Morphological and humidity sensing characteristics of $\text{SnO}_2\text{--CuO}$, $\text{SnO}_2\text{--Fe}_2\text{O}_3$ and $\text{SnO}_2\text{--SbO}_2$ nanoco-oxides

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Abstract. This paper reports the synthesis of $\text{SnO}_2\text{--CuO}$, $\text{SnO}_2\text{--Fe}_2\text{O}_3$ and $\text{SnO}_2\text{--SbO}_2$ composites of nano oxides and comparative study of humidity sensing on their electrical resistances. CuO , Fe_2O_3 and SbO_2 were added within base material SnO_2 in the ratio 1 : 0.25, 1 : 0.50 and 1 : 1. Characterizations of materials were done using SEM and XRD. SEM images show the surface morphology and X-ray diffraction reveals the nanostructure of sensing materials. The pellets were annealed at 200, 400 and 600°C respectively for 3 h and after each step of annealing, observations were carried out. It was observed that as relative humidity (%RH) increases, there was decrease in the resistance of pellet for the entire range of RH. Results were found reproducible. $\text{SnO}_2\text{--SbO}_2$ shows maximum sensitivity for humidity (12 M Ω /%RH) among other composites.

Keywords. Nanoco-oxides; humidity sensors; morphology; porous media; XRD; SEM.

1. Introduction

The metal or metal oxide additives to nanostructure metal co-oxides, used as base materials for semiconductor humidity and gas sensors are of great interest due to the influence that they exert on the physical and chemical properties (Matsuura and Matsuoka 1976; Nitta *et al* 1980; Yamamoto and Shimizu 1982; Katayama *et al* 1990; Yoshimura *et al* 1990; Cantalini *et al* 1993; Ushio *et al* 1993; Han Sang-Do *et al* 2000; Galatis *et al* 2003; Han Chi-hwan *et al* 2005; Kim and Gong 2005; Srivastava and Jain 2005; Jain *et al* 2006; Yadav *et al* 2008). These additives determine the catalytic properties and sensitivity of the base material on its electrical response under a given atmosphere. The presence of these additives influences the size and morphology of the so generated nanostructured oxides. The additives also influence the formation of new phases, which improves the properties of the base material.

The majority of existing sensors are intended for specialized measurement in two ranges—micro humidity or relative humidity under certain conditions (temperature, volume, etc). The importance of humidity sensing has been well understood and much research has been focused on the development of humidity-sensitive materials (Nitta 1988; Kulwicki 1991; Fagan and Wamarakoon 1993; Traversa 1995; Lee and Lee 2005; Chen and Lu 2005).

Various humidity sensors based on electrical (Montesperelli *et al* 1995; Traversa and Bearzotti 1995; Faia *et al* 2004; Faia *et al* 2005; Hernandez-Ramirez *et al* 2007; Yadav *et al* 2007a) and optical (Yadav and Shukla 2003; Shukla *et al* 2004; Yadav *et al* 2005; 2007b) properties have been described. Different groups to investigate their humidity sensing characteristics have studied various ceramic materials but very few papers have suggested the possible sensing mechanism for resistive type humidity sensors. Since humidity is a very important environmental factor therefore its measurement is important not only for human beings but also for many industries and technologies. Recently, major domestic applications of humidity sensors have been utilized for automatic humidity control in air conditioners, the automatic cooking in microwave ovens, in chemical industries, in production of electronic devices and in green houses. A significant change in electrical resistance may be caused by adsorption of water vapour on the surface of semiconductor oxides. Further, the measurements were made on ZnO , TiO_2 and SnO_2 , etc. Tin oxide is a wide band gap n-type semiconductor (~ 3.6 eV). It shows outstanding electrical, optical and electrochemical properties (Angelis and Riva 1995; Gopel and Schierbaum 1995; Martinelli *et al* 1995; Bose *et al* 2005) and it is the most used material due to its low cost, long life and good reproducibility. In this paper, we report the comparative study of humidity sensing properties of different composites made of SnO_2 at different annealing temperatures.

