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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATIONS OF NANO STRUCTURED SnO_2 THICK FILMS AND THEIR MICRO STRUCTURAL ANALYSIS

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ABSTRACT

This paper presents synthesis, thick film fabrication and characterizations of the nanostructured SnO_2 powder by disc type ultrasonicated microwave assisted centrifuge technique. The selected material is low cost and readily available. Synthesis procedure is quite simple. The obtained SnO_2 particles are in nanometer scale and dispersed with very large surface areas. Nano-scaled grains exhibit high surface to volume ratio. Thick films of as synthesized powder were fabricated by simple screen printing technique followed by the calcinations at 500°C for 1 hr. Optimizing the particular conditions, the thick films can be used for gas sensing applications. The film samples were characterized by X-ray diffraction (XRD), energy dispersive analysis by X rays (EDAX), field emission scanning electron microscopy (FE-SEM), etc.

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INTRODUCTION

Tin is principally found in the ore cassiterite (tin oxide). Tin(IV) oxide crystallizes with the rutile structure. As such the tin atoms are six coordinate and the oxygen atoms are three coordinate (Greenwood *et al.,* 1984). It has tetragonal symmetry. Each tin atom is surrounded by distorted octahedron of six oxygen atoms and each oxygen atom has three tin nearest neighbors at the corners of an almost equilateral triangle. SnO_2 is usually regarded as an oxygen-deficient n-type semiconductor (Lesley Smart *et al.,* 2005). Hydrous forms of SnO_2 have been described as stannic acid. Such materials appear to be hydrated particles of SnO_2 where the composition reflects the particle size (Holleman *et al.,* 2001). It is obtained commercially by reducing the ore with coal in a furnace. SnO_2 is a wide band gap semiconducting oxide having energy gap of 3.59 eV (Reimann and M. Steube, 1988; Frohlich *et al.,* 1978). Tin(IV) oxide has been used as an opacifier and as a white colorant in ceramic glazes (Searle, 1935). The use of tin(IV) oxide has been particularly common in glazes for earthenware, sanitary ware and wall tiles (Bourry, 1926). Tin oxide increases the opacity of the glazes (Parmelee and Harman, 1973). SnO_2 is used in sensors of inflammable and toxic gases, viz. CO, H_2, H_2S, LPG, NH_3, C_2H_5OH, Cl_2, etc. (Joseph Watson). In these, the sensor area is heated to a constant temperature (few hundreds of degrees Celsius) and in the presence of a combustible gas the electrical resistivity drops.

EXPERIMENTAL

Synthesis of Nanostructured SnO_2 Powder: Microwave treatment followed centrifuge technique Tin dioxide powders have been synthesized by various synthesis methods such as sol-gel, spray pyrolysis, gel combustion technique, hydrothermal synthesis, etc. Among these methods, conventionally accepted method is the synthesis of tin dioxide particles from precursor hydroxides precipitated by the direct addition of aqueous alcohol solution to tin chloride aqueous solutions. In the present study, the pure nanostructured SnO_2 powder has been synthesized by disc type ultrasonicated microwave treatment followed by centrifuge technique (Jun Zhang *et al.,* 2009; Kapse *et al.,* 2012; Khamkar *et al.,* 2012; Patil *et al.,* 2006 & 2007; Gawas *et al.,* 2011). Fig. 1 (a) shows disc type ultra-sonicator and Fig. 1 (b) shows microwave treatment followed centrifuge technique. Distilled water and propylene glycol is taken in the ratio of 1:1, and an initial aqueous alcohol solution was prepared. This solution was then mixed with aqueous solution of tin chloride with the alcohol to water ratio as 1:1. The special arrangement was made to add drop wise aqueous ammonia (0.1ml / min.) with constant stirring until the optimal pH of solution becomes 8.3. After complete precipitation and centrifugation, the hydroxide was washed with distilled water until chloride ions were not detected by $AgNO_3$ solution. Then the precipitate was allowed for ultrasonication and then placed in a microwave oven for 10

minutes with on-off cycles, periodically. The dried precipitate was ground by agate pestle-mortar and annealed in a muffle furnace at 450°C for 3 hours, to eliminate the organic impurities, if present. Thus, the dried powder of SnO_2 is now ready to fabricate thick films. Fig. 2 depicts the synthesis route for nanostructured SnO_2 material.

