Nanostructural and surface morphological evolution of chemically sprayed SnO_2 thin films

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Abstract

Physical properties of a nanocrystalline thin film is greatly influenced by its morphological and structural evolution. We try to understand the transition of SnO_2 thin films from amorphous to nanocrystalline structure with XRD, IR, SEM, AFM and surface profiler studies. A 2D layer like structure resulting from quantum confinement is found for the films prepared at 400 °C. We observed a new IR band at 530 cm\(^{-1}\) that was theoretically predicted and report it for the first time. A correlation of population of defects in SnO_2 films with change in lattice parameters and FWHM of IR bands are reported. The electric and optical properties of the films have been discussed.

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1. Introduction

Research in semiconductor metal oxide nanocrystalline thin films is of fundamental importance due to its wide range of applications in optoelectronic devices, gas sensors, low and medium diodes, heterojunction solar cells, varistor, etc., [1,2]. The use of polycrystalline SnO_2 as transparent electrodes and solid state gas sensor is gaining much interest with regard to the relationship between its electrical properties and crystalline size. SnO_2 thin films have good adhesion to many polycrystalline and amorphous substrates such as glasses, metals and oxides. Different methods have been employed to synthesise SnO_2 thin films such as chemical vapour deposition, sol–gel, sputtering, spray pyrolysis, pulse laser deposition, etc., [3–8]. Among these methods, spray pyrolysis gets considerable importance because of its economical advantage, easy accessibility and good results [9,10].

The interface and surface microstructure of nanomaterials have been extensively and intensively investigated by researchers in the past few years [11]. Although peculiar properties of nanomaterials are explained in terms of the interface and surface structures, the effects from the microstructure of the grains are usually overlooked. The microstructure of thin films depend upon the method of preparation and the associated changes in microstructure can influence the physical and chemical properties of the film. Since grains are the basic components in nanomaterials, its study, in addition to explaining many experimental results, will offer exciting opportunities for both fundamental research and technological applications.

The IR techniques can reveal local structural information on amorphous and poorly crystallised samples. Usually, the disorder induces spectral changes which are discussed in reference to bulk crystal spectra and on their vibrational density of states. The purpose of this study is to characterise the crystalline structural changes and microstructure evolution of nanocrystalline SnO_2 thin films by X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM) and atomic force microscopy (AFM). In this study, an effort has been made to explain nanostructural and surface
morphological properties of chemically sprayed SnO2 thin films with the observed change in crystal dimensions. The IR study is an extension of the work by Dieguez et al. [22] in Raman spectra. We report a new IR peak that was predicted by theory but to the best of our knowledge has not been observed before.

2. Experimental

SnO2 nanocrystalline thin films have been prepared by spray pyrolysis technique. 0.1 M hydroethanolic solution has been prepared by dissolving SnCl4·5H2O in a mixture of absolute ethanol and high purity water in the ratio 1:1. A few drops of concentrated HCl has been added to the solution to breakdown the polymer molecules that are formed when diluted with ethanol. The solution has been sprayed on to glass substrates placed over a temperature controlled oven in air atmosphere using a spray rate control atomizer. The spray rate was 40 mL/min and spray time was 90 s. The films have been prepared at different substrate temperatures 375 °C (Sample A), 400 °C (Sample B), 425 °C (Sample C), 450 °C (Sample D), 475 °C (Sample E) and 500 °C (Sample F). Since Sample A is amorphous and Samples E and F have comparable properties, we have not discussed Samples A and E in detail in this paper.

Structural analysis of the grown films were carried out by Philips PW 1830 X-ray diffraction spectrometer with an accelerating potential 40 kV and current 30 mA using Cu Kα1 radiation (1.54056 Å) as an X-ray source that is equipped with Ni filter. The IR studies were carried out using Shimadzu IR prestige spectrometer. Surface morphological studies were carried out using a spray rate control atomizer. The spray rate was 40 mL/min and current 30 mA using Cu Kα1 radiation.

Fig. 1. XRD patterns of spray pyrolytically grown nanocrystalline SnO2 thin films with deposition time 90 s at different substrate temperatures (a) 375 °C, (b) 400 °C, (c) 425 °C, (d) 450 °C, (e) 475 °C and (f) 500 °C.

where h, k, l are integers and (h k l) is the lattice plane index and a and c are lattice constants. For a normal crystal, the calculated values of a and c are the same for different crystal planes.

