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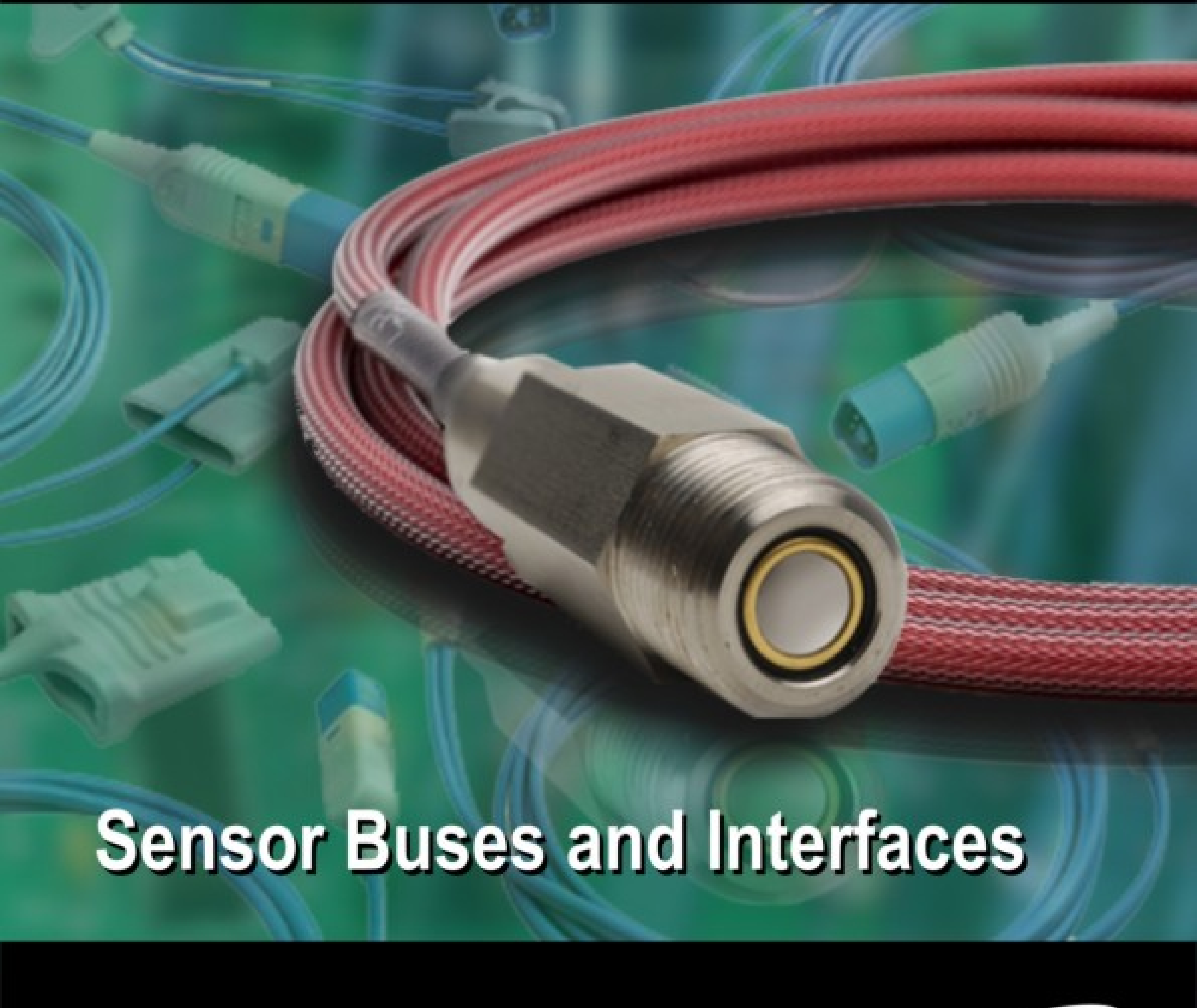

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Synthesis of Antimony Doped Tin Oxide and its Use as Electrical Humidity Sensor

