Water vapour sensing mechanism of pristine SnO_2 nanoparticle based thick film sensor

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Abstract

The SnO_2 was synthesized by co-precipitation method. The gross structure and phase purity of the pure SnO_2 nano powder were examined by powder X-ray diffraction technique. It reveals that the sample crystallize in tetragonal structure. The surface morphology investigated through field emission scanning electron microscope(FE-SEM) results that pure SnO_2 possesses uniform grains and is almost homogeneously distributed, which indicates the high packing density of the materials and nano spheres like structures. Further, Water vapour or humidity sensing investigations of pristine SnO_2 nano powder were study. Our result indicates that pristine SnO_2 in form of thick film was most sensitive for humidity under same conditions. The hysteresis plot between increasing and decreasing the RH range of 30–90% Rh and vice versa. The samples resistance decreases from 10^{11} Ω to 10^{8} Ω. The similar change was also observed in sensitivity. The response and recovery time were also studies. The results were re- producible up to ± 79% after 2 months of observations.

Key words: *SnO_2 nanoparticle, Humidity sensor.*

1. Introduction

Humidity plays a significant role in every part of the Earth in biology factors and varrious industrial processes. To have a desirable surrounding atmosphere, it is essential to monitor, detect and control the ambient humidity under different conditions ranging from low temperature to high or in combinations with other gases by precise and provident sensors [1,2]. Due to the different operating conditions of moisture sensors in different areas of application ranging from indoor to open air uses, various types of humidity sensing instruments have been developed based on different work principles and diverse hygroscopic sensing materials [3-5]. The operating principle of metal oxide semiconductor sensors is based on the change in conductivity of the sensitive layer by the chemical adsorption of molecules. Typically, the metal oxides semiconductors (SnO_2, In_2O_3, WO_3, ZnO, etc.) are used to create sensitive layers [6-8]. Tin oxide is an n- type wide band gap semiconductor (Eg = 3.6 ~3.97eV) and its electrical properties critically depend on its stoichiometry with respect to oxygen, on the nature and amount of impurities or dopants present and on its size as well as shape of nanostructures [9-11]. Stannic oxide is formed in the structure of rutile, the spatial group being P4/mnm. The unit cell is tetragonal, it consists of six atoms – two stannum and four oxygen atoms – and is characterized by the lattice parameters a and c and intrinsic parameter u. The optimized cell parameters obtained in the calculation are as follows: a=b= 4.738Å, c= 3.188Å and u = 0.30756. In the bulk all Sn atoms are six-fold coordinated to threefold coordinate oxygen atoms. The SnO_2 is an anisotropic polar crystal, which crystallizes in tetragonal rutile structure [12-16]

In this work, SnO_2 nanoparticles is synthesized by using co-precipitation method. The humidity sensing properties of the synthesized material such as hysteresis cycle, sensitivity and response time of pure synthesized material were studied.

2. Experimental

2.1 Synthesis of SnO_2 nanoparticle

All the chemicals used in this study were of GR grade purchase from Sd-fine, India (purity 99.99%). In preparation of SnO_2, 2 g (0.1 M) of stannous chloride dehydrate ($SnCl_2.2H_2O$) is dissolved in 100 ml distilled water. After complete dissolution, about 4 ml ammonia solution is added to above prepared aqueous solution with magnetic stirring. The solution was stirred for 20 minutes to make homogeneous solution. White gel precipitate is immediately formed and it is allowed to settle for 12 hrs. Then it is filtered and washed with deionised water 2-3 times. The obtain precipitate were mixed with 0.27 g carbon black powder (charcoal activated). The obtained mixer is kept in vacuum oven at 70 ºC for 24 hours so that the mixer gets completely in to dried powder. Then this dry product was crushed into a find powder by grinder. Now obtained product of fine nano powder of SnO_2

was calcinated at 800°C up to 8 hours in the auto-controlled muffle furnace (*Gayatri Scientific, Mumbai, India.*) so that the impurities from product will be completely removed.

Preparation of thick films

The thick film was prepared by screen printing technique on a glass substrate. Initially, for the screen printing the thixotropic paste was formulated by mixing the sintered fine powder of pure nano SnO_2 powder a with a solution of ethyl cellulose (as 10% temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The paste of pure SnO_2 and it was screen printed on a glass substrate in the form of thick films. The prepared films were dried at 80-110°C in oven for 1hrs then the dried films are kept for fired at 500°C for 25 min in muffle furnace (Kumar make Mumbai), so that all the organic materials (in the form of binders) and organic impurities can be evaporated form the sensor material. For the surface conductance measurement, the electrodes of silver paint were formed on adjacent sides of the films and again, the films were subjected to heating at 80°C for 15 min for drying the silver paint.

