Microstructural, Optical and Dielectric Properties of Al-Incorporated SnO$_2$ Nanoparticles

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Abstract: In this work, Pure SnO$_2$ and Al doped SnO$_2$ nanoparticles with the composition Sn$_{1-x}$Al$_x$O$_2$ (x = 0, and 0.05) have been successfully prepared using sol-gel technique. The effect of Al dopant on microstructural, optical and dielectric properties has been investigated by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Ultraviolet (UV-Visible) absorption spectroscopy and Impedance spectroscopy (LCR meter) respectively. The XRD patterns indicated tetragonal rutile structure with single phase without any detectable impurity for all samples and incorporation of Al ions into the SnO$_2$ lattice. Crystalline size decreased with aluminum content. The results of SEM confirm nanoparticles size decreases with Al dopant. UV-Visible results showed that optical band also decreases when Al is doped into pure SnO$_2$ lattice. Frequency dependent dielectric properties of pure and doped SnO$_2$ nanoparticles have been also studied.

Keywords: Band gap, SEM with EDAX, Tin oxide, XRD

1. INTRODUCTION

Tin dioxide (SnO$_2$) is well known as a multifunctional material having various applications such as gas sensors[1], catalysts[2], optoelectronic devices[3], and so on. In particular, SnO$_2$ based semiconductors offer great potential for gas sensors because of their detection accuracy and high sensitivity to combustible gases. SnO$_2$ in its pure form is an n-type wide band gap semiconductor having direct band gap of 3.68 eV at room temperature. The co-ordination geometry of SnO$_2$ is octahedral (Sn$^{4+}$) and oxygen is trigonal planar (O$^{2-}$) with co-ordination number 6 for Sn atom and 3 for oxygen respectively. The unit cell parameters or lattice constants of SnO$_2$ are $a = 4.737$ Å, $c = 3.185$ Å and $u = 0.672$; its space group is $P4_2/mnm$. The electrical and optical properties of SnO$_2$ can be largely modified by dopants. Up to now, SnO$_2$ has been doped separately with group III, V, VI and VII elements of the periodic table such as In, Ti, P, As, Sb, Te, F, Cl, Br and I to affect these properties [4–5]. SnO$_2$ nanoparticles are considered as potential materials for device fabrication due to enhancement of property when it
is doped with Al [6]. Similar types of results have been observed for Al doped ZnS. In the present report, effect of Al dopant on microstructural, optical and dielectric properties of SnO$_2$ nanoparticles has been studied.

2. Methodology

Pure and Al doped SnO$_2$ nanoparticles were prepared by sol-gel process with the help of Stannous Chloride (SnCl$_2$.2H$_2$O), Citric Acid and PEG (Polyethylene glycol). 0.5M Stannous Chloride and 0.5M Citric Acid were dissolved in 50ml distilled water with continuous stirring on magnetic stirrer in a beaker (B$_1$). A solution of PEG was prepared with 50ml distilled water in other beaker (B$_2$). Solution of B$_1$ is added to B$_2$ drop wise with continuous stirring. Complete solution was stirred for half an hour. After that liquid Ammonia was added drop by drop to maintain its pH around 8. A dark milky gel was obtained which then washed by water and ethanol several times to remove the impurity. Then the gel was dried at 100ºC for 24 hours. The dried material was crushed for half an hour and further calcined for 4 hours at 500ºC resulting in the formation of SnO$_2$ nanoparticles. To prepare Al doped samples, the same process was repeated by adding 5 mol% of Al from the source of Al(NO$_3$)$_3$.9H$_2$O to get 5% Al-SnO$_2$ nanoparticles.

3. Results and Discussion

3.1 Structural and Morphological Analysis

The crystal structure of all samples has been studied using Cu-K$_\alpha$ radiations in 20 range of 20º-80º. Fig.1 shows the XRD patterns of pure and Al doped SnO$_2$ nanoparticles annealed at 500ºC for 4 hours. The strong peaks corresponding with their planes obtained at diffraction angles 20 = 25.815º, 33.107º, 51.081º, arising out of reflections from (110), (101) and (211) planes respectively as identified using the standard JCPDS file no.41-1445, which belong to tetragonal SnO$_2$ rutile structure and on doping with Al a similar pattern is observed except that the diffraction peaks shift to the lower angle in comparison to pure SnO$_2$. The average crystallite sizes of as prepared samples are determined by using the Debye-Scherer formula[7] as given in equation in (1).

