

Synthesis of nano-crystalline tin oxide powder through fine crystallization in liquid phase

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The simple and inexpensive technique to synthesis nano crystalline tin oxide powder has been reported in this work. The nano crystalline tin oxide powder has been derived from stannic chloride, prepared through fine crystallization in liquid phase. Tin oxide powder has been characterized using SEM, TEM & XRD techniques which revealed crystal size around 13 nm. The slurry blobs deposited on alumina substrate of the powder thus prepared have been studied for sensing response of ethanol at various temperatures. The observations revealed that the material prepared is self-binding whereas commercial tin oxide powder required binders for sensor applications. Sensing response of nano particles of tin oxide deposited on alumina substrate has been investigated it was found very significant even without catalyst. These properties may have been attained by the prepared material due to the shift in the nano-scale range.

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1. Introduction

Nanomaterials (nano crystalline materials) are materials possessing grain sizes on the order of a billionth of a meter. They manifest extremely fascinating and useful properties, which can be exploited for a variety of structural and non-structural applications. All materials are composed of grains, which in turn comprise of many atoms and are usually invisible to the naked eye. Conventional materials have grains varying in size anywhere from 100's of microns (μm) to millimeters (mm). A nano crystalline material has grains of the order of 1-100 nm. The average size of an atom is of the order of 1 to 2 angstroms (\AA) in radius. One nanometer comprises of 10 \AA , and hence in one nm, there might be 3-5 atoms, depending on the atomic radii. Nano crystalline materials are exceptionally strong, hard, ductile (at high temperatures), wear-resistant, erosion-resistant, and corrosion-resistant. Further the nano crystalline materials or nano materials may be easily synthesized in laboratory. To prepare desired nano crystalline structures, several chemical techniques have been developed and reported in the literature, namely co-precipitation, sol-gel, spray pyrolysis, hydrothermal routes and freeze drying etc [2, 8, 9]. Tin Oxide is an n-type semiconductor crystallizing in tetragonal rutile structure. Tin (IV) oxide has been extensively studied as a potential candidate for gas sensing applications because of its relatively low operating temperature ($\sim 200\text{ }^\circ\text{C}$) and ability to detect gases at ppm levels [7, 2]. A Sensor is a device, which can selectively respond to certain properties of the environment and transfer this response into an electrical/ optical signal [1]. The mechanism of gas sensing is generally explained in terms of modulation of conductance due to interaction of test gas with sensor surface. [3, 4, 5, 6]. In recent times nano-sized materials have gained much interest for

fabricating new gas sensors due to their enhanced surface activity [8]. In this paper we are reporting a detailed description of technique for preparation of nano crystalline tin oxide powder through fine crystallization in liquid phase [2, 10, 5] and its deposition in the form of thick film [11, 12] for sensor fabrication. Using a simple technique we were able to synthesis tin oxide particles of size around 13 nm. The powder thus prepared was deposited on alumina substrate without any binding material. The sensitivity and response time of the sensor for ethanol vapors at different temperatures will be discussed as well. The emphasis in present study is laid upon the advent of simple and inexpensive technique for the preparation of nano crystalline tin oxide powder, which interestingly is self-binding and very sensitive to ethanol vapors.

2. Experimental details

2.1 Preparation of nanocrystalline SnO_2 powder and gas sensor

Tin oxide powder was prepared through fine crystallization in liquid phase. Following the technique, molar solution of tin chloride $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was prepared in distilled water and ammonium hydroxide was added drop wise with continuous stirring to yield precipitates of tin hydroxide. Precipitates formed were allowed to sediment for four hours, which followed decantation. The resulting gel was then dried into powder at about $120\text{ }^\circ\text{C}$.

The powder thus obtained was crushed and sintered in air at $500\text{ }^\circ\text{C}$ for three hours. To obtain a certain degree of homogeneity in grain size, powder was further grounded. To study the crystalline structure, size, and surface property of the fine tin oxide powder, various techniques such as XRD^a, SEM^a and TEM^b were employed.

Water based homogenous slurry of tin oxide powder in the form of slurry blob was deposited on alumina substrate having pre-deposited gold contacts. Hence, the fabricated SnO_2 chip was re-sintered at about 300°C for 30 minutes. Due to small particle size, tin oxide powder required no inorganic/ organic binder.

2.2 Sensor testing techniques

The measurements of sensing response of the gas sensor were made with the use of simple potentiometric arrangement, where potential drop across the resistor connected in series with sample was observed. With the injection of testing gas through an injector and circulator arrangement, we observed significant voltage variation across the resistor in real time. The sensor response was investigated at various temperatures ranging from 200°C to 450°C .

3. Results and discussion

3.1 Material characterization

The fine powder obtained by above-mentioned method was then subjected to various characterization investigations.

Fig-1 is the X-ray diffraction graph which clearly depicts the crystalline structure of tin oxide powder. The observed d-lines values match with the reported values of rutile phase of SnO_2 . The crystallite size measurements were also carried out using Scherrer equation $D = k \lambda / \beta \cos \theta$.

