

Effect of grain size and temperature on DC electrical conductivity of tin oxide nanoparticles synthesized by gel combustion method

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Abstract

Tin oxide (SnO_2) nanomaterials of different grain size have been prepared using gel combustion method by varying the fuel ($\text{C}_6\text{H}_8\text{O}_7$) to oxidizer (HNO_3) molar ratio as a process parameter. The prepared samples were characterized by using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Analysis X-ray Spectroscopy (EDAX). The XRD patterns showed the formation of single phase Tetragonal rutile structure. The average particle size is found to be in the range of 19–34 nm. SEM images show high porosity in the material. The DC electrical conductivity of SnO_2 thick film increases with the temperature significantly from 308K to 670K. The DC electrical conductivity of SnO_2 thick film decreases with decrease in grain size due to the effect of surface to volume ratio while activation energy increases with decrease of grain size.

Keywords: Tin oxide; Combustion synthesis; Thick film; DC conductivity; Activation energy.

1. Introduction

Nanostructured metal oxides have attracted an extensive research interest due to their unique electrical, physical, chemical and magnetic properties as well as their potential for technological applications. In recent years, great interest has been focused on SnO_2 nanomaterial due to its importance in many technical fields, such as gas sensors[1][2], solar cells[3][4] and optoelectronic devices[5]. The nominally undoped (unintentional doped) SnO_2 is a transparent metal-oxide which is natively n-type semiconductor. Inherent oxygen vacancies in the tetragonal rutile structure of SnO_2 are responsible for its n-type conductivity. It has a wide band gap of 3.6 eV (bulk SnO_2), plasma frequency in IR region and when suitably doped, it can be used both as p-type and n-type semiconductors [6,7].

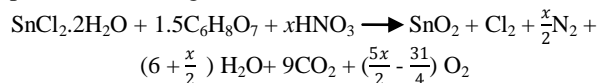
It is generally accepted that the practical performances of SnO_2 based sensors are relative to its crystallinity, morphology, crystal size, presence of dopants, crystal defects and surface properties, etc., which ultimately depend on the preparation methods and conditions. There is much progress has been achieved in the synthesis and structural characterization of SnO_2 nanostructures. SnO_2 has been synthesized by different methods such as the sol-gel method[8], chemical vapor deposition (CVD)[9],

magnetron sputtering[10] and hydrothermal treatment[11] etc. In the present work SnO_2 nanomaterial was prepared by combustion method which is very cheap and facile because of not requiring any complex equipment and complicated operation. The reaction is environmentally friendly since by-products are CO_2 , N_2 , Cl_2 , O_2 and H_2O , and it is safe and quick. In this preparation technique we have obtained tin oxide nanoparticles with different size simply by varying the amount of oxidizer during synthesis as nowadays applications require a high surface area and controlled defects which determine the optical and electrical properties [12]. There are many reports [13-15] on the electrical property of SnO_2 , however few reports available on electrical property of SnO_2 nanomaterial synthesized by the gel combustion method. So there is need to concentrate on different method of preparation of the sample and study the electrical conductivity. The aim of this work is to give an insight on how the grain size and temperature influence electrical properties of the SnO_2 nanopowder. In this paper, the effect of grain (crystallite) size and temperature on electrical property of tin oxide thick film prepared by doctor blade method has been reported. We have chosen the doctor blade technique because of the ease of preparation, quality and uniformity in thickness of the films.

2. Experimental

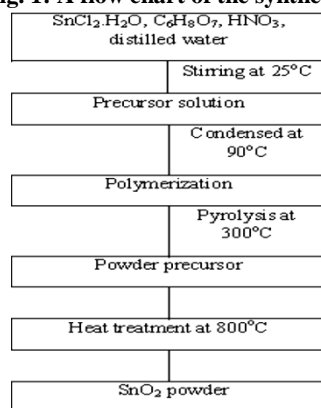
2.1. Sample preparation

SnO₂ was prepared by gel combustion method. The raw materials used were tin (II) chloride dihydrate (SnCl₂·2H₂O, 99.99%, Merck) and Nitric acid (HNO₃, 70%, Merck) which is used as an oxidizer. These raw materials were dissolved in distilled water and mixed in an appropriate ratio to form a tin nitrate solution. Then Citric acid (C₆H₈O₇, 99.5%, Merck) which acts as fuel was added to this solution. In this study, the amount of citric acid was fixed at 1.5 mol. The solution was heated with constant stirring at a temperature of about 90°C in a Pyrex vessel. Then the concentration of the solution slowly became higher. Eventually a polymeric precursor formed. When the temperature was raised to about 300°C, the polymeric precursor underwent a strong, self-sustaining combustion reaction with evolution of large volume of gases and swelled into voluminous and foamy ashes. The entire combustion process ended in a few seconds. The resulting ashes were then calcined at a temperature of 800°C (for 1 hour) until complete decomposition of the carbonaceous residues was achieved. Then the obtained white powder was nano SnO₂. A flow chart of the synthesis of SnO₂ by the combustion method is as shown in Fig. 1. In this synthesized method precursors undergo reaction as follows,