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]  

where $D$ is the crystallite size, $\beta$ is the full-width at half maximum (FWHM), $\theta$ is the Bragg angle and $\lambda = 0.154$ nm. Crystallite size of each sample has been calculated using most intense peak (110) of pure SnO$_2$ and doped SnO$_2$ nanoparticles and found to be 14.3nm and 9.7nm respectively. Al content in the host material, decreases the crystallite size. This Minor shifts in peaks can be explained by fact that the ionic radii of Sn$^{4+}$ is 0.069 nm and Al$^{3+}$ is 0.053 nm. The difference in their ionic radii results in small changes in crystal micro-structure.

The observed decrease in particles size on doping is due to formation of nanostructures which is confirmed by scanning electron microscopy (SEM) images. SEM image demonstrates clearly the formation of aggregated spherical SnO$_2$ NPs as shown in fig. 2(a & b).
The existence of Al is confirmed from the selective area EDAX analysis (Fig. 2(c)). It can be verified from the results of XRD and EDAX that the Al is successfully doped in the SnO$_2$ NPs. No incredible changes in the morphology of the particles were observed with the Al dopant in the SnO$_2$ lattice site, however the particle size seemed to be influenced by the dopant concentration.

![Figure 1](image1.png)

**Fig. 1.** XRD spectra of Pure and Al doped SnO$_2$ NPs

![Figure 2](image2.png)

**Fig. 2.** a) SEM and EDAX images Pure SnO$_2$  b) Al-SnO$_2$
3.2 Optical Study

The direct optical band gap $E_g$ is obtained by optical absorption measurements using the following relation [8].

\[(a h \nu)^2 = A(h \nu - E_g)\] \hspace{1cm} (2)

Where $\alpha$ is the absorption coefficient, A the constant and $E_g$ is the direct band gap of the material.

![Tauc Plots of pure and Al doped SnO$_2$ NPs](image)

The band gap energy for all samples has been obtained by extrapolation of the rising part to the x-axis as shown in fig. 3. The band gap energy has been observed for pure sample 3.9eV which is larger than the value of 3.6eV for the bulk SnO$_2$ due to quantum confinement. Doping of Al ions into the host material, decreases band gap i.e. (3.84eV) as compared to pure i.e. (3.9eV) as shown in fig. 3. It may be due to the formation of defect sub-bands below the conduction band.

3.3 Dielectric Properties

The dielectric constant is represented by $\varepsilon = \varepsilon' - i\varepsilon''$. The first term on R.H.S is real part of dielectric constant and describes the stored energy while second term on R.H.S is imaginary part of dielectric constant, which describes the dissipated energy. The dielectric constant as a function of frequency for all compositions is shown in the fig. 4. It is clear from the figure that it has strong frequency dependence in the lower frequency region. The dielectric constant decreases with the increase in frequency and become constant at high frequencies for all compositions. This type of behavior can be explained on the basis of Maxwell –Wagner model [10].
It has been observed that ac conductivity gradually increases with the increase in frequency of applied field. Due to increase in frequency enhances the electron hopping frequency of charge carriers $\text{Sn}^{4+}$ and $\text{Sn}^{2+}$ [11]. It can also be seen from the fig. 5 that conductivity increases with the increase in dopant concentration.

**Fig. 4.** Variation of dielectric constant with frequency

**Fig. 5.** Variation of ac conductivity with frequency
4. CONCLUSION

We have successfully synthesized pure tin oxide and Al doped SnO$_2$ nanoparticles calcined at 500ºC having particle sizes from 14.3-9.7 nm through the chemical sol-gel method. From XRD data, it is confirmed that all samples are in the tetragonal structure. No secondary phase is observed. FESEM images of pure and Al doped SnO$_2$ nanoparticles showed the formation of spherical nanoparticles. It is observed that the band gap of the doped samples is decreased. The variation of dielectric properties with frequency reveals that the dispersion is due to Maxwell–Wagner type of interfacial polarization in general. Hence, results indicated that the nanocrystalline nature of SnO$_2$ and Al doped SnO$_2$ can be used for applications in thin film electrodes, sensors, batteries and solar cells.

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