The absence of XRD peaks in Sample A indicates that it is amorphous. With increase in temperature, small peaks corresponding to SnO2 crystalline phase were observed to grow in strength and all the films prepared at and above 400 °C reveals that all of them are of polycrystalline nature and are of tetragonal (rutile) structure with a major reflex along (2 0 0), (1 1 0) planes. Other phases like β-SnO, α-SnO, Sn2O3, S3nO4, SnO, etc., are not observed. The FWHM of the peaks are found to decrease with increase in substrate temperature. In Sample B, planes corresponding to (1 1 0), (1 0 1), (2 0 0) and (2 1 1) were observed with weak intensities. The presence of broad and weak peaks indicates that SnO2 particles have a very small crystalline size or that they are semicrystalline in nature [14]. All diffraction lines are assigned well to cassiterite tetragonal crystalline phase of SnO2 with a reference pattern of JCPDS (41-1445).

It is manifested that as the substrate temperature increases to 425 °C (Sample C), the intensity corresponding to major (2 0 0) plane gets enhanced indicating the preferential orientation of the film along (2 0 0) direction. A close examination of this pattern reveals that generally the crystalline nature of the films is improved with respect to that of film prepared at 400 °C. All other planes appear with weak intensities. The decrease in FWHM of the preferentially oriented peak (2 0 0) of Sample C indicate an increase in particle size as seen in Table 1. Similar reports of increase in crystallinity with substrate temperature can be seen in literature [15,16]. For Samples C–E, all the diffraction lines are assigned well to cassiterite tetragonal crystalline phase of SnO2 with a reference pattern (JCPDS 46-1088).

SnO2 film prepared at 500 °C showed a peculiar enhanced intensity shift towards (1 1 0) plane from (2 0 0) plane with a random orientation along (1 1 0) and (2 0 0) planes indicating the influence of substrate temperature on the preferential growth of the film. All the diffraction lines are assigned well to cassiterite tetragonal crystalline phase of SnO2 with a reference pattern (JCPDS 41-1445).

The d values of X-ray diffraction shown in Fig. 1 estimated with X’Pert software were compared with the standard d values and are tabulated in Table 2. The observed values are in good agreement with the standard values.
agreement with the standard values and confirms that the material deposited is SnO₂. The absence of other peaks from lattice planes such as (2 2 0), (0 0 2), (3 1 0), (2 0 2), (1 1 2) of rutile lattice of SnO₂ may be due to vacant lattice sites resulting from the non-stoichiometry and lattice disorders generally observed in thin films [5].

We have calculated the lattice parameters of different samples with Eq. (2). The calculated lattice constants along with standard values are tabulated in Table 1. It is found that there are deviations from the standard values of the lattice parameters for the as-prepared SnO₂ thin films. It can be seen that the value of Δa and Δc are sensitive to substrate temperature. However, significant deviation in values of Δa and Δc can be observed for films prepared at 400 °C. This change in values of Δa and Δc can be attributed to presence of large number of oxygen vacancies, vacancy clusters and local lattice disorders [5]. A recent study has shown that the change in unit cell parameters a (Δa) and in c (Δc) is a measure of the population of oxygen vacancies [17].

### 3.2. IR studies

The IR techniques can reveal local structural information of amorphous and poorly crystalised samples. Usually, the disorder induces spectral change which is discussed in reference to the bulk crystal spectra and on their vibrational density of states. Tin oxide gives rise to well defined IR spectra extensively studied [19–21]. Tin oxide has a tetragonal rutile crystalline structure with a space group $D_{4h}^1$. The six unit cell atoms give a total of 18 branches for the vibrational modes in the first Brillouin zone [5,22–24].

$$
\Gamma = A_{1g} + A_{2g} + A_{1u} + B_{1g} + B_{2g} + 2B_{1u} + E_g + 3E_u
$$

In these 18 modes, two are active in infrared (the single $A_{2u}$ and triply degenerate $E_u$), four are Raman active (three nondegenerate modes $A_{1g}, B_{1g}, B_{2g}$ and a doubly degenerate $E_g$) and two are silent ($A_{2g}$ and $B_{1g}$).

The aim of the present study is focused on the IR spectrum of SnO₂ nanocrystalline thin films grown at different substrate temperatures. Fig. 2 shows the relevant portion of the IR spectrum of the nanocrystalline thin films prepared at different substrate temperatures. It can be seen that two fundamental IR bands at 399, 775 cm⁻¹ corresponding to $A_{2g}$ and $E_u$ vibration modes are in good agreement with the values for rutile bulk SnO₂. $E_u$ mode is absent in Samples B and D. The fundamental mode $A_{2g}$ shows a minor shift from 399 cm⁻¹ to higher wave numbers (401, 403 cm⁻¹) as the particle size increases with substrate temperatures. When the size of SnO₂ crystal is changed, the IR spectrum is modified because of the interaction between electromagnetic radiation and the dependence on crystal size, shape and state of aggregation of the particle [25,26]. Several authors have reported that some Raman peaks have been found to be closely related to grain size [22,23,27–29]. The main feature of XRD spectra is the narrowing of XRD peaks as the substrate temperature is increased, which reveals that there is an increase in grain size and higher crystalline quality. In all the samples, a peak is observed around 29° which may be due to the librational mode of H₂O molecule present in the sample.

