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Preparation, Characterization and Humidity Sensing Properties of nanocrystalline SnO_2 thin films prepared by Spray Pyrolysis technique

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ABSTRACT

This paper presents preparation, characterization and humidity sensing properties of SnO_2 thin films. In the present investigations, the nanocrystalline SnO_2 thin films were prepared by spray pyrolysis technique. These films were characterized by X-ray diffraction (XRD) measurements, and scanning electron microscopy (SEM).The humidity sensing properties of prepared SnO_2 thin films were investigated in lab-built sensing unit. The prepared SnO_2 thin films show excellent response to humidity changes with fast response and recovery time.

Introduction

All Recent developments in automated systems have made ever-increasing demands for various kinds of physical and chemical sensors. As humidity is a very common parameter in our environment, measurements and /or control of humidity are important not only for human comfort but also for a broad spectrum of industries and technologies. So for many methods of sensing humidity and moisture have been introduced, and almost all of them are still in use. Sensors of great variety of application have been developed, numerous materials have been utilized for humidity sensing of which the metal oxides that are physically and chemically stable, have been extensively used at both room and elevated temperature [1-3]. The sensing materials are roughly classified in to three groups, i.e. electrolytes, organic polymers and porous ceramics. In spite of the differences in materials, most sensors utilize a common phenomenon, that is physical or chemical adsorption (or absorption) of water molecules [4].

Among the different types of humidity sensors, those based on electrical properties such as resistance and capacitance is best suited to modern automatic control systems. Various sensors for humidity have been introduced [4, 5], some recent ones [4] of which are of miniature solid state type. Different materials are used for these solid state sensors [4-10]. The semiconductor humidity sensors are characterized by their conductance change due to chemical absorption of water molecules, thus resulting in electron conductivity. These types of humidity sensors are now under development by several researchers [4, 8, 10-13, 20-21]. Stannic Oxide (SnO_2) is an n-type wide band gap semiconductor of which electrons are majority carrier, and electron concentration of conduction band affected by gas.

A variety of techniques have been used to prepare tin oxide (SnO2) thin films. It includes spray pyrolysis [12], ultrasonic spray pyrolysis [13], chemical vapour deposition [14], activated reactive evaporation [15], ion-beam assisted deposition [16], sputtering [17] and sol–gel [18] methods. Among these techniques, spray pyrolysis has proved to be a simple, reproducible and inexpensive, as well as suitable for large area applications. Besides the simple experimental arrangement, high growth rate and mass production capability for large area coatings make them useful for industrial as well as solar cell applications. In addition, spray pyrolysis opens up the possibility to control the film morphology and particle size in the nanometer range. As demonstrated [19] spray pyrolysis is a versatile technique for deposition of metal oxides.

In the present investigations, nanocrystalline SnO_2 thin films were prepared by spray pyrolysis technique. Structural properties and grain size were studied using X-ray diffraction. Microstructure was studied using FESEM. The prepared SnO_2 thin films were tested for humidity sensing.

Experimental Methods

A. Preparation of nanostructured SnO_2 thin film by spray pyrolysis method

Fig.1 shows spray pyrolysis technique for preparation of nanostructured SnO_2 thin films. The set-up of spray pyrolysis system consists of spraying chamber, spray nozzle (gun), compressor for carrier gas, heating system, and temperature indicator.

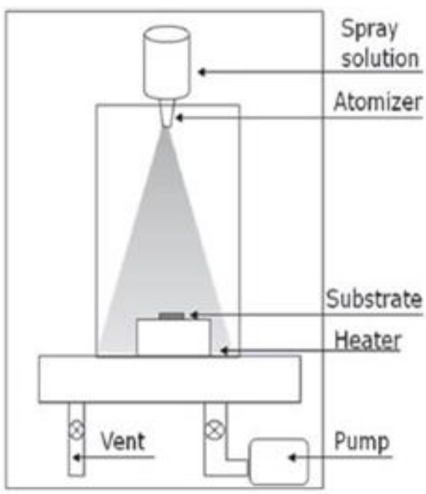

Fig.1: Schematic diagram of spray pyrolysis system for the preparation of nanostructured

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Nanostructured SnO_2 thin films were prepared from aqueous solution of Tin (II) chloride dehydrate ($SnCl_2.5H_2O$), Purified Merck) dissolved in (20%) deionized water and (80%) methanol to a concentration of 0.2 M for the preparation of thin films. The spray produced by nozzle (diameter 0.4 mm) was sprayed onto the ultrasonically cleaned glass substrates heated at 350 ± 5°C.Various parameters such as nozzle-to-substrate distance, deposition time and flow rate of solution, deposition temperature and concentration were optimized to get good quality films. The films were prepared by spraying the prepared solution (20ml) at the rate of 5ml/min.