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2. Principle of operation

Adsorption of water vapour is totally responsible for changes in conductivity of pellet (Andersons and Parks 1968; Morimoto *et al* 1969; Shimizu *et al* 1985; Sagnella 1998; Chou *et al* 1999). 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 in enhanced sensitivity. Chemistry involved in adsorption of water on metal oxide 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 under-saturated metal (figure 1a), and next step is dissociative chemisorption, which results in hydroxylated surface (figure 1b). Overall the conduction is due to protonation and deprotonation of surface hydrolysis. The morphology of the sensing element influences water vapour adsorption and desorption processes. These processes are the functions of ceramic pore size and its distribution (Chou *et al* 1999).

Sensitivity of humidity sensor (S) is defined as the change in resistance (ΔR) of sensing element per unit change in relative humidity (%RH) (Yadav *et al* 2007a).

$$S = \frac{\Delta R}{\Delta \%RH} \text{ M}\Omega/\%RH,$$

3. Preparation of sensing element

3.1 Preparation of SnO_2 -CuO nanoco-oxide (S_1)

3.1a Synthesis of Cu_2O/CuO : The cupric oxide (CuO) had a special importance in the application of humidity sensors. Benedict reagent was prepared by dissolving 173 g of sodium citrate and 90 g of anhydrous sodium carbonate in 500 ml of deionized distilled water. The contents was heated slightly to dissolve and the solution filtered and its volume made to 850 ml. Further 17.3 g of $CuSO_4 \cdot 5H_2O$ was dissolved in 150 ml of water separately. This solution was added slowly with stirring to the

previous solution, the mixed solution was ready for use. Subsequently a mixture was prepared by adding 50 ml glucose solution (0.2 g/ml) to 150 ml Benedict's reagent and reducing glucose to get pure Cu_2O . After cooling the boiled mixture, brick red precipitate of cuprous oxide was obtained, which was filtered and washed several times by deionized water. The dried powder was heated at $200^\circ C$ to change cuprous oxide into cupric oxide (Yadav and Yadav 2009).

3.1b Synthesis of SnO_2 -CuO (S_1): For preparing sensing element SnO_2 -CuO (S_1), CuO was mixed in SnO_2 powder in different weight per cent i.e. 25, 50 and 100% which was dispersed in isopropyl alcohol and stirred for six hours for preparation of co-oxide. Further it was dried at $50^\circ C$ for 1 h and converted into fine powder by grinding in mortar with pestle for 6 h. Pellets of this material were made by hydraulic pressing under uniaxial pressure of 616 MPa at room temperature.

3.2 Preparation of SnO_2 - Fe_2O_3 (S_2)

Stannous chloride ($SnCl_2 \cdot 2H_2O$) solution was made in deionized water containing a very small amount of hydrochloric acid (1–2%) and ferric chloride ($FeCl_3$) solution was prepared in deionized water. Both solutions were added to ammonium hydroxide solution under stirring for 6 h so that all the hydroxides precipitated simultaneously.

The co-precipitates were washed to make them chloride free and finally calcined at $600^\circ C$ for 3 h to get the co-oxide powder of SnO_2 - Fe_2O_3 (S_2). On vigorous grinding of the material in mortar with pestle for 6 h, a very fine powder was obtained. Various ratios e.g. 1:0.25, 1:0.5 and 1:1 were taken for comparative study.

3.3 Preparation of SnO_2 - SbO_2 (S_3)

The SnO_2 - SbO_2 composite (S_3) was prepared from chlorides in the laboratory. The SnO_2 solution was prepared by dissolving 1 g of $SnCl_2 \cdot 2H_2O$ and $SbCl_3$ in deionized water. This mixture was stirred for 3–4 h. The solution was filtered to get a paste, which was heated at $50^\circ C$ for 1 h. Finally the powder of SnO_2 - SbO_2 (1:1) was obtained. Similarly SnO_2 - SbO_2 co-oxide of ratios 1:0.25 and 1:0.5 were prepared. On vigorous grinding of the material in mortar with pestle for 6 h, a very fine powder was obtained.