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Abstract: In this paper we report the humidity sensitive electrical properties of antimony doped tin oxide. Antimony has been doped within SnO_2 in the ratio 1:1. The pellet has been made by hydraulic pressing machine at pressure 30 MPa and room temperature 24°C. This pellet, has been annealed at 200ºC, 300ºC, 400ºC, 500ºC and 600ºC successively for 3 hrs and after each step annealing, observations were taken. It has been observed, as Relative Humidity (%RH) increases, there is decrease in the resistivity of pellet for the entire range of RH i.e. from 10% to 95%. Linear decrease is observed for the range of RH from 10 % to 85 % for annealing temperature 200ºC and 300ºC, from 10 % to 60 % for annealing temperature 400ºC and from 10 % to 30 % for annealing temperature 500ºC and 600ºC respectively. Scanning electron micrographs show the surface morphology and X-ray diffraction reveals the nanostructure of sensing element. Results have been found reproducible with hysteresis of ± 2% after 3 months. *Copyright © 2008 IFSA.*

Keywords: Humidity sensors, nanostructure, morphology and resistivity.

1. Introduction

With in past decades, solid-state sensors based on tin oxide have been an important analytical device for air monitoring in domestic and industrial environment [1]. Most of the commercially available sensors are produced by ceramic fabrication technologies or by thick film technology with SnO_2 pastes as the starting material [2-4]. It is well known that the resistivity of metal oxide semiconductors can be affected by temperature. Since the interaction of these materials with humid medium depends on their structure and surface, impedance spectroscopy is a useful tool for its detail characterization [5]. Recently, the interest of the scientific community is devoted to the progress achieved in the synthesis, structural characterizations and physical property investigation of nanostructures. Due to their peculiar characteristics and size effects [6-7], these materials often show some novel physical properties that are different from these of the bulk and are of great interest both for fundamental studies and for potential nano-device applications [8-10].

It is known that properties of doped SnO_2 are mainly determined by chemical states of dopants and their distribution on the surface and in the bulk of SnO_2 grains [11-20]. Tin oxide is a wide band gap n-type semiconductor (~3.6eV). It shows outstanding electrical, optical and electrochemical properties [1-2] and it is the most used material due to its low cost, long life and good reproducibility. These are many factors affecting the sensing properties. Besides the intrinsic factors of materials some extrinsic factors, such as grain size and operating temperature are also very important. It is well known that the presence of noble metal elements (Pt, Pd, Sb etc) on the surface of the tin oxide can enhance the interaction of water vapor/ moisture with the adsorbed oxygen on the surface [14-15, 20]. This improvement involves on increase of the response and a decrease of the temperature needed to obtain it. The introduced metal must be dispersed on the surface of the SnO_2 grains forming small clusters in order to increase their effectiveness. Then, in the presence of oxygen some catalytic elements can turn up in some oxidizing states that can be easily reduced in the presence of OH^- [18]. Thus antimony has been added with tin oxide because it is known to exhibit high level of catalytic activity. It increases the rate of adsorption and desorption of water vapour with tin oxide pellet.

The present paper focuses on the investigation of humidity sensing properties of antimony doped tin oxide pellet synthesized by conventional precipitation route.

2. Experimental Procedure

The material Sb doped SnO_2 has been prepared by the conventional precipitation route. After drying the powder, pellet has been made by using hydraulic pressing machine (KBR Press, Germany) at pressure 30 MPa. Heat treatment of pellet has been done at temperatures 200°C, 300°C, 400°C, 500°C and 600°C successively in an electric furnace (Ambassador, India). This pellet has been inserted between the electrodes of a conductivity-measuring holder and then it is exposed to humidity in the controlled humidity chamber [21]. Variations in the resistivity have been noted by using sinometer (VC 9808). Relative humidity (% RH) is measured by using standard hygrometer along with a thermometer (Huger, Germany). Potassium sulphate has been used as humidifier and potassium hydroxide has been used as dehumidifier. Temperature variation of chamber throughout the experiment is 1°C. SEM Photographs have been taken by using Scanning Electron Microscope (LEO-0430, Cambridge) and XRD has been done using X-Pert, PROXRD System (Netherland).

3. Principle of Operation

Adsorption of water vapours is totally responsible for changes in conductivity of pellet. Adsorption is the process in which gas molecules or rarely liquid molecules accumulate on the surface. If sensing material is porous, it will provide more surfaces for adsorption, resulting enhanced sensitivity. Chemistry involved in adsorption of water on Sb-SnO_2 surface can be understood as follows. Surface associated with dry oxide is characterized by the presence of low coordinated metal ions. First step of water adsorption is the coordination of H_2O molecules with undersaturated metal (Fig. 1a), and next step is dissociative chemisorption, which results hydroxylated surface (Fig. 1b). Overall the conduction is due to protonation and deprotonation of surface hydrolysis.