As in the above reaction formula, the gaseous products, N₂, H₂O, CO₂, and O₂, which are released during the gel combustion reaction, are dependent on the amounts of HNO₃ added to solution during the reaction as an oxidizer [16]. The obtained SnO₂ powder calcined at 800°C was formed into thick film on Silicon glass substrate. The thick film was coated on silicon glass substrate using doctor blade method [17][18]. The thickness of films was determined by mass difference method [19].

Fig. 1: A flow chart of the synthesis



2.2. Structural characterizations

Crystal structure of SnO₂ was analyzed by XRD method using Cu-Kα radiation (λ=1.5418Å)

operating at 30 kV and 15 mA. The scan rate was 5°/min and the range was between 20° and 80°. The average grain size was calculated using the Scherrer relation[20],

$$d = 0.89 \frac{\lambda}{\beta \cos \theta} \quad (1)$$

Where d is the crystallite size, λ the wavelength of X-rays, β the full width at half maximum and θ the diffraction peak angle. The surface morphology and shape of the nanoparticles of powdered samples were investigated by scanning electron microscope (Hitachi Model S-3200N). The elemental analyses of the powdered samples were carried out by using EDAX spectra.

2.3. Electrical conductivity measurement

The DC electrical conductivity was calculated using the relation [21],

$$\sigma = \frac{t}{RA} \quad (2)$$

Where t is thickness of the film, R the Resistance of the film measured using Keithley source meter (Model-2000) and A is the area of the film. The activation energy is obtained using the relation

$$\sigma = \sigma_o \exp\left(-\frac{E_A}{kT}\right) \quad (3)$$

Where E_A is activation energy of the sample, T temperature and k Boltzmann constant.

3. Results and discussion

The X-ray diffraction investigation carried out on the prepared SnO₂ (lattice constants of a = 4.738Å and c = 3.187 Å) revealed that the obtained SnO₂ is pure single phase having tetragonal rutile structure with a good crystalline character according to the standard data (JCPDS, card file No. 41-1445) [22]. No reflection peaks were observed from the impurities such as unreacted Sn or other tin oxides this indicating the high purity of the products. The lattice constants a and c for the tetragonal phase structure were determined by the relation [23],

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2} + \frac{k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (4)$$

Where d and (hkl) are the interplanar distance and Miller indices respectively.

Fig. 2: XRD pattern SnO₂ nanoparticles.

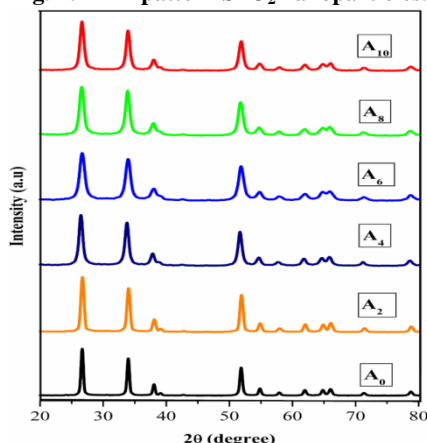
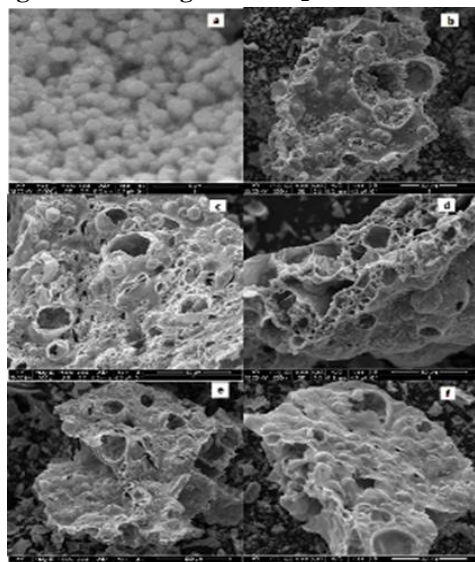


Fig. 3: SEM images of SnO₂ nanomaterials.