2.2 Characterization

X-ray diffraction (XRD)

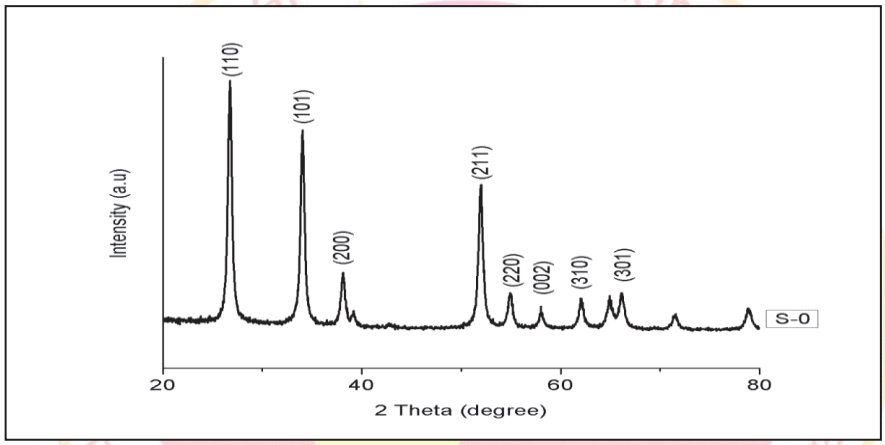

Figure 1 XRD pattern of pristine stannic oxide (SnO_2)

Figure 1. shows the XRD pattern of pristine stannic oxide (SnO_2) nanostructure synthesized by liquid phase via co-precipitation method calcinated at 400°C it is clearly observed that the highest intensity peak is obtained at (110) crystal planes and other peaks lying at (101), (200), (211), (220) and (002) of SnO_2. All the peaks match well with the standard tetragonal structure of SnO_2 with lattice constant a = 4.723 nm and c = 3.238 nm and its unit cell volume (V=72.24A^{o3}) with JCPDS card no. 71-0652. All the peaks are perfectly match with pure SnO_2 nanostructure, which indicates the high purity of obtained SnO_2 nanoparticles. The average crystalline size was found to be 23.19 nm calculated by using Debye-Scherer formula [17].

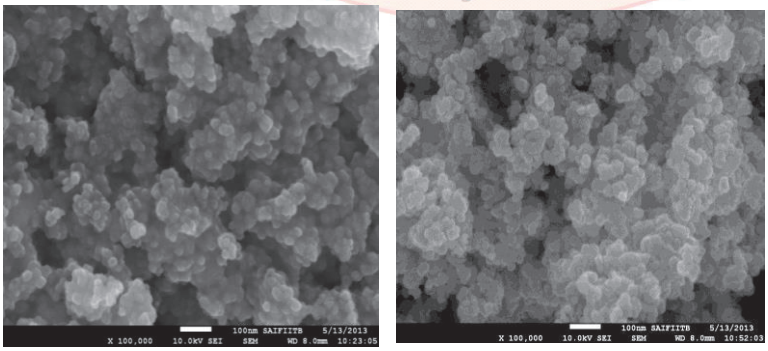

Figure 2. FE-SEM of pure SnO_2

Figure 2. shows the micrograph of sample pure SnO_2 thick films in this the particles are found to in the tetragonal shape within the particle size in the range of about 15 nm to 31.2 nm.

3. Result and Discussion

Hysteresis Plot

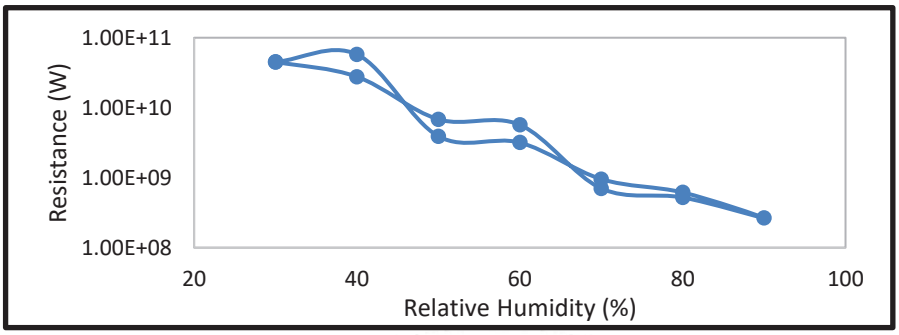

Figure 3. Hysteresis Plot

Hysteresis plot of pristine SnO_2 shows the variation between resistances of sample with respect to the relative humidity in increasing and decreasing order from 30 to 90 % RH as shown in the figure 3. A very small hysteresis present during forward and reverse cycle of relative humidity, where as a very significant average change observed in the value of resistance from 10^{11} Ω to 10^{8} Ω, these is a very remarkable change in the observed in the value of resistance in pristine SnO_2 material. In all the prepared sample the hysteresis is present which shows processes of regeneration is quite slower. Apart from these a sample shows comparable decrease in resistance with an increase in % RH which indicates that the conduction occurred at the grain surface by release of electron from the water molecule and possessed a high sensitivity factor due to large surface area and porosity in the form of thick films.

