Research Article Adv. Mat. Lett. 2010, 1(1), 55-58 ADVANCED MATERIALS Letters
www.amlett.com, DOI: 10.5185/amlett.2010.3101 Published online by the VBRI press in 2010

Study of structural and electrical properties of pure and Zn-Cu doped SnO_2

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Received: 7 March 2010, Revised: 5 April 2010 and Accepted: 7 April 2010

ABSTRACT

Numerous metal oxide semiconductor materials were reported to be usable as semiconductor gas sensor, such as ZnO, SnO_2, and TiO_2 and so on. The samples of Zn and Cu doped SnO_2 ($SnZnO_3$ and $SnCuO_3$) have been synthesized by solid-state reaction method. Some aspect of crystal structure of the compound at room temperature was studied using X-ray diffraction technique. The XRD study of the compound shows that there is a change in the basic crystal structure of SnO_2 on substitutions of ZnO and CuO. The patterns of the SnO_2 sample are indexed as tetragonal perovskite type with a = 7.3928 Å, c = 5.2879 Å but on substitution of ZnO and CuO the structure becomes orthorhombic with lattice constant a = 23.5237Å, b = 8.2183 Å and c =5.8017 Å or a = 21.8594 Å, b = 5.3200 Å, and c = 5.1803 Å, respectively. The temperature variation of resistance shows that compounds have negative temperature coefficient of resistance. The gas sensitivity for LPG (liquefied petroleum gas) showed a drastic change in conductivity.

Keywords: Ceramics; scanning electron microscope, XRD, gas sensors

Radheshyam Rai did PhD (Physics) from the Magadh University Bodh Gaya, India in 2004. During his PhD he worked on PLZT ferroelectric materials with different dopants and also worked on LPG and CNG gas sensor devices at the National Physical Laboratory and the Indian Institute of Technology, New Delhi, India. He has quite significant list of publications and research activities. After his PhD, he joined Department of Physics, Indian Institute of Technology, Delhi, India as a young scientist. In his stay, he worked on ferroelectromagnetic materials for devices application. At present, he is working as post-doctoral fellow at the Universidade de Aveiro under the Fundacão para a Ciênciaea Tecnologia, Lisboa, Portugal. His research is devoted on the non-lead based piezoelectric materials for energy harvesting and ferromagnetic applications.

Introduction

In the field of optoelectronics [**1–3**], catalysis [**4**], gas sensors [**5,6**] and radioactive waste management [**7-8**], the tin oxide nanoparticles is very useful materials. Several Commercial gas sensors make use of SnO_2 sensing elements. Gas sensors detecting a trace amount of the gases have been applied to processes in chemical, pharmaceutical, and fermentation industries to control the amount of harmful wastes discharged from the plants, the explosion of the combustible gases and incomplete combustion, exhaust gases from automobiles [**9-13**]. The sensors show many advantages over optical or electro chemical sensors. The main advantages are their low cost, low consumption of electrical power and high sensitivity [**14**]. Highly sensitive and selective detection of various gases has become increasingly important in the recent years especially for the purpose of emission control and environmental monitoring. Because of some high sensitivity of the electrical conductivity of SnO_2, to gaseous environment, gas sensors based on these semiconducting oxides can be used for the detection of combustible and noxious gases in air **[15].** Two main mechanisms are responsible for gas sensing (1) the bulk diffusion of oxygen from outside into the oxide, compensating an original deficiency of oxygen, which is typical of most oxides. (2) The low-temperature chemisorptions of environmental gases on the surface of multiple grains, charging the surface state and charge distribution inside the grain. SnO_2 is an n-type semiconductor with wide energy gap. It is particularly interesting because it has semi conducting properties and has been widely used as catalyst for oxidation of organic compounds, gas sensors, rechargeable Li batteries and optical electronic devices. It is believed that sensors sensitivity can be improved by increasing the surface areas of sensitivity materials. The materials will provide more surface site available for more oxygen to be absorbed on these sites and to make contact with surrounding gases [**16-17**]. The intrinsic conduction mechanism of SnO_2 is usually linked to bulk oxygen vacancies [**18-19**]. Choi et al. [**20**] also reported that CuO and ZnO addition abruptly decreased the eclectriacl conductivity of SnO_2. Co-doping SnO_2 based ceramics with Sb and Zn, showed profound

effects on ceramic density and electrical properties. Doping with Sb atom enhanced the ceramic electrical conductivity, with no densification. But Zn-doped ceramics showed enhanced ceramic densification with low conductivity. A considerable amount of current research activities has been devoted to the development of stable; pure or doped tin dioxide sensors. Our present investigation mainly deals with synthesis of high surface area of SnO_2 and mechanisms of gas sensing.