The average crystallite size was determined by the Scherrer's formula which confirmed the formation of nanoparticles SnO₂ and calculated values are in the range of 12nm to 31 nm as recorded in Table. 1. Fig. 2 depicts the XRD patterns of the pure SnO₂ samples sintered at 800°C. All the diffraction peaks in the patterns can be indexed to the tetragonal rutile structure of SnO₂. The broadened peak width in the XRD pattern indicates the gel combustion reaction would give an opportunity to make an ultrafine powder. Among the samples, the sample synthesized using 6.2 mole has broadened peak which indicates lesser grain size for A₆ sample as compared to others.

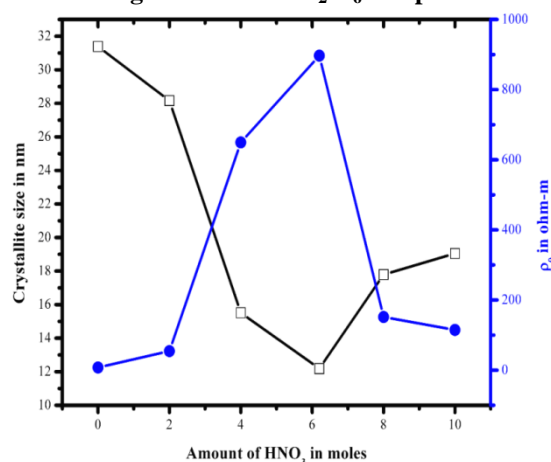
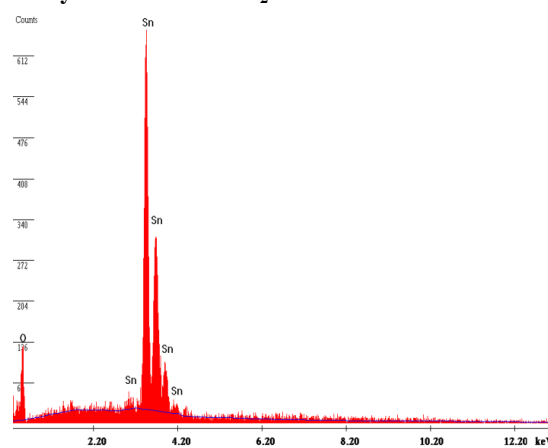
The effect of fuel to oxidizer molar ratio in the control of grain size was investigated by calculating the average crystallite size of SnO₂ powder. If the amount of HNO₃ is more than 6.2 moles, the atmosphere of reaction may change to an oxidizing one. In contrast, if the amount of HNO₃ is less than 6.2 moles, the atmosphere of reaction may change to a reducing one. In other words, both reactions mentioned above were serving as incomplete combustion reactions. Consequently, when the amount of HNO₃ is 6.2 moles, the reaction atmosphere may be neither oxidizing nor reducing, that is, it seems to serve as a complete combustion reaction condition.

This combustion reaction is as follows,

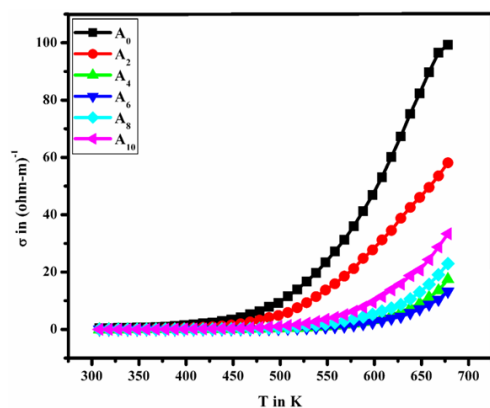
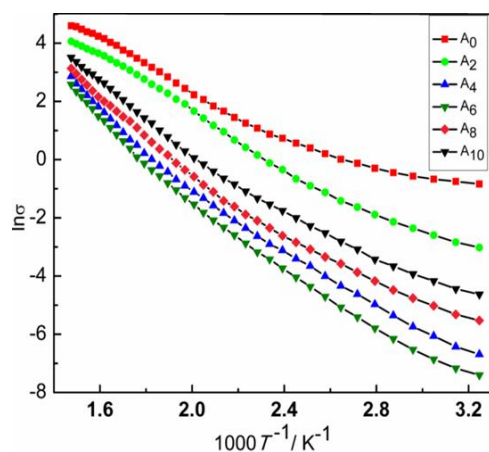
$$\text{SnCl}_2 + 1.5\text{C}_6\text{H}_8\text{O}_7 + 6.2\text{HNO}_3 \rightarrow \text{SnO}_2 + \text{Cl}_2 + 3.1\text{N}_2 + 9.1\text{H}_2\text{O} + 9\text{CO}_2$$

According to the above reaction, when the amount of HNO₃ is around 6.2 moles, the stoichiometric combustion reaction can occur. At the same time, it is very likely that this stoichiometric combustion reaction condition gave rise to an optimized combustion reaction which included a very high reaction temperature and rapid release of gaseous by-products to produce well crystallized fine powders so that crystallites size is minimum for the sample which was prepared by using 6.2 moles of HNO₃.