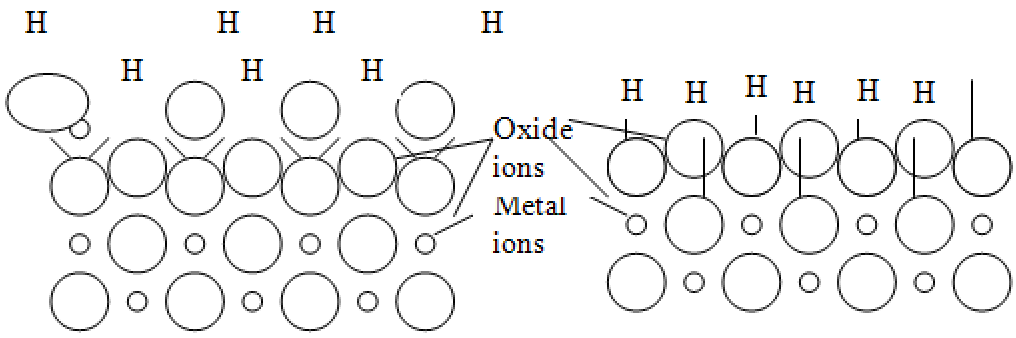

Fig. 1. (a) Coordination of surface metal ions with water molecules.

Fig. 1. (b) Dissociative chemisorptions produces hydroxylated surface.

The morphology of the sensing element influences water vapour adsorption and desorption process. These processes are the functions of ceramic pore size and its distribution.

Sensitivity of humidity sensor (S) has been defined as the change in resistivity ($\Delta\rho$) of sensing element per unit change in relative humidity (% RH).

4. Results and Discussion

4.1. Static Responses of SnO_2 Based Sensor

Variations in resistivity with % RH has been shown by curves 'a', 'b', 'c', 'd' and 'e' in Figs. 2 and 3 for the sensing elements annealed at 200°C, 300°C, 400°C, 500°C and 600°C respectively. Curves 'a' and 'b' of Fig. 2 show that as % RH increases, the resistivity decreases drastically up to 85 % and then decreases more slowly up to 95 %. Sensitivity of sensing element annealed at 300°C is found better than sensing element annealed at 200°C. Curves 'c' and 'd' of Fig. 3 for sensing element annealed at 400°C and 500°C are very close to each other and show that as relative humidity increases up to 30 %, resistivity of sensing element decreases linearly, resulting reliable sensitivity, then further on increase of % RH, resistivity decreases very sharply up to 95 %. Curve 'e' for sensing element annealed at 600°C shows better sensitivity. Resistivity decreases abruptly up to 60 % and then it becomes slowly. This curve shows approximate linear characteristics and useful for device fabrication.

4.2. Sensitivity Response with Temperature

Fig. 4 shows that as the annealing temperature of the sample increases the average sensitivity increases and it is found maximum (11.79) for sensing element annealed at 600°C.

4.3. Porosity with Temperature

It can be seen clearly in all the SEMs that material is porous and its porosity increases with the increasing annealing temperature. Variation of pore size with annealing temperature has been shown in Fig. 5.

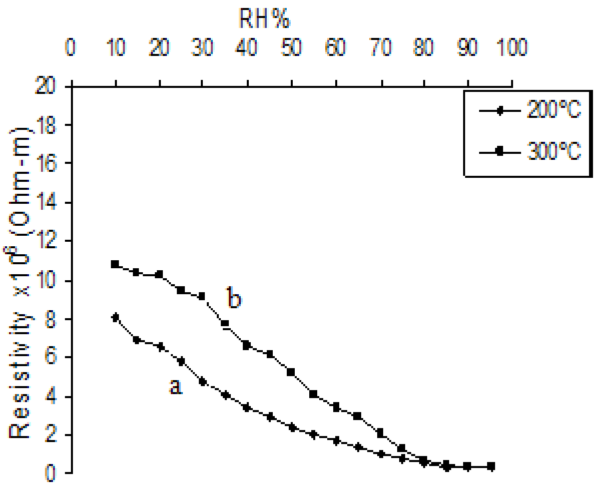

Fig. 2. Variations of resistivity against RH% for sensing element Sb: SnO_2 annealed at 200°C and 300°C respectively.

