoping reduces the grain size. From the above results, the lattice constant $a$, $c$ and lattice volume of sample increases as Ni content increases, indicating the oxidation state of Mn and Ni is 2+ and 2+ respectively and no extra peaks due to Mn, Ni ions substituted at the Sn site without changing the rutile tetragonal structure.
Fig 4.3b Dependence of lattice parameters as a function of concentration

Fig 4.4 shows X-ray diffraction patterns for Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ prepared at different temperatures. The samples are polycrystalline, and a preferred orientation could not be detected. The samples are characteristic of Tin Oxide in the tetragonal structure, and all peaks can be indexed according to the JCPDS card for Tin Oxide. Note that only major reflections are indexed in Fig 4.4. In all the samples there is no presence of any sort of impurity in the phase. The dependence of lattice parameter $a$ on the annealing temperature is shown in Fig 4.4.a as we can see from Fig 4.4.a lattice parameter $a$ decrease from $a=4.705$ Å to $a=4.697$ Å at $T=500^\circ$C, lattice parameter $a$ increases steadily with increasing annealing temperature, reaching maximum of $a=4.739$ Å for the temperature $T=700^\circ$C.
When the temperature increases from 500°C to 700°C, the grain size also increases. This indicates that the crystallinity of the sample grown and also the FWHM decreases when temperature increases reveals the increase of crystal size. Yet, two important factors might have played a role in such result. Firstly, the doping was of the “double doping” type, secondly the temperature. We have calculated the lattice parameters for all the above mentioned samples. A comparison of the lattice parameters among temperature is given in Table 4.4.
Table 4.4 Lattice parameters and Grain size of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ at different temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Lattice Constant a(Å°)</th>
<th>Lattice Constant c(Å°)</th>
<th>Grain Size (D) nm</th>
<th>Cell Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4.705</td>
<td>3.192</td>
<td>2.7</td>
<td>70.6</td>
</tr>
<tr>
<td>500</td>
<td>4.697</td>
<td>3.191</td>
<td>3.7</td>
<td>70.3</td>
</tr>
<tr>
<td>600</td>
<td>4.716</td>
<td>3.174</td>
<td>7.1</td>
<td>70.5</td>
</tr>
<tr>
<td>700</td>
<td>4.739</td>
<td>3.182</td>
<td>15.9</td>
<td>71.4</td>
</tr>
</tbody>
</table>

4.2.2 Morphology and Chemical composition

In order to investigate the morphology and homogeneity of our samples, we used the Energy dispersive X-ray analysis technique in conjunction with scanning electron microscopy. Figure 4.5a and 4.5b shows the overall surface morphology of Mn-doped SnO$_2$ nanopowders. SEM pictures are taken for all the Sn$_{1-x}$Mn$_x$O$_2$, where 0.04≤x≤0.10 samples sintered for one hour at 500°C. All SEM pictures have been magnified to the same magnification order, which is useful when comparing the sizes of the crystallites of various samples. The images show that the samples comprise of nanocrystalline grains. The grain size of the samples is also determined manually from the SEM micrographs. It is clearly observed that the samples are comprised of nanoparticles of extra fine; with an average grain size of 8 nm. The results are similar to that obtained from XRD analysis. The chemical composition of the sample Sn$_{1-x}$Mn$_x$O$_2$, (x=0.10) as determined by EDAX analysis is shown in Figure 4.5c. It shows that no large deviation from the chemical composition of the sample as described by the nominal chemical formulas. This is in a good agreement with the XRD results, which show no trace of any impurities in the sample. The calculated chemical composition of the samples is given in Table 4.5.
Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO$_2$ and codoped SnO$_2$

Figure 4.5a SEM micrographs of Sn$_{1-x}$Mn$_x$O$_2$ samples with x=0.04 and x=0.06
Figure 4.5b SEM micrographs of $\text{Sn}_{1-x}\text{Mn}_x\text{O}_2$ samples with $x=0.08$ and $x=0.10$
Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO$_2$ and codoped SnO$_2$

Table 4.5 Chemical composition of the Sn$_{0.90}$Mn$_{0.10}$O$_2$ samples as determined by SEM–EDAX analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>App Conc.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>32.77</td>
<td>0.4737</td>
<td>39.64</td>
<td>0.84</td>
<td>78.82</td>
</tr>
<tr>
<td>Mn K</td>
<td>24.32</td>
<td>0.8672</td>
<td>16.07</td>
<td>0.40</td>
<td>9.31</td>
</tr>
<tr>
<td>Sn L</td>
<td>68.54</td>
<td>0.8868</td>
<td>44.29</td>
<td>0.70</td>
<td>11.87</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.5c SEM–EDAX spectrum of Sn$_{0.90}$Mn$_{0.10}$O$_2$