Fig. 1 (a): Disc type ultrasonicator Fig. 1 (b): Microwave treatment followed centrifuge technique

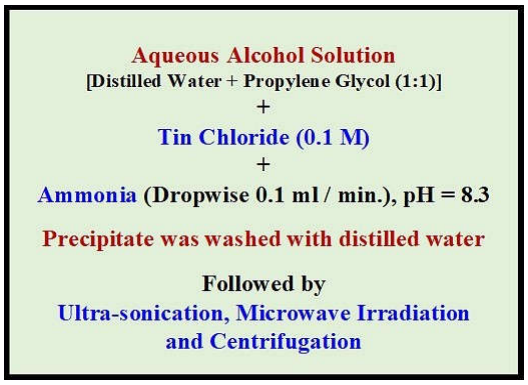

Fig. 2. Synthesis route for Nano structured SnO_2

Thick Film Fabrication

Fig. 3. Thick film fabrication route

The uses of thick film technology in the production of chemical sensors have opened up the possibility of manufacturing sensors in a cost effective manner. Such properties of a thick film sensor are highly desirable for chemical applications. Thick film technology based on glass, and ceramic compositions is very stable in severe conditions such as high temperature or corrosive environments. Deposition of the layers is most commonly carried out by using screen printing for high volume, and low cost production. Each layer is printed with a paste comprising a functional material and a temporary organic vehicle. After deposition, solvent was removed by drying followed by firing, to eliminate the organic binder and sinter the materials. Glass frits are commonly used alone for over glazes and as a permanent binder in thick film technology (Greenwood *et al.,* 1984; Turekian *et al.,* 1961; Kihlborg, 1963; David Scanlon *et al.,* 2010; Ivanova *et al.,* 2001; Tomas *et al.,* 2009). Commonly ceramic substrates made of mostly alumina (Al_2O_3), silicon, glass-ceramic and sapphire with appropriate surface finish is used. The change in resistance for thicker films is large as compared to thinner ones (Jacq *et al.,* 2009). Thick film technology involves screen printing methodology and thick film fabrication. The main aim of the present work is to study the microstructural analysis of SnO_2, that can be used for gas sensing application by employing thick film technology which gives response to different toxic, and hazardous gases (Ansari *et al.,* 1996; Wagh *et al.,* 2007; Patil *et al.,* 2006; Kamalpreet Khun Khun *et al.,* 2009; Srivastava *et al.,* 2014; Pandav *et al.,* 2015), which contribute substantially in the detection of global environmental pollution explosion. The thick film technique is the process of screen printing followed by firing. This offers a good control over the thickness and micro structure. The lifetime of thick films is expected to be larger. The synthesized ultrafine powder of pure SnO_2 was calcined at 500°C for 3 hrs. it was further grounded to ensure a fine particle size. By mixing the synthesized nanostructured powder of pure SnO_2 with a solution of ethyl cellulose in a mixture of organic solvents, viz. butyl cellulose, butyl carbitol acetate and turpineol (Fig. 3), the thixotropic paste (Ansari *et al.,* 1996; Wagh *et al.,* 2007; Patil *et al.,* 2006; Kamalpreet Khun Khun *et al.,* 2009; Srivastava *et al.,* 2014; Pandav *et al.,* 2015; Patil Snehal *et al.,* 2015) was prepared. While in formulating the paste, the ratio of inorganic to organic part was kept as 80:20. The thixotropic paste was screen printed on the glass substrates in desired patterns. Films prepared were dried at 80°C under an IR lamp, followed by firing at 500°C for 30 min. in ambient air. Silver contacts were made by vacuum evaporation for electrical measurements and monitoring the gas sensing performance of thick films.