B. Characterization

In the present study nanostructured SnO_2 thin film were characterized by X-ray diffraction ((Miniflex Model, Rigaku, Japan). The microstructure of the films was analyzed using a field emission scanning electron microscope (FE-SEM, JEOL. JED 6300). Humidity sensing properties were measured using a static humidity measurement system.

C. Humidity measurement system

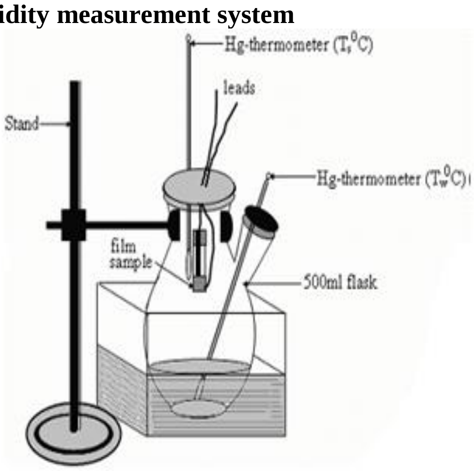

Fig 2. Humidity measurement system

Fig. 2. shows the schematic diagram of the closed humidity system used for measurement of relative humidity (RH). It consists of a closed flask (total volume 2000 ml) with two necks for inserting thermometers and the sprayed SnO_2 thin film sensor. The flask is partially filled with water and kept in a cooling container [3, 14-16].

The % *RH* of the air in the system is given by [14]

$$RH\% = \frac{E_W(T_W)}{E_W(T_S)} \times 100$$

where $E_w(T_w)$ is the saturated vapour pressure at the temperature of the water bath T(w) and $E_w(T_S)$ is the saturated vapour pressure at the temperature of the prepared SnO_2 thin film sensor element (T_S) (connected at a time). The RH is adjusted by changing the temperature of the humidity system. The thin film sensor is kept and stabilized inside the system for humidity sensing measurement. The D.C resistance of the thin films was measured by using directly by a sensitive digital multimeter.

D. Sensitivity

It is defined as the change in resistance due to a change in %RH with respect to the initial resistance Ra, i.e. % S= [(ΔR/Ra)] x100; It is measured by keeping the sample at different RH values at stabilized condition.

Results and discussions

Fig 3. Photograph of spray pyrolysis system used for deposition of SnO_2 thin film