To make the sensing elements, pellets of prepared materials were made using hydraulic pressing machine under a pressure of 616 MPa at room temperature. These pellets were annealed at 200, 400 and $600^\circ C$ for 3 h in an electric furnace. Each pellet was kept within an electrode holder and exposed to humidity in the self-designed humidity chamber and variations in resistance with

Figure 1. (a) Coordination of surface metal ions with water molecules and (b) Dissociative chemisorptions produce hydroxylated surface.

humidity were recorded using a digital multimeter (VC 9808, India). Relative humidity was measured using standard Hygrometer (Huger, Germany). The least count of Hygrometer used here is 1% RH.

4. Characterization of materials

4.1 X-Ray powder diffraction

X-ray diffraction by X-Pert PRO XRD system (Netherlands) with $\text{Cu-K}\alpha$ radiation source having wavelength $1.54 \text{ \AA}$ shows extent of crystallization of the sensing element $\text{SnO}_2\text{-CuO}$, $\text{SnO}_2\text{-Fe}_2\text{O}_3$ and $\text{SnO}_2\text{-SbO}_2$ annealed at 600°C and the diffraction patterns are shown in figures 2–4. For sensing element $\text{SnO}_2\text{-CuO}$, the minimum crystallite size is 16 nm corresponding to the plane (113) and maximum size is 114 nm corresponding to plane (200). Thus the average is 73 nm. For sensing element $\text{SnO}_2\text{-Fe}_2\text{O}_3$, the minimum crystallite size is 28 nm corresponding to the plane (113) and maximum size is 152 nm corresponding to plane (202) resulting in an average crystallite size of 74 nm. The minimum crystallite size is 11 nm corresponding to the plane (002) and maximum crystallite size is 134 nm corresponding to

plane (200) for sensing element $\text{SnO}_2\text{-SbO}_2$, the average being 44 nm. Overall this sensing material has minimum crystallite size among other composites under investigation.

The average crystallite size of each oxide based sensing element is estimated to be below 100 nm and is well within the nanometer regime. This, therefore, authenticates that the present work deals with nanomaterials and since the two oxide based materials are synthesized together, these are considered to be a composite.

4.2 Scanning electron microscopy

Surface morphology was studied using scanning electron microscope (SEM, LEO-0430, Cambridge). Figures 5a–c show the micrographs of sensing material $\text{SnO}_2\text{-CuO}$ annealed at 200, 400 and 600°C respectively. These images clearly show the spherical morphology with certain degree of elongation and that the sensing material is highly porous and were 0.099 , 0.110 and $0.117 \mu\text{m}$ respectively at the three different adopted temperatures. Macro-pores of so-obtained materials are therefore considered as a good candidates for humidity sensing application.

Figures 6a–c reveal that the molecules of $\text{SnO}_2\text{-Fe}_2\text{O}_3$ at annealing temperatures of 200, 400 and 600°C look like mushrooms and the porosity increases as annealing temperature increases. These images show the surface morphology of the composite with varying and irregular size. Average pore size at 200, 400 and 600°C are 0.73 , 4.65 and $6.70 \mu\text{m}$ respectively which again could be very useful for studying sensing properties.

Figures 7a–c show that the particles of $\text{SnO}_2\text{-SbO}_2$ are highly agglomerated, random in size and un-evenly distributed. Micrographs show that the sensing material is highly porous having porosity approximately in the range $1\text{--}7.5 \mu\text{m}$. Higher porosity increases surface to volume ratio of the materials and therefore, helps in achieving good sensitivity.

Figure 2. XRD pattern of sensing element S_1 .

Figure 3. XRD pattern of sensing element S_2 .

Figure 4. XRD pattern of sensing element S_3 .