Where, D is the crystallite size, k is a factor of crystal figure, λ is the wavelength of X-Ray (0.1541 nm), β is the line width (after correction for instrumental broadening) and θ is the angle of diffraction. The average particle size calculated was about 14nm.

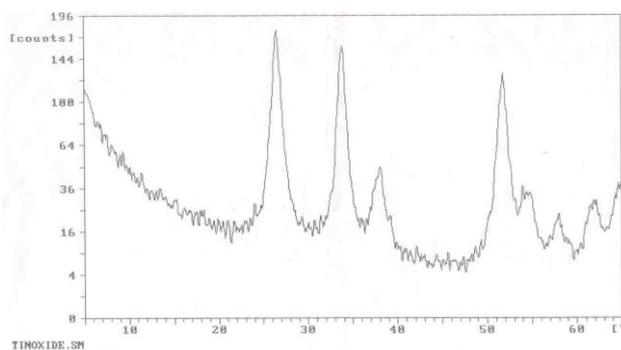


Fig. 1. XRD of SnO_2 powdered sample prepared.

Fig. 2 represents the scanning electron microscope image of calcined SnO_2 . The image revealed general surface morphology, which clearly indicates agglomeration due to clamping.

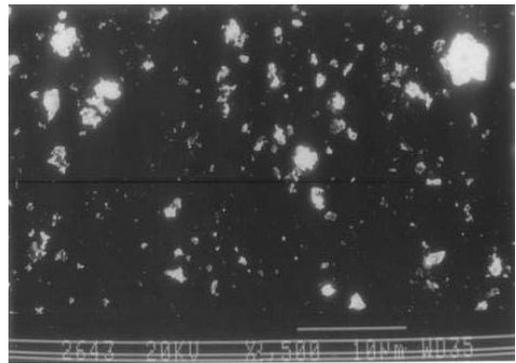


Fig. 2. SEM of SnO_2 powder.

Fig. 3 represents TEM micrograph of tin oxide powder, which confirms agglomeration of particles and average particle size comes out 13nm. This is almost similar to the value calculated using Scherrer's equation from X-Ray diffraction.

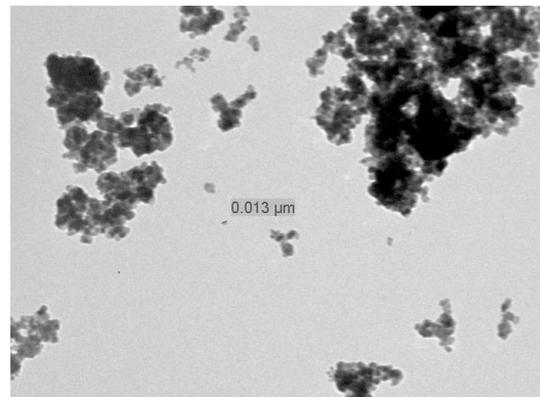


Fig. 3. TEM micrograph of prepared Tin oxide, clearly revealing average size of 13 nm.

Thus SEM, XRD and TEM studies confirmed that powder thus prepared was polycrystalline SnO_2 having particle size of 13nm. Due to small size, it is having enhanced surface activity that induces self binding characteristic in the powder.

3.2 Sensor testing results

The sensor chip fabricated out of polycrystalline nano-sized tin oxide powder was subjected to fixed volume of ethanol gas through the injector and circulator arrangement, at different temperatures in a closed chamber. The voltage variation across the resistor connected to the sensor in series was found to correspond to the sensing characteristic of the sample chip. The sensing characteristics of sensor for 120ppm ethanol at various temperatures (200°C - 450°C) were recorded by home-made data acquisition system. The sensitivity was found to be optimum around 250°C and is shown in Fig-4. It is evident that at optimum temperature, the conductance

change of sensor is sufficiently large for 120 ppm ethanol and response is quite fast as it is below one minute.

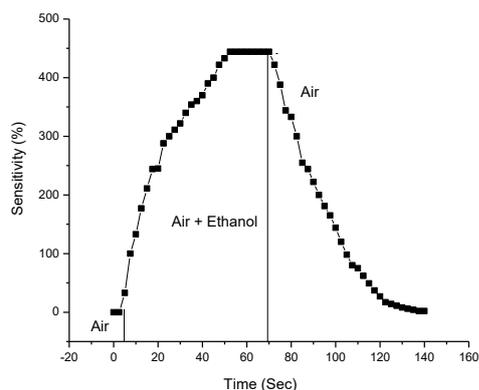


Fig. 4 Sensitivity $[(G-G_0)/G_0]$ versus Time at 250 °C. G_0 is the conductance in the absence of ethanol & G is conductance in air ethanol mixture.

4. Conclusion

In this work we have been able to synthesis polycrystalline tin oxide powder with particle size of 13nm, due to small particle size material exhibits enhanced binding property. The material under study was very sensitive to ethanol vapors without any catalyst and optimum operable temperature is around 250 °C.

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a) XRD, SEM studies were carried out at CIL, Panjab University, Chandigarh.

b) TEM study was carried out at SAIF, All India Institute of Medical Sciences, New Delhi.

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