Experimental

$Sn_{1-x}Y_xO_3$ (where Y = Zn and Cu) powder with concentration x = 0.00, 0.10 were synthesized by a high temperature solid-state reaction technique using high purity of oxides; SnO_2 (99.9% M/s Aldrich chemical USA), ZnO (99.9% M/s Sdfine-Chem ltd), and CuO (99.99% M/s Aldrich Chemical USA) in air atmosphere. The above compounds in a suitable stoichiometry were thoroughly mixed in an agate mortar for 2 h. The mixed materials were then calcined in alumina crucible at 900 ^oC for 2h. The fine powder was pressed into cylindrical pellets of 1-3 mm thickness and 10mm in diameter using PVA (polyvinyl alcohol) as a binder at a pressure of 2 × 10^5 N/m^2. Finally the pellets were sintered at 1000 ^oC for 2 h. The formation and quality of SnO_2 and doped compound were checked with X-ray diffraction technique. Bruker AXS DQ Advance X-ray Powder diffractometer was used for recording the X-ray diffraction patterns. The X-ray diffraction of the compounds was recorded at room temperature using X-ray powder diffractometer (Rigaku-Minifiex, Japan) with CuKα radiation (λ = 1.5418 Å) in a wide range of Bragg angles 2θ (20° <2θ <70°) with scanning rate of 2° min^{-1}. The morphologies and dimensions of the powders were observed by transmission electron microscopy (TEM). The dc resistance of the compounds was measured using a Keithley-628 current source meter with a laboratory-fabricated experimental setup. The sensor characteristics were recorded by measuring the resistance in presence of gas and in air at different temperatures. The gas sensitivity is measured by homemade measurement setup with keithely-247 multimeter, mass flow meters and a thermocouple (K-type chromal alumna) attached to the sensor.

Results and discussion

The XRD pattern of samples shows very sharp and single diffraction peaks, which indicate a better homogeneity and crystallinity of the samples (**Fig 1**). The diffraction lines of the samples with the different doping, suggested that there is change in the basic crystal structure of SnO_2 on substitutions of ZnO and CuO. All the reflection peaks were indexed and lattice parameters of samples were calculated using a computer program based on a least squares refinement method (POWD) [**21**]. The patterns of the SnO_2 sample are indexed as tetragonal Perovskite type with a = 7.3928 Å, c = 5.2879 Å but on substitution of ZnO and CuO the structure becomes orthorhombic with lattice constant a = 23.5237Å, b = 8.2183 Å and c = 5.8017 Å or a = 21.8594 Å, b = 5.3200 Å and c = 5.1803 Å, respectively. In XRD pattern the peaks of copper oxide and zinc oxide becomes observable, but intensities of the peaks remain low, suggesting that the concentration of copper or zinc oxide phase in the SnO_2 is small. This is due to the, volatization of (Cu or Zn) oxide during sintering and doping of oxide into SnO_2.

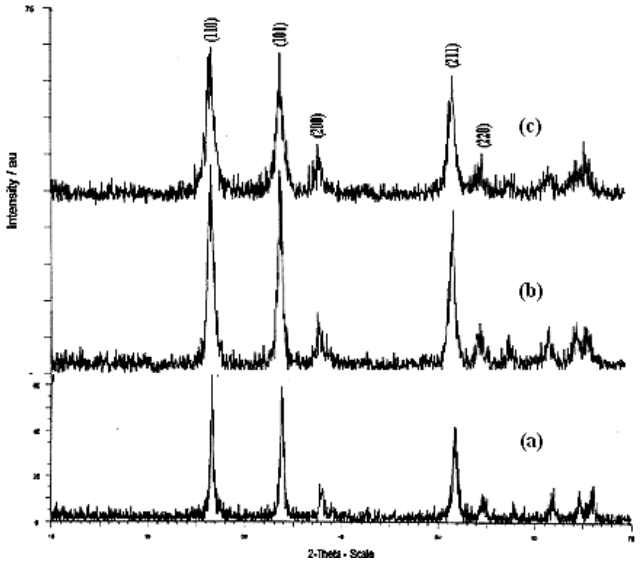

Fig. 1. XRD graph of (a) pure, (b) Zn doped and (c) Cu doped SnO_2 powder.

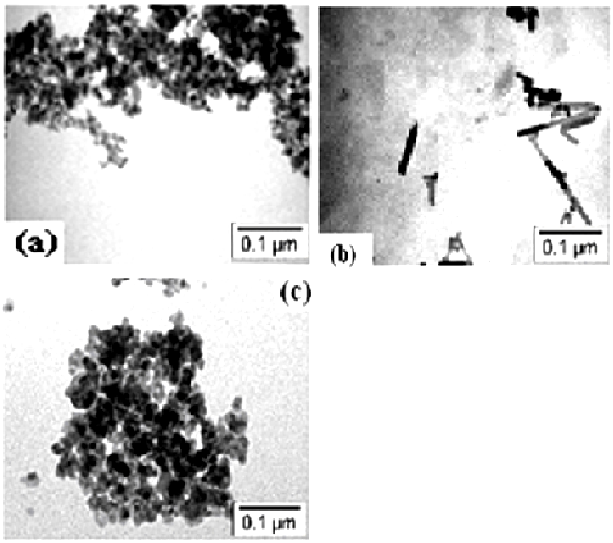

Fig. 2. TEM micrographs of powder specimen of pure SnO_2, (b) Zn doped SnO_2 and Cu doped SnO_2.