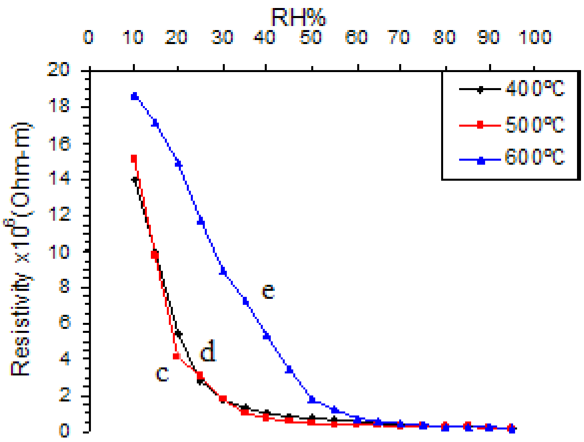

Fig. 3. Variations of resistivity against RH% for sensing element Sb: SnO_2 annealed at 400°C, 500°C and 600°C respectively.

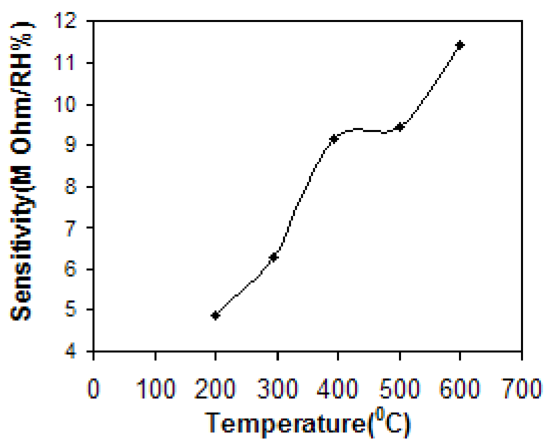

Fig. 4. Graph between annealing temperature and sensitivity.

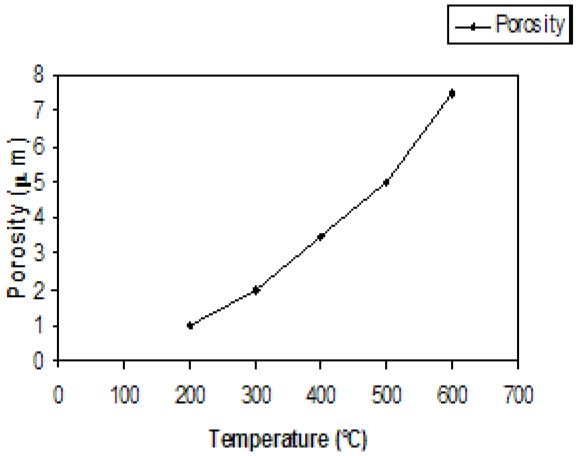

Fig. 5. Graph between annealing temperature and porosity.

4.4. SEMs & XRD Analysis

Micrographs show that the molecules of Sb doped SnO_2 are highly porous having porosity lying between 1 to 7 µm approximately. SEMs of the sample annealed at different temperatures are shown in Figs. 6-10.

X-ray diffraction pattern shown in Fig. 11, reveals that sensing material consists of tin oxide with antimony. Larger peaks are of SnO_2 and smaller peaks may be of antimony. Average particle size of tin oxide calculated by Scherer's formula is 18 nm approximately.

Antimony has been added with tin oxide because it is known to exhibit high level of catalytic activity. It increases the rate of adsorption and desorption of water vapor with tin oxide pellet. After three months results have been found to be reproducible with very small hysteresis ± 2 %. No aging effect was observed.