In a disordered crystal, its imperfections modifies its symmetry, preventing atoms from vibrating in phase and
preventing their displacements to be correlated. The changes in the local symmetry of the crystal can produce changes in some of the components of the polarisability tensor and is applicable even to usually forbidden vibration modes. The remarkable aspect of IR spectrum for the as-prepared SnO$_2$ thin film is the appearance of new IR peak at about 530 cm$^{-1}$. An interesting aspect is that this new IR peak appears in all samples with a minor shift of wave number and a change in peak width. This result agrees well with the theoretical prediction$^{[22]}$ of a new band in region from 542 to 486 cm$^{-1}$. Thus we attribute this new band to the microstructural evolution which results from disorder or defect of nanoparticles in nanocrystalline SnO$_2$ thin films. It may also be correlated to change in lattice parameters.

Fig. 3 shows that not only has the position of the peaks shifted towards higher frequencies, but the width of these peaks have also changed. For the sample prepared at 400 °C the FWHM of the new IR peak is a maximum which is having the maximum $\Delta \alpha$ value. For the sample prepared at 425 °C, both FWHM and $\Delta \alpha$ are minimum. In fact, the IR activity in nanostructured materials are sensitive to surface disorder, example, oxygen defects and compositions in the surface regions. It is known that changes in local symmetry or local lattice disorder of the crystal can produce changes in the components of the vibrational energy states, even for the normally forbidden vibration modes. As a result, in an intermediate case, a shift of the classical modes accompanied by broadening and the appearance of some SnO$_2$ forbidden modes should be observed. This is indeed what occurs with modes $A_{2g}$ and $E_{u}$. However, the band 530 cm$^{-1}$ cannot fit any of the SnO$_2$ IR forbidden modes. A possible explanation for the new IR band is that it arises from the surface layer of non-stoichiometric SnO$_{x}$ lattice disorders caused by oxygen vacancies$^{[30,31]}$. This observation is substantiated by the observed change in lattice parameters ($\Delta a$ and $\Delta c$) given in Table 1$^{[17]}$.

3.2.1. SEM studies

Fig 4 shows the SEM micrographs of undoped SnO$_2$ thin films deposited at 400 and 425 °C. Physical parameters of the thin films are given in Table 3. The figures reveal the surface morphological evolution of the samples prepared at two significant substrate temperatures. Transition of semicrystalline to crystalline phase is also seen indicating the role of temperature in the synthesis of nanostructures with varied morphologies. The dependence of film quality on substrate temperature can be interpreted by the mobility and diffusion of the reactants on the substrate surface.

Fig 4a shows the SEM micrograph of Sample B. It has more asperity than other samples with no well defined crystallites. It looks like arrays of two dimensional layers that resulted from quantum confinement. The growth of thin films from atoms deposited is intrinsically a non-equilibrium phenomenon governed by a competition between kinetics and thermodynamics. Precise control of growth and thus of the properties of deposited films becomes possible only after an understanding of how this competition is achieved$^{[32]}$. The break in translational symmetry at a crystal surface creates surface electronic properties that can differ from those in bulk crystal and that localize at the surface layer$^{[33,34]}$. The formation of surface states and resonances is a general property of solid surfaces. The delicate interplay between the surface electronic structure and the atomic position often leads to complex surface reconstructions in which the atoms in the top layer rearrange to minimize the surface energy. In analogy to the surface of a bulk solid, it is possible to observe similar physics in reduced dimensions at the edge or end of a nanostructure. Similar to two dimensional (2D) surface states formed at the surface of a bulk sample, an edge or step in a 2D structure breaks the 2D symmetry and can form a 1D edge state$^{[35]}$. XRD studies on the sample indicates (large $\Delta \alpha$) the presence of large number of oxygen vacancies$^{[17]}$. SEM studies on the samples show the absence of well defined grain boundaries and this explains the increase in conductivity (Table 3). The grain formation process is found to have initiated and pinholes can be observed on the
film. Sample C (Fig 4b) has more uniform surface than Sample B. The film surface was found to be regularly textured with uniform spherical grains. Because of the smaller grain size, the grain boundary phase is more and reduces electrical conductivity [36]. Fig 4 c and d shows the surface profile of films prepared at 400 and 425 °C. These profiles indicate sharp reduction in roughness that resulted during the transition from semicrystalline to nanocrystalline structure. A reduced value of...
Fig. 5. 2D topographic view of AFM images and section analysis of spray pyrolytically grown nanocrystalline SnO$_2$ thin films at different substrate temperatures (a and e) 400 °C, (b and f) 425 °C, (c and g) 450 °C, (d and h) 500 °C.
$\Delta a$ indicates a decrease in population of oxygen vacancies. It is to be noted that although it might be expected that a decrease in $\Delta a$ should result in a decrease in conductivity and increase in transmittance [17], the increase in grain boundaries explains the decrease in conductivity of the samples and the regular texture explains the increase in transmittance.