Sensitivity

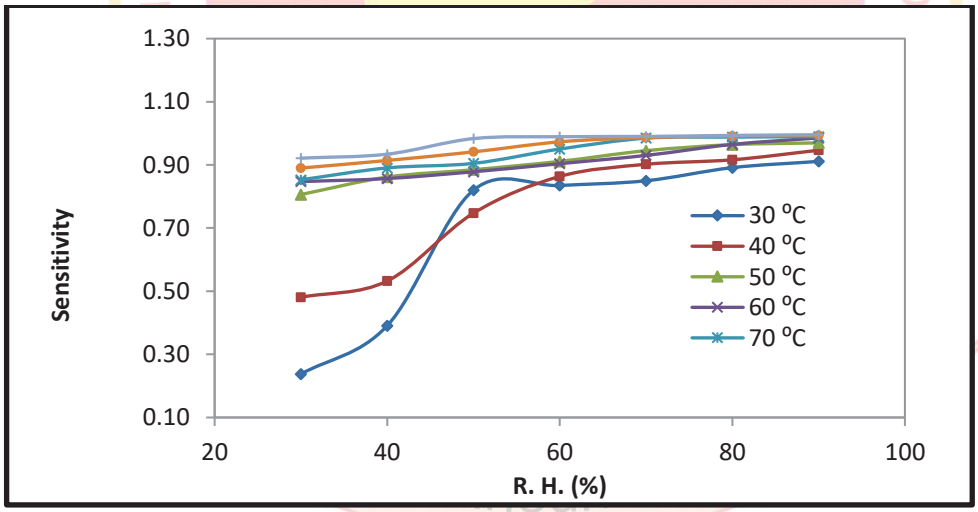

Figure 4. Sensitivity curve

The sensitivity is found to be increasing with the RH for the thick films and it is increasing up to some particular RH and then afterward it remains constant as shown in figure 4. For higher RH the sensitivity curve is found to be higher for the thick film of pristine SnO_2. It also state that the change in conductivity is more in SnO_2 nano materials the similar change is observed in sensitivity also. The Pure SnO_2 nanoparticle-based sensors exhibits significantly higher sensitivity it is due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapuors. The fall in resistance is mainly due to the increased amount of conduction electron or charge carrier upon adsorption of water vapours by the surface layer of the thick films.

Response Time

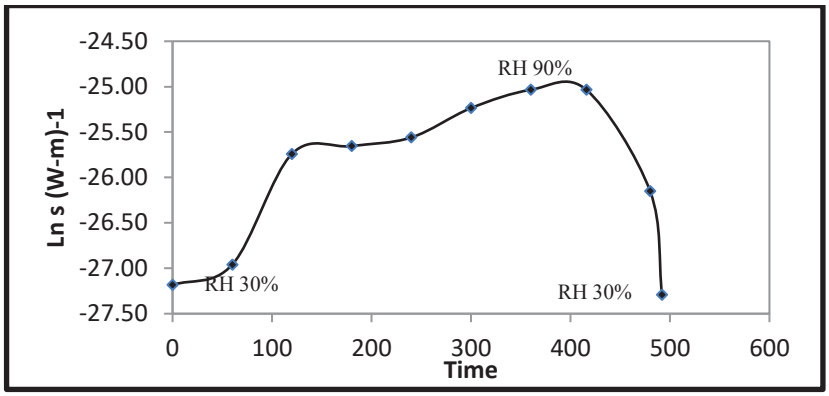

Figure 5. Response Curve

The responses curve pristine SnO_2 at constant temperature is as shown in figure 5. From the response curve, on time and recovery times are measured. Under the condition of constant temperature, the relative humidity is increases from 30 % RH to 90% RH in some appropriate time and then at the 90 % RH it is stopped, (ON response time) 360 sec which is after, it was allowed to fall up to 30 % RH (OFF recovery time) which is 127 sec. It is observed that response and recovery time is nearly fast in the pristine SnO_2.

4. Conclusion

SnO_2 nanoparticle was successfully synthesise co-precipitation method. Minimum crystallite size was found to be 23.19 nm for SnO_2 nanoparticle. The Surface morphology of pure SnO_2 shows that most particles are spherical in shape leaving more space as pores and hence it was most sensitive for humidity sensing. The Hysteresis plot shows very significant average change in the value of the resistance from 10^{11} Ω to 10^{8} Ω during forward and reversed cycles. Sensitivity is found to be increasing with the RH in pure SnO_2 thick film and it is increasing up to some particular RH and then afterward it remains constant. This shows that it has good scope for the development of moisture sensor in the range of relative humidity 30% to 90% RH. The response and recovery time of pristine SnO_2 based thick film sensors were satisfactory i.e. the sensors were found to be fast in operation. The recovery time found to 127 s at constant temperature respectively.

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