Figure 4.6a, 4.6b and 4.6c show SEM images of Ni doped SnO$_2$ nanopowders. SEM pictures are taken for all the Sn$_{1-x}$Ni$_x$O$_2$, 0.04≤$x$≤0.10 samples sintered for one hour at 500°C. The morphology of the samples shows that particles are well separated forming small crystallites. All SEM pictures have been magnified to the same magnification, which is useful when comparing the sizes of the crystallites of various samples. The size of the particles is approximately 8nm. No phase segregation can be seen in the SEM figures, which confirms the homogeneity of the samples. Chemical compositions of the samples were obtained from EDAX spectrum is in a good agreement with the nominal chemical formula.
Figure 4.6a SEM image of Sn$_{1-x}$Ni$_x$O$_2$, x = 0.04 sample
Figure 4.6 b SEM image of Sn$_{1-x}$Ni$_x$O$_2$, $x = 0.06$ and $x = 0.08$ sample
Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO$_2$ and codoped SnO$_2$

Figure 4.6c SEM image of Sn$_{1-x}$Ni$_x$O$_2$, ($x=0.10$) sample

Figure 4.6d SEM–EDAX spectrum of Sn$_{0.90}$Ni$_{0.10}$O$_2$
Table 4.6 Chemical composition of the Sn$_{0.90}$Ni$_{0.10}$O$_2$ samples as determined by SEM – EDAX analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>App Conc.</th>
<th>App Corrn.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>23.49</td>
<td>0.5329</td>
<td>32.51</td>
<td>0.89</td>
<td>70.67</td>
<td></td>
</tr>
<tr>
<td>Ni K</td>
<td>41.04</td>
<td>0.9489</td>
<td>31.90</td>
<td>0.66</td>
<td>18.90</td>
<td></td>
</tr>
<tr>
<td>Sn L</td>
<td>41.55</td>
<td>0.8609</td>
<td>35.59</td>
<td>0.67</td>
<td>10.43</td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.7 Shows SEM micrograph of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ and Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ sample. Figure 4.7c, and Figure 4.7d Shows TEM micrograph of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ and Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ samples. The particles are well formed, and the approximate size is 5 to 7 nm. Figure 4.8a and Figure 4.8b shows SEM micrographs of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ sample sintered at different temperature. As we can see, in the case of (Mn, Ni) - codoped tin oxide samples the particles are well formed. The size of the particles varied from 6 nm to 8 nm. When the temperature increase from 400 to 700°C, the crystalline size increases. Formation of big crystallites, which are surrounded by areas of much small particles are shown in the micrographs. Figure 4.7a and 4.7b shows, the EDAX spectrum of Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ and Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$. The EDAX spectrum shows the composition wt% of the used materials. The weight percentage of Sn, Mn and Ni as prepared sample was observed as 56.89, 2.30, 5.23 and 64.73, 9.24, 9.81 respectively.
Figure 4.7 SEM micrograph of (a) Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ and (b) Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ samples
Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO$_2$ and codoped SnO$_2$

Figure 4.7a SEM–EDAX spectrum of Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$

Table 4.7a Chemical composition of the Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ samples as determined by SEM–EDAX

<table>
<thead>
<tr>
<th>Element</th>
<th>App Conc.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>25.21</td>
<td>0.3882</td>
<td>35.58</td>
<td>1.14</td>
<td>78.38</td>
</tr>
<tr>
<td>Mn K</td>
<td>8.27</td>
<td>0.8670</td>
<td>5.23</td>
<td>0.31</td>
<td>3.35</td>
</tr>
<tr>
<td>Ni K</td>
<td>3.98</td>
<td>0.9500</td>
<td>2.30</td>
<td>0.30</td>
<td>1.38</td>
</tr>
<tr>
<td>Sn L</td>
<td>93.15</td>
<td>0.8973</td>
<td>56.89</td>
<td>1.06</td>
<td>16.89</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO$_2$ and codoped SnO$_2$

![Figure 4.7b SEM –EDAX spectrum of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$](image)

Table 4.7 b Chemical composition of the Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ samples as determined by SEM –EDAX