It is well known that gas-sensing properties of a metal oxide strongly depend on its morphological features. A high surface area facilitates the chemisorptions process by increasing the adsorption and desorption rates [**22**]. The grain neck and grain boundary feature also influences the gas sensing properties. It has been shown that smaller grain size increases gas sensitivity [**17**, **23-25**]. As shown in **Fig 2(a-c)** the morphology of SnO_2, $SnZnO_3$ and $SnCuO_3$ is different. More information regarding the structure and morphology were obtained from the TEM microstructure of the samples. The TEM micrographs, **Fig. 2 (a-c)** shows particle size and shape morphology.

Fig. 2(a-c) shows the powder morphology of SnO_2, $SnZnO_3$ and $SnCuO_3$ powders. The powder consisted of agglomerated grains, having a wide particle size distribution. From EDX (energy dispersive X-ray) analysis of sintered pellets revealed some loss (5–10%) is present in high temperature sintering. The average grain size was about 2-5 nm.

The resistance-operating temperature relations of sensors in air were measured between 50-250^{0}C (**Fig 3**). In first temperature region the resistance of sensors decreases with temperature. It appears to follow exponent law approximately [**25**]. It is the result of the ionization of donor impurity and defect. In last temperature region, the change in resistance is small. It is because the electrons of donor level are ionized completely, and the electronic concentration of intrinsic excitation is less than the concentration of donor at this temperature region with increasing temperature. It is due to SnO_2 molecule has the uncharged conductance at the certain temperature range. The compounds have good thermal stability when their operating temperature is at this range. It is significant to apply the sensor to certain control and monitoring.

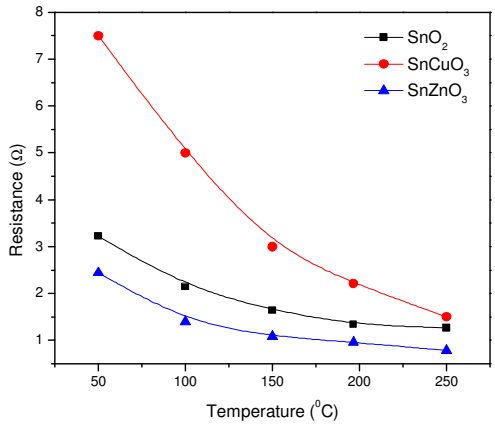

Fig. 3. Variation of resistance of SnO_2, $SnCuO_3$ and $SnZnO_3$ as a function of temperatures.

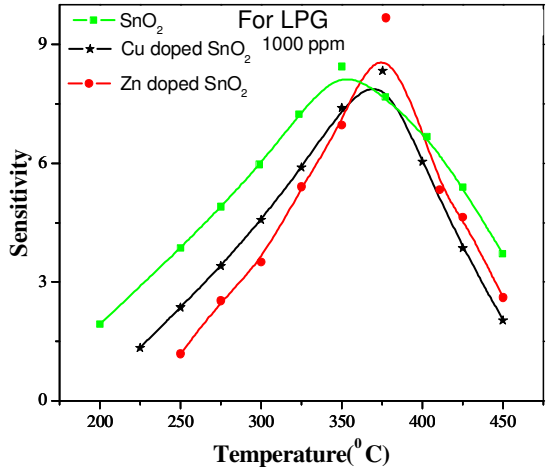

Fig. 4. Variation of resistance of SnO_2, $SnCuO_3$ and $SnZnO_3$ as a function of temperatures.

For the gas sensitivity (**Fig. 4**) measurements, the flow rate of carrier gas (air) was kept at 1000 sccm. For determining the optimum temperature of operation, the resistance and gas sensitivity of these samples was measured at different temperatures and different concentration levels of LPG. The LPG responds at 200° to 450°C. The sensitivity remains constant at 200 to 325°C temperature but above this temperature the sensitivity increased rapidly at 375°C and then decreased to 450°C. At different temperatures the sensitivity of samples exhibited the wave like shape due to the reaction with different oxygen species. The maximum sensitivity for doped ceramics is 11 and 8 at 375°C respectively.

Semiconductor gas sensors monitor changes in the conductance during the interaction of a chemically sensitive material such as SnO_2 with molecules to be detected in the gas phase; the reaction steps involved the low-temperature surface reactions and secondly, involved the high-temperature bulk reactions between point defects in the SnO_2 and oxygen (O_2) in gas phase. All of these reactions involved adsorbed negatively charged molecular (O^{2-}) or atomic (O^-) oxygen species as well as hydroxyl groups (OH) at different surface sites.

Conclusion

Cu and Zn doped ceramics, prepared by high temperature solid-state reaction techniques have an orthorhombic structure. Doping of transition metal oxides to SnO_2 dramatically influences the defect chemistry and the sintering behavior of SnO_2. Doping of Cu and Zn in SnO_2 exhibits many interesting features. The substitution of Sn ions by copper or zinc ions created more oxygen vacancies in the materials, which was good for sensor materials. From the present study we can say that the doping of Cu and Zn on SnO_2 enhances the electrical properties.

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