Fig 4. Photograph of Lab-built Humidity sensing unit

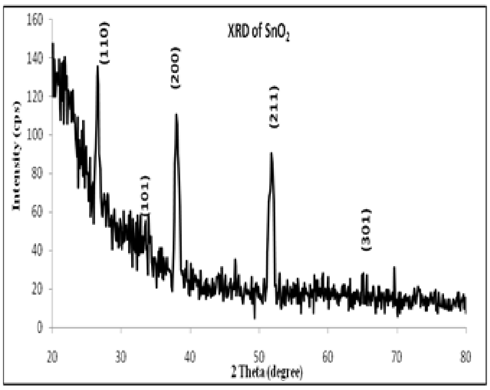

Fig 5. X-ray diffraction pattern of prepared SnO_2 thin film

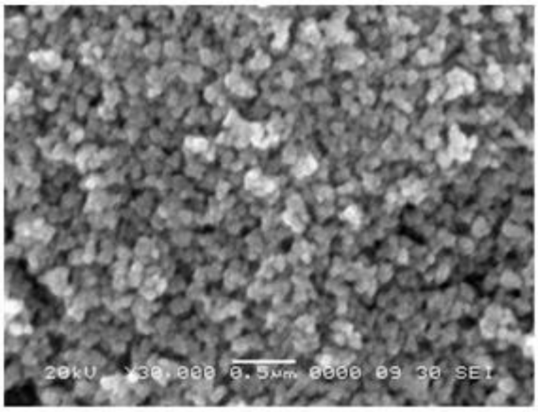

Fig 6. SEM photograph of prepared SnO_2 thin film

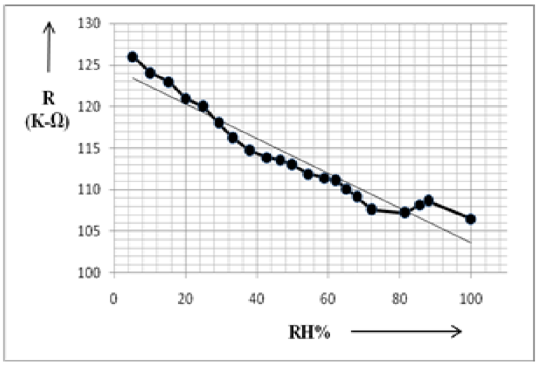

Fig 7. Change in resistance of SnO_2 thin film with respect to change in RH (%).

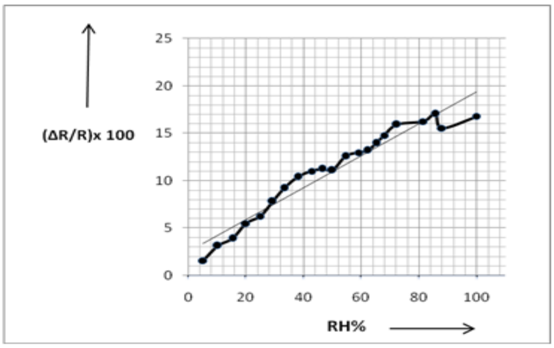

Fig 8. Sensitivity of SnO_2 thin film to change in RH (%)

The photo graph of Spray pyrolysis system used for the deposition of SnO_2 thin film is shown in fig 3. The photograph of humidity sensing system is shown in fig.4.

The XRD pattern of prepared SnO_2 thin film is shown in fig 5. It indicates the diffraction peaks at 2θ values of 26.6^o, 31.3^o, 38^o, 51.8^o and 66^o which reveal the formation of the SnO_2 film. The average grain size calculated by using D and S equation as follows-

$$d = 0.9 \lambda / \beta \cos \theta$$

where λ, β and θ are the X-ray wavelength (1.5405A °for Cu Ka), the full width at half-maximum of the diffraction peak (FWHM) and Bragg diffraction angle, respectively. The average particle size is found to be ~ 12 nm. It clearly indicates that prepared film is crystalline.

The thickness of the film is found to be ~ 169 nm.

The surface morphology of the screen printed SnO_2 thick film deposited on the glass substrate is as shown in Fig. 6. It clearly shows the surface of SnO_2 films is porous. Therefore, the spray prepared SnO_2 film can adsorb atmospheric oxygen very easily and its amount depends on the area of the exposed surface of the film.

Fig.7. shows change in resistance of the prepared SnO_2 thin film with respect to relativity humidity (RH %). The characteristics shows that the resistance of the prepared SnO_2 thin film almost changes linearly with respect to change in relativity humidity (RH %). The change in resistance is found to be almost linear from 5 to 100% RH value.

The decrease in resistance with increase in humidity is due to the dissociation of H_2O molecules [17], into proton (or another H_3O^+) and hydroxyl groups (OH^-). H_3O^+ is responsible for the reversible reaction. These hydroxyl groups combine with surface oxygen ions forming water and releases back an electron to the material. Thus the conductance of n-type semiconductor increases (resistance decreases) with increase in humidity [4,18-19]. The physi-absorbed water dissociates because of high electrostatic field in the chemisorbed layer. The possible reaction can be written as -

$$2H_2O \rightarrow H_3O^+ + OH^-$$

Fig. 8. shows sensitivity of prepared SnO_2 thin film with respect to change in relativity humidity (RH %). The characteristics shows that the prepared SnO_2 thin film almost shows linear sensitivity to change in relativity humidity (RH %). The change in (%) S per (RH %) is found to be almost linear from 5 to 100% RH value and its value is found to be ~ 0.25.

Conclusions

1. The SnO_2 thin films having thickness ~ 169 nm and having particle size ~ 12 nm can be prepared by spray pyrolysis system.
2. The prepared SnO_2 thin films can be characterized by X-ray diffractogram and by scanning electron microscopy.
3. The prepared SnO_2 thin film is found to be linearly sensitive for changes in relative humidity (RH%) within the range 5% to 100%.
4. The change in (%) S per (RH %) is found to be almost linear from 5 to 100% RH value and its value is found to be ~ 0.25.

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