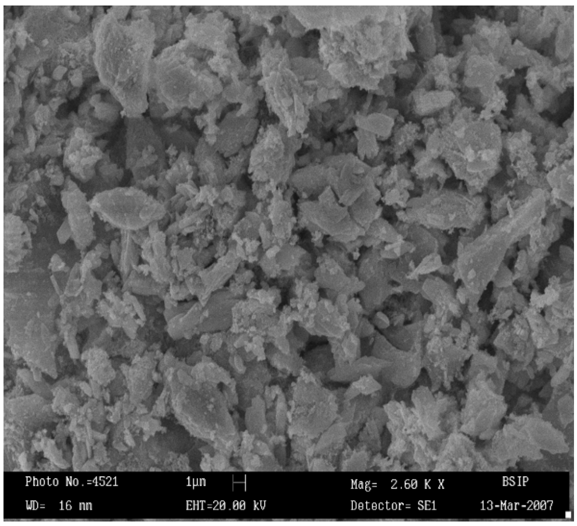

Fig. 6. SEM of sensing element annealed at 200°C.

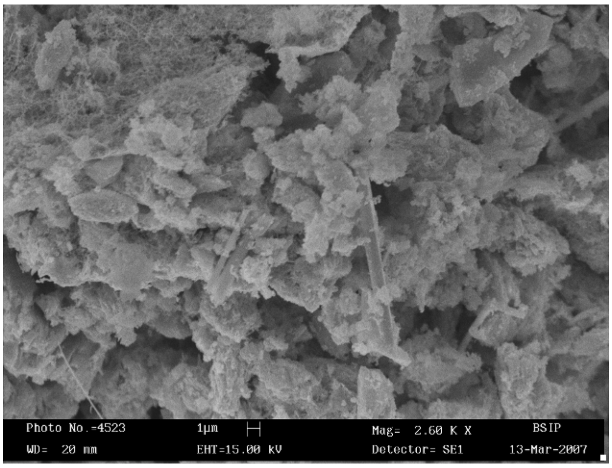

Fig. 7. SEM of sensing element annealed at 300°C.

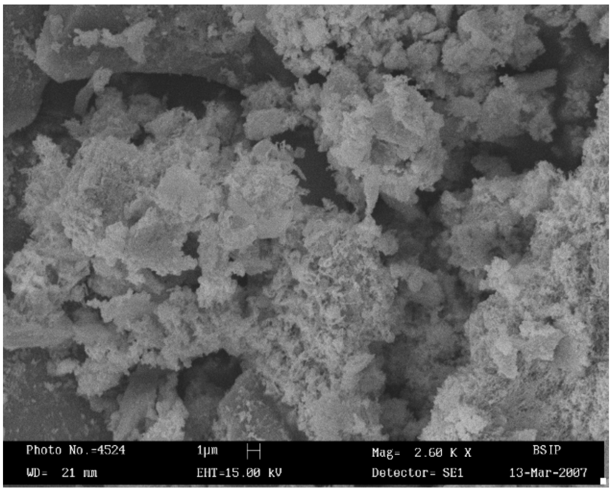

Fig. 8. SEM of sensing element annealed at 400°C.

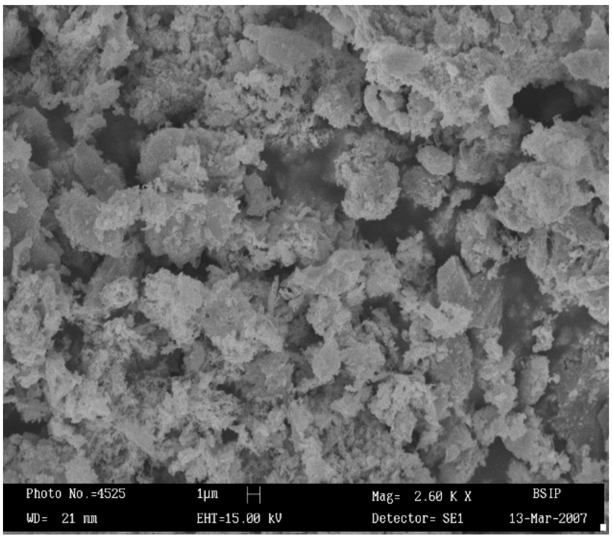

Fig. 9. SEM of sensing element annealed at 500°C.