### 3.2.2. AFM studies

Atomic force microscopy (AFM) revealed the smoothness of sample surface. Fig 5(a–d) and Fig 6 shows 2D and 3D surface morphology of samples prepared at different substrate temperatures. Section analysis of the AFM images are given in Fig. 5(e–h). Fig 5(b and c) indicates granular morphology of the samples. Figs. 5(a) and 6(a) stand different in nature with respect to the other images. It is observed that Sample B [Figs. 5(a) and 6(a)] has more asperity than other samples with no well defined boundaries. This depict the transformation from semicrystalline to nanocrystalline phase in accordance with the 2D quantum confinement observed in SEM micrographs. Figs. 5(b) and 6(b) show AFM topograph of SnO$_2$ thin films grown at 425 °C. The sample is polycrystalline with well defined grains in agreement with SEM observations. The smooth morphology observed for the films prepared at 425 °C is well understood from comparing the height profiles(Fig. 5 e–h). It is seen that the film prepared at 425 °C is extremely smooth whose surface roughness is only 0.983.

Higher deposition temperature favored increase in film roughness and lateral size [37]. There are two possible modes that occur in the kinetics of grain growth: ripening and coalescence. Ripening is the grain growth with mass transport from smaller to larger grain by surface diffusion to reduce the surface to volume ratio, and the coalescence is the combining of two grains with similar size into a larger grain. In both process, the total surface energy is decreased due to the change in surface area. Kinetics of grain growth of SnO$_2$ thin films is attributed to 3D diffusion limited process [38].

The degree of surface roughness of crystalline films is found to increase with increasing deposition temperature. It would generally be considered that the surface morphology of deposited films is related to surface thermal energy and mass diffusion of constituent elements. At higher temperatures (425 and 450 °C) the surface mobility of constituent elements increases and the growth of facet grains are preferred [39,1]. High substrate temperature stimulates migration of grain boundaries and causes the coalescence of small grains to form larger grains [40]. Increase in particle size suggests that the particle features in AFM image may be interpreted as

### Table 3

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Resistivity ($\Omega$ cm)</th>
<th>$\Delta a$ (Å)</th>
<th>$\Delta c$ (Å)</th>
<th>Transmittance (550 nm [%])</th>
</tr>
</thead>
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<tr>
<td>375</td>
<td>8.05</td>
<td></td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>400</td>
<td>$5.82 \times 10^{-2}$</td>
<td>0.108</td>
<td>$-0.032$</td>
<td>65</td>
</tr>
<tr>
<td>425</td>
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<td>0.013</td>
<td>$-0.004$</td>
<td>96</td>
</tr>
<tr>
<td>450</td>
<td>$1.1 \times 10^{-1}$</td>
<td>0.06</td>
<td>$-0.017$</td>
<td>68</td>
</tr>
<tr>
<td>500</td>
<td>$8.48 \times 10^{-3}$</td>
<td>0.015</td>
<td>$-0.005$</td>
<td>78</td>
</tr>
</tbody>
</table>

Fig. 6. 3D topographic view of AFM images of spray pyrolytically grown nanocrystalline SnO$_2$ thin films at different substrate temperatures (a) 400 °C, (b) 425 °C, (c) 450 °C, (d) 500 °C.
agglomerates of nanocrystalline SnO₂ grains. SnO₂ films with different surface roughness and low resistivity may be of importance in microelectronics (low roughness) or as gas-sensors (high roughness) [41].

4. Conclusion

In summary, for chemically sprayed SnO₂ thin films, substrate temperature plays a significant role in the nanostructural and surface morphological evolution. In the case of nanocrystalline SnO₂ films, which were prepared by spray pyrolysis techniques, it was found that the nanocrystalline SnO₂ grains posses some structure features of tetragonal rutile structure but have a large amount of defects such as oxygen vacancies, vacancy clusters and local lattice disorders at the interface and surface. We observe a 2D layer like structure resulting from quantum confinement for the films prepared at 400 °C. Starting from 425 °C, a transition from semicrystalline phase to nanocrystalline phase occurs that is confirmed by SEM, AFM and surface profiles studies. We report a new IR band at 530 cm⁻¹ caused by the defects in the films. A correlation between the population of defects in the films with change in lattice parameters and the FWHM of the IR bands is established.

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