<table>
<thead>
<tr>
<th>Element</th>
<th>App Conc.</th>
<th>App Corrn.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>18.33</td>
<td>0.4198</td>
<td>43.67</td>
<td>2.01</td>
<td>74.25</td>
<td></td>
</tr>
<tr>
<td>Cl K</td>
<td>2.03</td>
<td>0.8648</td>
<td>2.34</td>
<td>0.19</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td>Mn K</td>
<td>8.09</td>
<td>0.8756</td>
<td>9.24</td>
<td>0.43</td>
<td>4.57</td>
<td></td>
</tr>
<tr>
<td>Ni K</td>
<td>9.28</td>
<td>0.9463</td>
<td>9.81</td>
<td>0.55</td>
<td>4.55</td>
<td></td>
</tr>
<tr>
<td>Sn L</td>
<td>57.20</td>
<td>0.8837</td>
<td>64.73</td>
<td>1.05</td>
<td>14.83</td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>129.79</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO$_2$ and codoped SnO$_2$

Figure 4.7c TEM micrograph of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ sample
Figure 4.7d TEM micrograph of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ sample
Figure 4.8 a SEM micrographs of $\text{Sn}_{1.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_2$ sample sintered at temperature $T=400^\circ\text{C}$ and $T=500^\circ\text{C}$.

T=400

$20kV$ $X10,000$ $1\mu m$ $12\text{J0 SEI}$

T=500

$20kV$ $X46,000$ $0.5\mu m$ $0104$ $112x SEI$
Figure 4.8b SEM micrographs of Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ sample sintered at temperature T=600°C and T=700°C.
4.2.3 Photoluminescence properties and Hall measurements

One of the objectives of the present investigation is to clarify the effect of Mn ions on the photoluminescence for the SnO$_2$ host. The photoluminescence (PL) can be used to conveniently investigate the structure and defect or impurity levels [31]. Figure 4.9a shows the room temperature PL spectra for Sn$_{1-x}$Mn$_x$O$_2$, $0.04 \leq x \leq 0.10$ samples annealed at 500°C for one hour. There is a broad emission band when the concentration $x=0.04$.

Figure 4.9a Room temperature PL spectra for Sn$_{1-x}$Mn$_x$O$_2$, $0.04 \leq x \leq 0.10$

Samples annealed at 500°C
This emission band contributed to the twofold-coordinated tin oxygen-deficient centers. Meanwhile, the emission band is separated into two bands when the concentration rises above $x=0.08$. This may be due to the fact that the twofold-coordinated tin oxygen-deficient center is reduced with increasing concentration. The resistivities of Mn-doped SnO$_2$ samples are too high for our equipment to measure the carrier concentration. Figure 4.9b shows the room temperature PL spectra for Sn$_{1-x}$Ni$_x$O$_2$, 0.04≤$x$≤0.10 annealed at 500°C for one hour. The PL spectra of all the samples each show a broad blue emission near 450 nm. Since the emission are both lower than the band gaps of pure SnO$_2$ [29]. The emission cannot be assigned 2p valence band. Furthermore, Liu chun-Ming et al. [29] stated that the origin of the peak was related to defects, or nanocrystalline grains or defect levels associated with oxygen vacancies of tin interstitials resulting from the nanosize of the Ni-doped SnO$_2$ samples. The peak at 450 nm was due to Oxygen vacancies. In our samples, the nanocrystalline –SnO$_2$ grain assemblage has a large number of defects: vacancies of Oxygen, vacancy cluster, and local lattice disorders at the interface and interior surface. It is difficult to identify the origin of blue emission. It can be seen from Figure 4.9b that nickel doping changes the peak position. However, in this study, the blue shift effect is ascribed as a function of Ni concentration. The resistivities of Ni-doped SnO$_2$ samples are too high for our Hall equipment to measure the carrier concentration and charge density.
Figure 4.9 b Room temperature PL spectra for Sn$_{1-x}$Ni$_x$O$_2$, $0.04 \leq x \leq 0.10$ samples annealed at 500°C

Figure 4.9c shows the room temperature PL spectra of Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ and Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ samples sintered at 500°C. One of the main objectives of the present investigation is to clarify the effect of concentration of (Mn, Ni) ions on the photoluminescence for the SnO$_2$ host. The emission spectrum presents two bands at 400 nm and 415 nm, respectively. From Figure 4.9c, it can be observed that the addition of Ni to SnO$_2$ host lattice. F.Gu et al. [40] reported that in pure SnO$_2$ host, the emission attributes to electron transitions, mediated by defects levels in the band gap, such as Oxygen vacancies, Tin interstitials and so forth. Probably after increasing Ni ion concentration into the SnO$_2$ host, the defects still play a dominant role with respect to the luminescence processes.
Figure 4.9c Room temperature PL spectra of Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ and Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ samples sintered at 500°C.