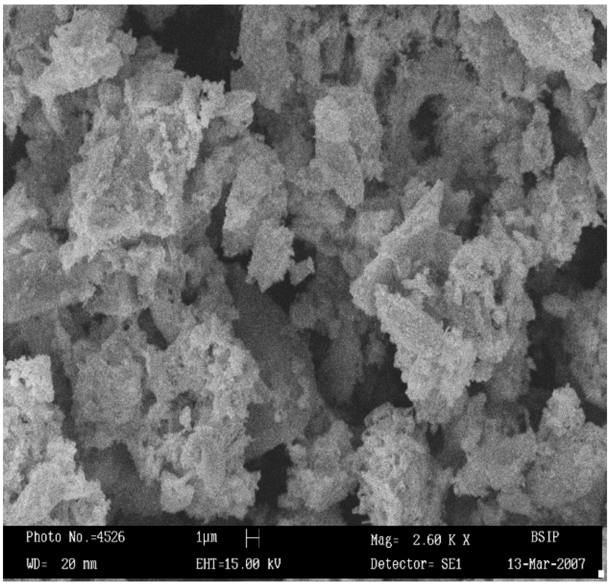

Fig. 10. SEM of sensing element annealed at 600°C.

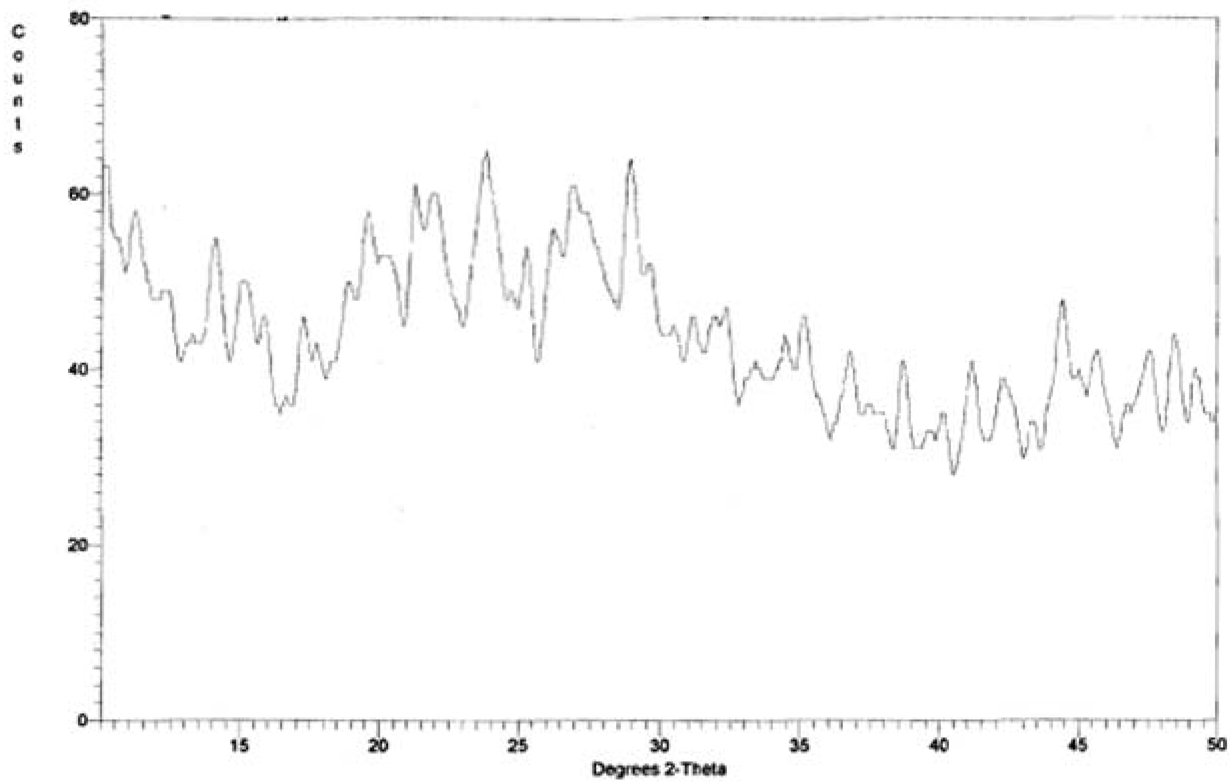

Fig. 11. XRD of sensing element annealed at 600°C.