Figure 5. SEM of sensing element S_1 prepared after annealing at (a) 200°C, (b) 400°C and (c) 600°C.

5. Results and discussion

Figures 8–16 show that for every sensing element, as %RH increases resistance decreases sharply or slowly. Figure 8 shows the variations in resistance with %RH for sensing element $\text{SnO}_2\text{--CuO}$ in the ratio 1:0.25 annealed at 200, 400 and 600°C respectively. Curve 'a' of this figure represents the variation in resistance with %RH for the sensing element annealed at 200°C and shows that resistance decreases drastically up to 25%RH and then decreases more slowly in the higher range of %RH. A marked decrease of resistance in the range 10–30%RH and again in the next range is shown in curve 'b'. Curve 'c' shows that resistance decreases rapidly up to 35%RH, a linear decrease in resistance from 35–50 and further decreases slowly. Figure 9 shows the variation in

resistance with %RH for the sensing element $\text{SnO}_2\text{--CuO}$ in the ratio 1:0.50 annealed at temperatures 200, 400 and 600°C respectively. Curve 'a' of this figure shows that resistance decreases linearly in the entire range of %RH. Curve 'b' shows that resistance decreases linearly up to 25%RH, sharply decreases in the range 25–40%RH and again decreases slowly. Curve 'c' exhibits sharp decrease from 10–55%RH and beyond this, resistance decreases slowly. Figure 10 shows the variation in resistance with %RH for the sensing element $\text{SnO}_2\text{--CuO}$ in the weight ratio 1:1 annealed at temperatures 200, 400 and 600°C respectively. Curves 'a' and 'b' express the variation in resistance with %RH for the sensing element annealed at 200 and 400°C respectively. Both curves show that as humidity increases, resistance of sensing element decreases with small value in $\text{M}\Omega$ over the entire range of

Figure 6. SEM of sensing element S_2 prepared after annealing at: (a) 200°C, (b) 400°C and (c) 600°C.

RH. Curve 'c' shows variation in resistance with the variation in %RH for sensing element annealed at 600°C. It exhibits similar behaviour like curve 'a' up to 30%RH, slow decrease in resistance from 30–65%RH and again linear decrease in resistance in the next range of humidity.

Figures 11 shows the variations in resistance with %RH for sensing element $\text{SnO}_2\text{-Fe}_2\text{O}_3$ in the ratio 1 : 0.25 annealed at 200, 400 and 600°C respectively. Curve 'a' shows that resistance decreases drastically up to 35%RH and then decreases slowly. Curve 'b' also shows that resistance decreases drastically up to 35%RH, then decreases sharply in the range 35–50%RH after which it decreases slowly up to the saturation region. Curve 'c' shows linear decrease in resistance in the range 10–25%RH and drastic decrease from 25–40%RH after which resistance decreases more slowly up to 95%RH.

Figure 12 illustrates the variations in resistance with %RH for the sensing element $\text{SnO}_2\text{-Fe}_2\text{O}_3$ in the ratio 1 : 0.50 annealed at temperatures 200, 400 and 600°C respectively. Curves 'a' and 'b' show that resistance decreases sharply up to 25%RH and then decreases linearly up to saturation range. Curve 'c' shows that resistance decreases drastically up to 85% and then decreases slowly up to 95%. Figure 13 exhibits the variation in resistance with %RH for the sensing element $\text{SnO}_2\text{-Fe}_2\text{O}_3$ in the ratio 1 : 1 annealed at temperatures 200, 400 and 600°C respectively. Curve 'a' shows that as RH% increases, resistance decreases linearly up to 20 and a sharp decrease in resistance up to 35%RH can be seen. After that again the resistance decreases in the range 30–95%RH. Curve 'b' shows the same behaviour as curve 'a' up to 25%, drastic decrease from 25–40%RH and slow decrease in the next higher range.