Generally, Oxygen vacancies are known to be the most common defects and usually act as radiative centers in photoluminescence processes. The Oxygen vacancies present in three different charge states: $V^0_o$, $V^+_o$, and $V^{2+}_o$ in the Oxide. As $V^0_o$ is a very shallow donor, the most Oxygen vacancies will be in their paramagnetic $V^+_o$ state under flat-band conditions and the origin of photoluminescence is assigned to the recombination of electrons in singly occupied Oxygen vacancies with photo excited holes in the valence band. After the increasing the concentration of (Mn,Ni)–codoped to the host lattice, it is easy for Mn or Ni ions to substitute for Sn$^{4+}$ ion, which can be due to the fact that the radius of Sn$^{4+}$ (76 pm) is similar to that of Mn$^{2+}$ (80 pm) ion [40]. In addition, the 2-charge of the Mn$_{Sn}$ ion has to be compensated for somewhere in the lattice in the form of
Oxygen vacancy. That is the reason why the PL intensity becomes larger after increasing (Mn, Ni)-codoping to the SnO$_2$ host. Doping increases photoluminescence of SnO$_2$ host particles and photoluminescence emission which is due to the contribution of oxygen vacancies in the SnO$_2$ host. Hall instrument is used to measure the carrier concentration, mobility and Hall resistance of the prepared samples. It is noted that the Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ codoped sample is annealed at 500°C for one hour, it remains conductive with a carrier concentration of 1.161x10$^{18}$ cm$^{-3}$. The resistivity of Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ sample prepared same condition are too high for our equipment to measure the carrier concentration. The increase in electron concentration and conductivity in the Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ sample is believed to have resulted from defects due to increasing Ni doping.

Table 4.8 Electrical properties of the Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ sample annealed at 500°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carrier Concentration $n$ [cm$^{-3}$]</th>
<th>Mobility $\mu$ [cm$^2$/Vs]</th>
<th>Resistivity $\rho$ [Ω cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$<em>{1.8}$Mn$</em>{0.1}$Ni$_{0.1}$O$_2$</td>
<td>-1.161x10$^{18}$</td>
<td>8.3335</td>
<td>2.348</td>
</tr>
</tbody>
</table>

4.2.4 Magnetic properties of Transition metal doped [Mn, Ni] and Transition metal codoped SnO$_2$ samples.

The magnetic properties of transition metal [Mn, Ni] doped SnO$_2$ were investigated by using vibration sample magnetometer (VSM). To see how the Mn incorporation changes the magnetic behavior of diamagnetic SnO$_2$, the Mn concentration increases up to 10 at %, the sample starts showing antiferromagnetic behavior in its hysteresis loop up to 8.0 at %. The magnetic behavior of the samples having a Mn concentration of x=4 at % to x=10 at % in SnO$_2$ is shown in Figure 4.9d that the saturation magnetization attains a value of 17.323 E$^-$. 

89
Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO\(_2\) and codoped SnO\(_2\)

3 emu.

Figure 4.9d Room temperature magnetic hysteresis loops of Sn\(_{1-x}\)Mn\(_x\)O\(_2\), 0.04≤x≤0.10 annealed at 500°C for one hour.

The magnetic-field dependence of Magnetization for the samples Sn\(_{1-x}\)Ni\(_x\)O\(_2\), 0.04≤x≤0.10 at room temperature is illustrated in Fig 4.9e. The samples upto x=0.08 shows diamagnetic loop. Magnetization data of the sample with x=0.10 show a trace of weak ferromagnetism at room temperature. It is well known that the bulk [23] NiO is antiferromagnetic. Consequently, the weak ferromagnetic behavior in this sample probably originates from the super imposition of the antiferromagnetic and intrinsic ferromagnetic effects. The saturation Magnetization (Ms) value 1.2596 E\(^3\) emu and Coercivity (Hci) 524.13 G for a Ni concentration of 10 at %.
Figure 4.9e Room temperature magnetic hysteresis loops of Sn$_{1-x}$Ni$_x$O$_2$, 0.04$\leq x \leq$0.10 annealed at 500°C for one hour.