5. Conclusion

Antimony doped tin oxide was investigated for its humidity sensing characteristics annealed at 200°C, 300°C, 400°C, 500°C and 600°C respectively. It has been observed that as the annealing temperature increases, the sensor becomes more sensitive to humidity with different range of % RH and it is found that sensor shown by curve 'e' has linear change in resistivity up to 60 %, therefore, it can be used to fabricate resistive type humidity sensor for this range. Thus the humidity sensor reported here based on electrical resistivity is cost effective and user friendly. It can be used for selective range of relative humidity for indoor and outdoor applications.

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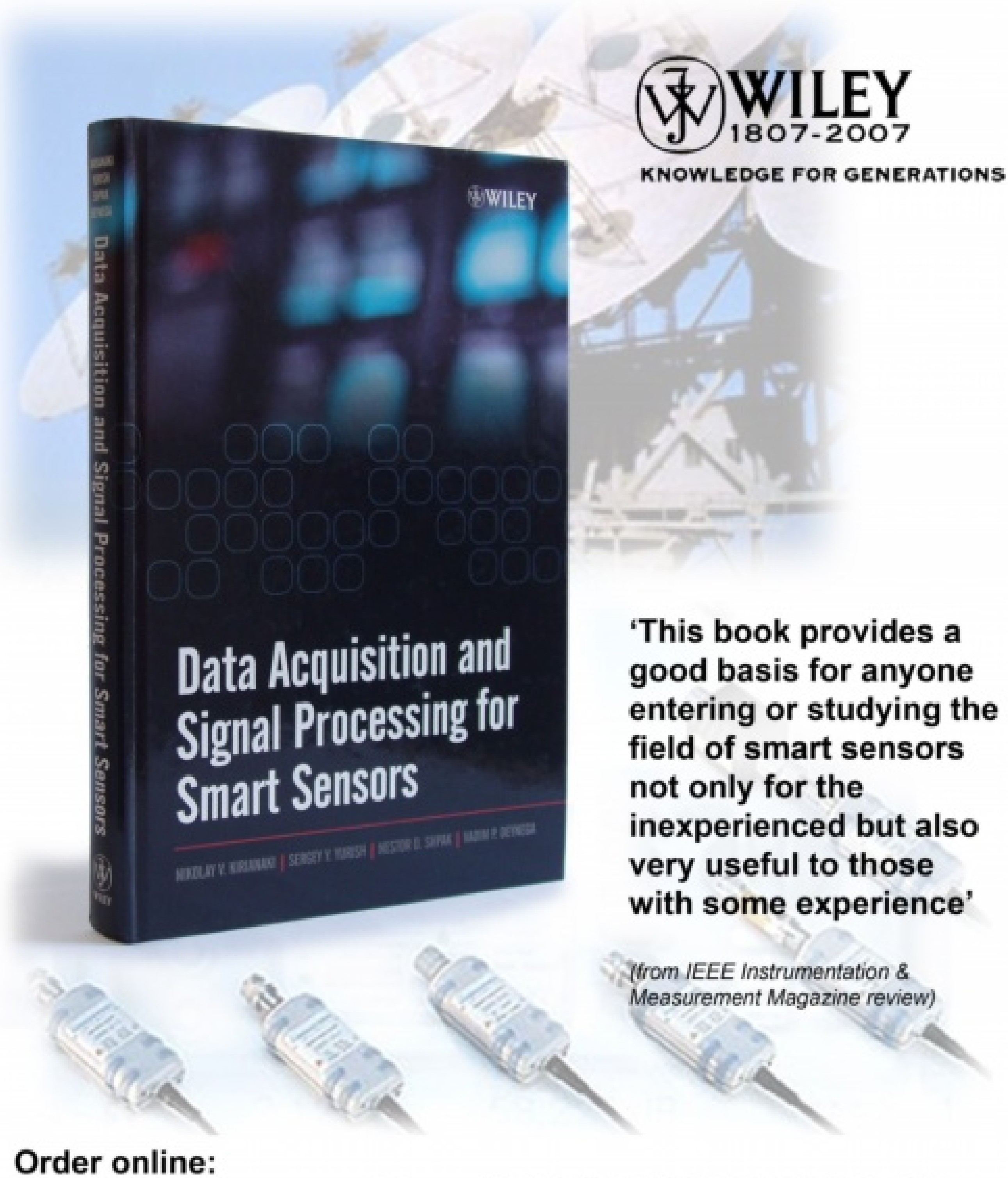

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