Figure 7. SEM of sensing element S_3 prepared after annealing at: (a) 200°C, (b) 400°C and (c) 600°C.

Figure 8. Variations in resistance (MΩ) against %RH for sensing element (S_1) 1 : 0.25 annealed at different temperatures.

Figure 9. Variations in resistance (MΩ) against %RH for sensing element (S_1) 1 : 0.5 annealed at different temperatures.

Table 1. Sensing elements $\text{SnO}_2\text{-CuO}$, $\text{SnO}_2\text{-Fe}_2\text{O}_3$ and $\text{SnO}_2\text{-SbO}_2$ annealed at temperatures 200, 400 and 600°C vs average sensitivity ($\text{M}\Omega/\%\text{RH}$) with 25% composition i.e. 1 : 0.25.

Sensing elements	Average sensitivity ($\text{M}\Omega/\%\text{RH}$) with 25% composition i.e. 1 : 0.25		
	200°C	400°C	600°C
$\text{SnO}_2\text{-CuO}$ (S_1)	2.5	5.5	7.0
$\text{SnO}_2\text{-Fe}_2\text{O}_3$ (S_2)	1.8	2.8	3.8
$\text{SnO}_2\text{-SbO}_2$ (S_3)	0.4	0.9	3.4

Table 2. Sensing elements $\text{SnO}_2\text{-CuO}$, $\text{SnO}_2\text{-Fe}_2\text{O}_3$ and $\text{SnO}_2\text{-SbO}_2$ annealed at temperatures 200, 400 and 600°C vs average sensitivity ($\text{M}\Omega/\%\text{RH}$) with 50% composition i.e. 1 : 0.5.

Sensing elements	Average sensitivity ($\text{M}\Omega/\%\text{RH}$) with 50% composition i.e. 1 : 0.5		
	200°C	400°C	600°C
$\text{SnO}_2\text{-CuO}$ (S_1)	1.1	2.4	6.2
$\text{SnO}_2\text{-Fe}_2\text{O}_3$ (S_2)	2.5	2.6	6.7
$\text{SnO}_2\text{-SbO}_2$ (S_3)	0.6	2.9	5.3

Figure 10. Variations in resistance ($\text{M}\Omega$) against %RH for sensing element (S_1) 1 : 1 annealed at different temperatures.

Curve 'c' shows similar behaviour as curve 'c' of figure 12 with slight improvement.

Figure 14 shows the variations in resistances with %RH for sensing element $\text{SnO}_2\text{-SbO}_2$ in the ratio 1 : 0.25 annealed at 200, 400 and 600°C respectively. Curve 'a' of this figure exhibits variation in resistance with %RH for the sensing element annealed at 200°C; there is gradual variation in resistance over the entire range of %RH i.e. 10–95. Curve 'b' for the sensing element annealed at 400°C shows that as %RH increases from 10–15%RH, resistance decreases rapidly and further decreases gradually up to point of saturation. Curve 'c' shows variation in resistance with %RH for the sensing element annealed at 600°C and shows linear behaviour over the entire range of humidity and it is quite sensitive.

Figure 11. Variations in resistance ($\text{M}\Omega$) against %RH for sensing element (S_2) 1 : 0.25 annealed at different temperatures.

Figure 15 shows the variations in resistances with %RH for sensing element $\text{SnO}_2\text{-SbO}_2$ in the ratio 1 : 0.50 annealed at 200, 400 and 600°C respectively. Curve 'a' represents the variation in resistance with %RH for the sensing element annealed at 200°C and shows that sensor is highly sensitive in the lower RH range i.e. 10–30%, and then changes become smaller but significant. Curve 'b' represents the variation in resistance with %RH for the sensing element annealed at 400°C and shows improvement in sensitivity. Curve 'c' represents the variation in resistance with %RH for the sensing element annealed at 600°C. It shows that as %RH

Table 3. Sensing elements SnO₂–CuO, SnO₂–Fe₂O₃ and SnO₂–SbO₂ annealed at temperatures 200, 400 and 600°C vs average sensitivity (MΩ/%RH) with 100% composition i.e. 1 : 1.