Figure 4.9f shows the magnetic hysteresis loops measured at room temperature for the (Mn, Ni)-codoped SnO$_2$ samples with various concentrations. Yet several groups reported room-temperature ferromagnetism observed in Mn-doped SnO$_2$, Ni-doped SnO$_2$, our Mn-doped SnO$_2$ and Ni-doped SnO$_2$ samples synthesized under the same condition gives linear hysteresis loops under magnetic fields upto 2Tesla. Nevertheless, by
introducing a few percent of Ni, ~10 at % in Mn-doped SnO$_2$ study, the (Mn, Ni)-codoped sample exhibit stable and hysteretic ferromagnetism at room temperature.

Figure 4.9 Room temperature magnetic hysteresis loops of Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ and Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ samples annealed at 500°C for one hour.
The sample Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ exhibit weak hysteretic behavior and the saturation Magnetization (Ms) is 3.6081 E$^{-3}$ emu and Coercivity (Hci) is 692.28 G. Since the 10 at \% Mn-doped SnO$_2$ and Ni-doped SnO$_2$ samples exhibit weak ferromagnetic or super paramagnetic characteristics, respectively, it is believed that the magnetic moments in Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ sample come from the Mn$^{2+}$ ions whose numbers of unpaired 3d electrons (3d$^5$) and ion radius (80 pm) are both larger than those of Mn$^{3+}$ ions (3d$^4$ and 58 pm) [13]. More unpaired electrons and larger ion radius would increase the probability of ferromagnetic coupling between magnetic Mn$^{2+}$ ions. On the other hand, defects resulted from increasing Ni concentration and delocalized carriers originated from oxygen vacancies also enhance the ferromagnetic interaction. It is noted that the Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ codoped sample with a carrier concentration of 1.611x10$^{18}$ cm$^{-3}$. The resistivity of Sn$_{1.9}$Mn$_{0.07}$Ni$_{0.03}$O$_2$ sample synthesized under the same condition is too high for our equipment to measure the carrier concentration. The increase in electron concentration and conductivity in the Sn$_{1.8}$Mn$_{0.1}$Ni$_{0.1}$O$_2$ sample is believed to have resulted from defects due to Ni concentration increases. This result reveals that the itinerant carriers play a dominant role in the ferromagnetic interaction between the magnetic Mn$^{2+}$ ions. The dependence of the saturated magnetization on the carrier concentration is consistent with carrier-mediated model [13, 23].
The magnetic properties of $\text{Sn}_{1.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_2$ sample calcined at different temperature were shown in Fig 4.9 g.

Figure 4.9 g Magnetic properties of $\text{Sn}_{1.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_2$ sample calcined at different temperature.
It is seen that $\text{Sn}_{1.8}\text{Mn}_{0.1}\text{Ni}_{0.1}\text{O}_2$ sample annealed at 600°C has a Magnetization of $37.26 \times 10^{-3}$ emu and Coercivity is 812.10 G and the sample annealed at 400°C has a magnetization of $19.815 \times 10^{-3}$ emu, but when the annealing temperature was 700°C, the magnetization and Coercivity of the sample decrease to $12.626 \times 10^{-3}$ emu and 779.7 G. This is due to the difference in structural defects and particle size in the samples annealed at different temperatures [16]. Moreover, with the increase in temperature above 600°C, the number of Mn, Ni ions remains the same but oxygen vacancies decrease, which must be taken into account as an important source of ferromagnetism in codoped samples. Hence it is clear that the oxygen vacancies play an important role in inducing ferromagnetism in the samples.

### 4.3 Summary

In this chapter we have presented various data on Mn-doped SnO$_2$ and Ni-doped SnO$_2$ samples. We have also presented investigations of (Mn/Ni) –codoped SnO$_2$ samples. In the case of single Mn doping into SnO$_2$, and Ni doping into SnO$_2$ were found to be weak ferromagnetic at room temperature, while (Mn/Ni) –codoped had a large carrier concentration, which indicated that (Mn/Ni)-codoped samples were ferromagnetic at room temperature and showed a giant magnetization value, this value of the magnetization are the largest among published results of (Mn/Ni)-codoped SnO$_2$ samples.
Reference


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Chapter IV  Preparation and characterization of DMS based on Transition metal (Mn, Ni) doped SnO$_2$ and codoped SnO$_2$