MATERIAL'S CHARACTERIZATIONS

Structural Properties: X- Ray Diffraction

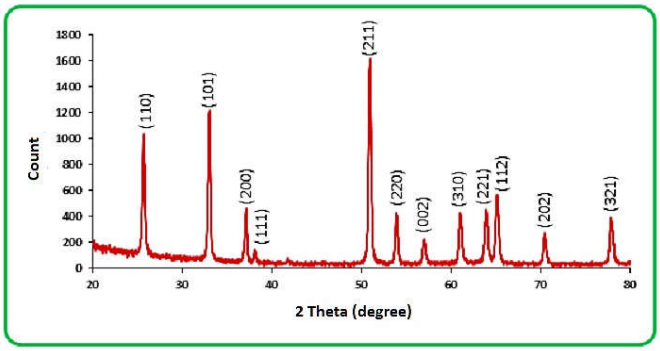

Fig. 4. XRD of pure SnO_2 powder

X-ray diffraction study of SnO_2 powder (Fig. 4) was carried out using BRUKER AXSD 8 (Germany) advance model. X-ray diffraction with $CuK\alpha_1$ (λ = 1.54060 Å) radiation is in 2θ range of 20° to 80°. The 2θ peaks observed at 26.61, 33.89, 37.95, 38.97, 51.78, 54.76, 57.82, 61.87, 62.59, 64.72,71.28 and 78.71 are correspond to the (110), (101), (200), (111), (211), (220), (002), (310), (221), (112), (202) and (321) planes of reflections. The XRD spectrum reveals that, the sharp peaks of the XRD pattern correspond to SnO_2 material and are

observed as polycrystalline in nature and tetragonal in structure. It was found that, the peaks observed, are matching well with the JCPDS reported data. The crystals show anisotropy due to different directions within the repeating pattern with incident radiations. The material was observed as nanocrystalline in nature. Lattice parameters were found as a = 4.73820 and c = 3.18710. A unit cell volume of the cubic system is, $V= a^2 c$ and it was evaluated as, 71.55 (JCPDS card no. 00-041-1445). The average crystallite size was determined from Scherer's formula,

$$d = \frac{0.94\,\lambda}{\beta cos\theta}$$

Where, λ is the wavelength of X-rays, β is the full width at half maximum (FWHM) of a diffraction peak and θ is the diffraction angle. It was found that, the average crystallite size is in the range of 14 nm -43 nm. It was also observed from XRD analysis that, the synthesized pure SnO_2 powder has less amorphous nature (12.5%) and more crystalline nature (87.5%) (Table 1).

Table 1. Percentage crystallinity and amorphous nature of synthesized SnO_2 powder

Material	Crystallinity (%)	Amorphous (%)
Pure SnO_2	87.5	12.5

Elemental Analysis of SnO_2 : E-DAX

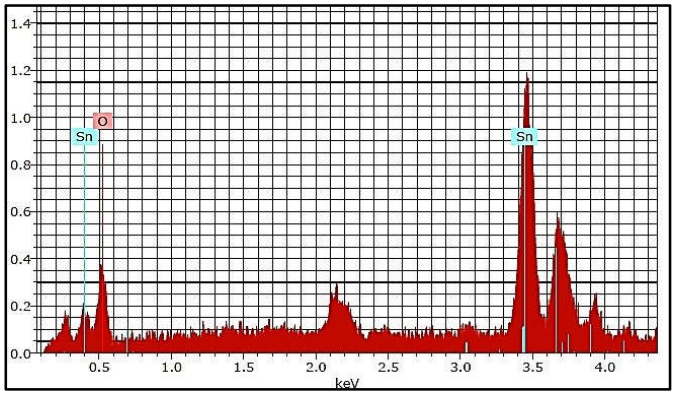

Fig. 5. Energy dispersive analysis by X- Rays (E-DAX)