Sensing elements	Average sensitivity (MΩ/%RH) with 100% composition i.e. 1 : 1		
	200°C	400°C	600°C
SnO ₂ –CuO (S ₁)	0.5	2.0	5.8
SnO ₂ –Fe ₂ O ₃ (S ₂)	4.8	6.5	8.0
SnO ₂ –SbO ₂ (S ₃)	5.0	8.8	11.8

Table 4. Sensing elements SnO₂–CuO, SnO₂–Fe₂O₃ and SnO₂–SbO₂ vs max. average sensitivity (MΩ/%RH), hysteresis and average sensitivity after six months.

Sensing elements	Maximum average sensitivity (MΩ/%RH)	Hysteresis (%)	Average sensitivity (MΩ/%RH) after 6 months
SnO ₂ –CuO (S ₁)	8.1	28	10.7
SnO ₂ –Fe ₂ O ₃ (S ₂)	8.0	11	9.5
SnO ₂ –SbO ₂ (S ₃)	11.8	22	14.4

Figure 12. Variations in resistance (MΩ) against %RH for sensing element (S₂) 1 : 0.50 annealed at different temperatures.

Figure 14. Variations in resistance (MΩ) against %RH for sensing element (S₃) 1 : 0.25 annealed at different temperatures.

Figure 13. Variations in resistance (MΩ) against %RH for sensing element (S₂) 1 : 1 annealed at different temperatures.

Figure 15. Variations in resistance (MΩ) against %RH for sensing element (S₃) 1 : 0.5 annealed at different temperatures.

Figure 16. Variations in resistance ($\text{M}\Omega$) against %RH for sensing element (S_3) 1 : 1 annealed at different temperatures 200, 400 and 600°C .

increases up to 50%, resistance decreases rapidly and after that as %RH increases, it decreases gradually up to 95%.

Figure 16 shows the variation in resistance with %RH for the sensing element $\text{SnO}_2\text{-SbO}_2$ in the ratio 1 : 1 by weight, annealed at temperatures 200, 400 and 600°C respectively. Curve 'a' shows the linear variation for the sensing element annealed at 200°C over the entire range of humidity. Similarly curve 'b' shows the variation in resistance with variation in %RH for sensing element annealed at 400°C . It shows significant slope up to 75%RH and is then almost constant up to point of saturation. Curve 'c' for the sensing element annealed at 600°C shows that as humidity increases, resistance of sensing element decreases drastically up to 50% and then decreases gradually up to 95%RH.

Comparative study of average sensitivities of all the three sensing elements made of $\text{SnO}_2\text{-CuO}$, $\text{SnO}_2\text{-Fe}_2\text{O}_3$ and $\text{SnO}_2\text{-SbO}_2$ each successively annealed at temperatures 200, 400 and 600°C were done and these are depicted in tables 1–3.

Maximum average sensitivity, percentage hysteresis and average sensitivity after 6 months of each humidity sensor were investigated (table 4) which shows that sensing element made of $\text{SnO}_2\text{-SbO}_2$ (S_3) and annealed at 600°C has maximum sensitivity. Also the sensing element exhibits positive aging effect i.e. after six months sensitivity increased.

6. Conclusions

We conclude that $\text{SnO}_2\text{-SbO}_2$ prepared on annealing at 600°C having maximum sensitivity of $11.8 \approx 12$, less hysteresis, smaller particle size and high porosity proved to be better humidity sensor as compared to sensors made

of $\text{SnO}_2\text{-CuO}$ and $\text{SnO}_2\text{-Fe}_2\text{O}_3$. The results show that the sensitivity of sensor improved after 6 months. Thus the humidity sensor reported in the paper based on electrical resistance is robust, sturdy and friendly for users and can be used for both indoor and outdoor applications with electronic modification for the entire range of relative humidity.

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