Fig. 3 shows the SEM images of nano SnO₂ powdered samples calcinated at 800°C. From the SEM analysis, it was found that the particles of powdered sample are spherical in shape with agglomerated status and porosity of the sample is high. As compared to other samples A₆ (Fig. 3d) has high porosity due to the rapid release of large volume of gaseous by-products during the combustion reaction. Fig. 4 shows the EDAX spectra, collected from the average scanned area of pure SnO₂. It was clear from the spectra that Sn and O are only the main elemental species in pure SnO₂ sample. Thus it advices, the gel combustion synthesis of nano tin oxide using above mentioned precursors yields a product with high purity.

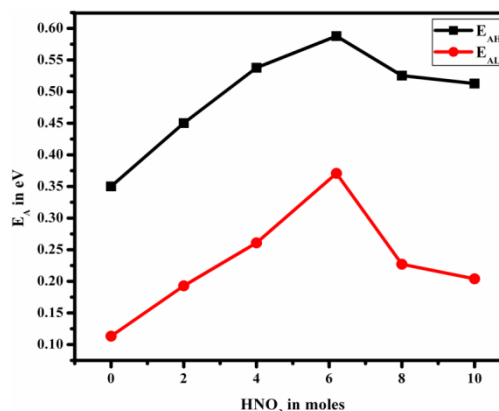
Fig. 4: EDAX SnO₂ A₆ sample.**Fig. 5: Variation of room temperature resistivity ρ_0 and the crystallite size of SnO₂ nanomaterials with oxidizer.****Table 1: Average particle size, ρ_0 , activation energy of SnO₂ samples.**

Sample	HNO ₃ in moles	Particle size in nm	Activation energy in eV	
			E _{AH}	E _{AL}
A ₀	0	31	0.35	0.11
A ₂	2	26	0.45	0.19
A ₄	4	15	0.53	0.26
A ₆	6.2	12	0.58	0.37
A ₈	8	17	0.52	0.22
A ₁₀	10	18	0.51	0.20

Fig. 6: Variation of electrical conductivity of SnO₂ samples with temperature.**Fig. 7: lnσ versus 1000/T.**

The resistivity of the thick films was measured for all the prepared samples of SnO₂. As shown in Fig. 5, the resistivity of A₆ sample is high as compared to the other samples due to its small grain size which is in the order of 896.8Ωm at room temperature. In polycrystalline SnO₂, the electrical conduction mechanism is related to the grain boundaries. It is known that the electrical conductivity increases with the increase in the crystallite sizes of the polycrystalline because of the decrease of the grain boundaries number (the decrease of the carriers scattering on these grain boundaries) [24, 25]. Fig. 6 depicts the temperature dependence of electrical conductivity of tin oxide thick films deposited at room temperature. From figure it was observed that the electrical conductivity of the samples increases with temperature in region 300-673K which indicates the semiconducting behavior [26] [27]. The electrical conductivity is also depends on fuel to oxidizer molar ratio due to the variation of grain size with fuel to oxidizer molar ratio [28, 29]. A plot logσ versus 1000/T (Fig.7) exhibits straight line with a slope E_A/k indicating activation energy of E_A. The activation energy is sensitive to the temperature so that E_a is higher in high temperature regime as compared lower regime as shown in Fig.8. The A₆ sample exhibits higher value of activation energy about E_A=0.58eV [JASR|VOL 01|ISSUE 10|2015

and 0.37eV at higher and lower temperature regime respectively while all other samples exhibit lesser values due to their higher grain size [30][31]and are comparable to the values reported[32].

Fig. 8: Variation of activation energies (E_A) of SnO₂ nanomaterials.

4. Conclusion

Tin oxide nanoparticles have been prepared successfully using gel combustion method by varying oxidizer molar ratio. From the XRD and SEM studies it was found that oxidizer places a very important role in the control of grain size and the porosity of samples. From the study of electrical conductivity of prepared sample it was found that the DC electrical conductivity of samples increases with the temperature from 300 to 673K which indicates the semiconducting behavior of prepared samples. Importantly from the study it was also found the dependency of electrical conductivity of samples on fuel to oxidizer molar ratio due to the variation of grain size with fuel to oxidizer molar ratio. Thus we can control the DC electrical conductivity of the Tin oxide nanomaterial simply by varying the fuel to oxidizer molar ratio during synthesis. According to the electrical data all samples exhibit n-intrinsic conductivity whose activation energy ranges within 0.35-0.58eV at high temperature regime and 0.12 - 0.47eV at low temperature regime.

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