Table 2. Elemental analysis of SnO_2 thick films

Mass %	Expected	Observed
Sn	78.77	80.82
O	21.23	19.18
SnO_2	100	100

The quantitative elemental compositions of the thick films of SnO_2 were analyzed using an energy dispersive spectrometer, and mass % of Sn, O and SnO_2 are represented in Table 2. Fig. 5 shows an E-DAX graph of synthesized SnO_2 material. The E-DAX analysis exhibited clear peaks of only Sn and O from the desired detected site. Pure stoichiometric SnO_2 is expected to be insulating. Stoichiometrically expected mass % of Sn and O (in SnO_2) are 78.77 and 21.23 respectively. However, the observed mass % of the respective elements are 80.82 and 19.18. Thus, the synthesized powder of SnO_2 is not exactly stoichiometric and hence is semiconducting in nature. The prepared powder of pure SnO_2 is deficient in oxygen, which increases its n-typeness characteristic. This leads to n- type semiconducting nature of SnO_2.

Micro structural Analysis of SnO_2 : SEM

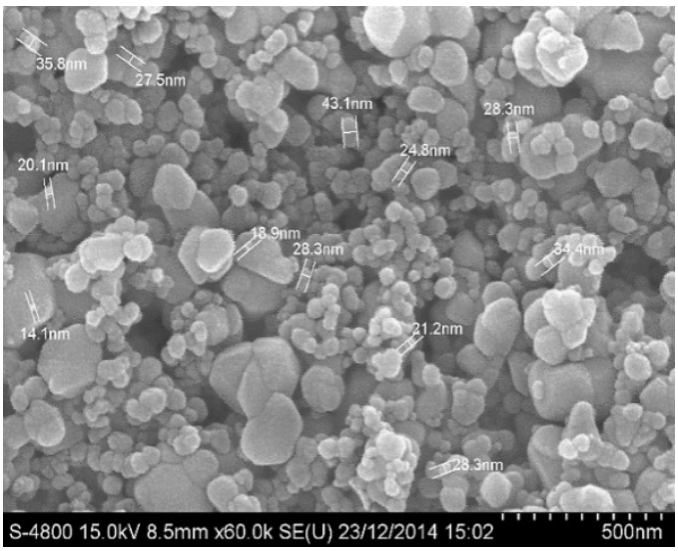

Fig. 6. SEM image of SnO_2 thick film

Fig. 6 depicts the SEM image of SnO_2 thick film fired at 500°C for 30 min. The SnO_2 thick film consists of voids, and a wide range of randomly distributed grains with sizes ranging from 14 nm to 43 nm distributed as smaller grains associated with agglomerated grains with porous nature. The Nanoscale grains exhibit high surface to volume ratio.

Conclusion

1. SnO_2 nanocrystalline powder was synthesized via disc type ultrasonicated microwave treatment followed by centrifuge technique.
2. Thick film fabrication technique is the most suitable, simple and economical method for the fabrication of samples.
3. The average crystallite size calculated by using the Scherer's formula was found in the range of 14 nm - 43 nm.
4. It was observed from XRD analysis that, the synthesized SnO_2 powder has less amorphous nature (12.5%) and more crystalline nature (87.5%). The formation of the SnO2 nano-grained powder with rutile tetragonal structure is also observed.
5. From the E-DAX analysis, it is clear that, the synthesized powder of SnO_2 is not exactly stoichiometric and hence is semiconducting in nature.
6. The prepared powder of SnO_2 is deficient in oxygen, this lead to n- type semiconducting nature of SnO_2.
7. From the SEM micrograph, it was found that, the Nanoscale grains exhibit high surface to volume ratio. This feature is very much useful for the detection of hazardous and inflammable gases (ppm / ppb level) present in the environment. Hence, the reported material can be used in the gas sensing applications.

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