Irradiation effect on ethanol sensing response of zinc and tin composite oxide

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ABSTRACT

Sensing response of synthesized composite oxide of zinc and tin to ethanol vapor before and after irradiation has been reported in this paper. Composite oxide powder has been synthesized by a chemical route followed by calcination. For structural and morphological characterization, these powders were exposed to XRD and TEM analysis. To construct sensors,thick films of these powders were deposited on the alumina substrates having pre-deposited gold electrodes. Irradiation of fabricated sensors was carried out with 100 MeV O^{7+} ions at fluences of 1×10^{11}, 1×10^{12} and 1×10^{13} ions/cm^2 using UD15 Pelletron tandem accelerator at Inter University Accelerator Centre, New Delhi. The sensing response of these sensors at different temperatures to ethanol vapor was examined before and after irradiation. The results disclosed that sensing response remained same before and after irradiation signifying that Zn-Sn composite oxide is a radiation hard material.

Keywords: Gas sensor, irradiation effects, semiconducting oxide, nanocomposites, powder

1 Introduction

Number of workers throughout the world have been trying to improve the sensing behaviour of the gas sensors based upon semiconducting oxides. It has been found that the particle size reduction and gas diffusion control are the main parameters which influence the gas sensing response [1-3]. Basically, sensing is a surface controlled phenomenon, therefore to develop an improved gas sensor it is necessary to have a material composed of nanoparticles which ultimately offers large surface to volume ratio and a large number of active sites for gas sensing.Recently composite oxides of zinc and tin have proved their worth as the promising candidates for gas sensing applications [4]. For preparation of these composite materials, different researchers have tried various techniques [5-10]. Since the gas to be sensed encounters with sensing surface so it can be obviated that even slight modification in the surface may lead to drastic change in the sensing response of sensor. In the literature various techniques have been reported to modify the sensor surface. Irradiation of materials with swift heavy ions (SHI) is one of the effective techniques that can modify the surface of materials [11-14]. In one of our work we have reported sensing behaviour of nanosized zinc-tin oxide towards LPG and ethanol [15]. In this paper we are reporting the sensing behaviour of nanocomposite oxides of zinc and tin films and their modification caused by bombardment of 100 MeV O^{7+} ions.

2 Experimental Details

The zinc and tin composite oxide has been synthesized by following co-precipitation technique. We started with 0.1 M solution of zinc chloride and stannic chloride in distilled water to which ammonia solution was added drop wise with continuous stirring. The precipitates obtained were filtered and dried at 120^{o}C and powder obtained was further annealed for 3 hours at different temperatures such as 400, 600 and 800^{o}C. These powders were subjected to XRD and TEM for structural and morphological characterizations. To fabricate sensor, water based thick films of these powders were deposited on the alumina substrate having pre-deposited gold electrodes. These sensors were then exposed to 250 ppm of ethanol for optimizing the sensing properties. The sensing response S is defined as Ra/Rg, where Ra is the resistance of the sensor in the air and Rg is the resistance in the presence of known volume of test gas injected in the air. Irradiation of fabricated sensors was carried out with 100 O^{7+} ions at fluences of 1×10^{11}, 1×10^{12} and 1×10^{13} ions/cm^2 using UD15 Pelletron tandem accelerator at Inter University Accelerator Centre, New Delhi. These modified sensors were again subjected to the 250 ppm of ethanol and their sensing responses were compared with responses obtained before irradiation.

3 Results and Discussion

The crystalline phases of the powders annealed at temperatures from 400 to 800^{o}C are identified using X-Ray diffraction techniques, as shown in Figure 1. The powder heated at 400^{o}C for 3 hours is a mixture of ZnO, SnO_2 and Zn_2SnO_4, whereas $ZnSnO_3$ phase has just shown its existence. It can be clearly observed from the Figure 1 that at an annealing temperature of 400^{o}C,

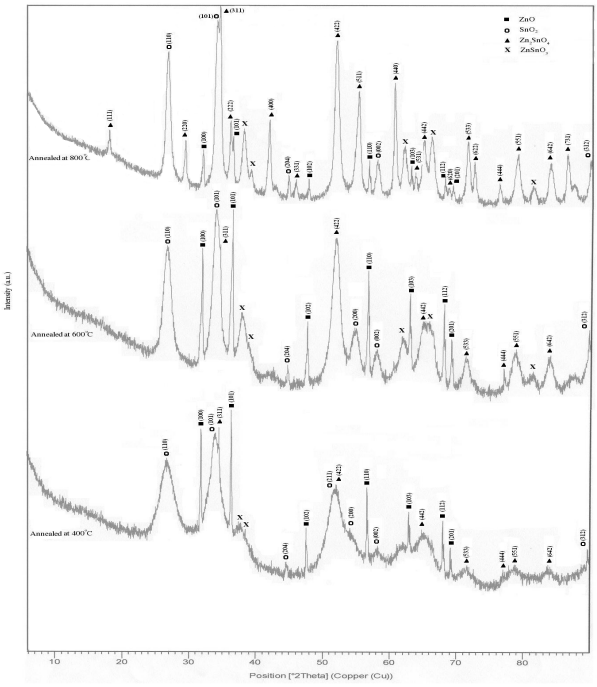

Figure 1: XRD image of zinc-tin composite oxides.

prominent phases are of pure ZnO and SnO_2, whereas composite oxides are scanty. At 600^{o}C the phases of composite oxide Zn_2SnO_4 have increased along with major phase of SnO_2 (tetragonal) in the blend instead of phases of ZnO. Moreover $ZnSnO_3$ phases have also increased under the influence of heat treatment. This increase can be interpreted as a one-way transfer of zinc to SnO_2 grains that is reaction proceeds only on the SnO_2 grains [4]. With the further increase in the heating temperature to 800^{o}C, phases of composite oxides grew at the expense of zinc, and Zn_2SnO_4 (cubic) has the most prominent peak in the blend whereas the phases of ZnO (hexagonal) have lost their prominence in the powder. Similarly perovskite phase of $ZnSnO_3$ has also improved significantly. This decrease in the amount of ZnO in the powder could be due to higher diffusion rate of zinc than that of tin in the overall solid-state reaction [4]. Hence one can clearly note from XRD image that composite oxides like Zn_2SnO_4 and $ZnSnO_3$ have grown at the cost of zinc whereas increased intensity of tin oxide peaks is only due to grain growth. Similar appearance of Zn_2SnO_4 phases at temperature above 700^{o}C have been reported by C. Liangyuan et.al [8] and Yu and Choi et.al [16] as well.

Figure 2 represents TEM images of thus prepared powders. In Figure 2(a) one can clearly see the highly agglomerated structures, where grains of zinc oxide and tin oxide have joined together to form the clusters in order to reduce the overall surface energy of small nanoparticles. We can see in Figure 2(b) that with increase of annealing temperature from 400 to 600^{o}C, the clusters

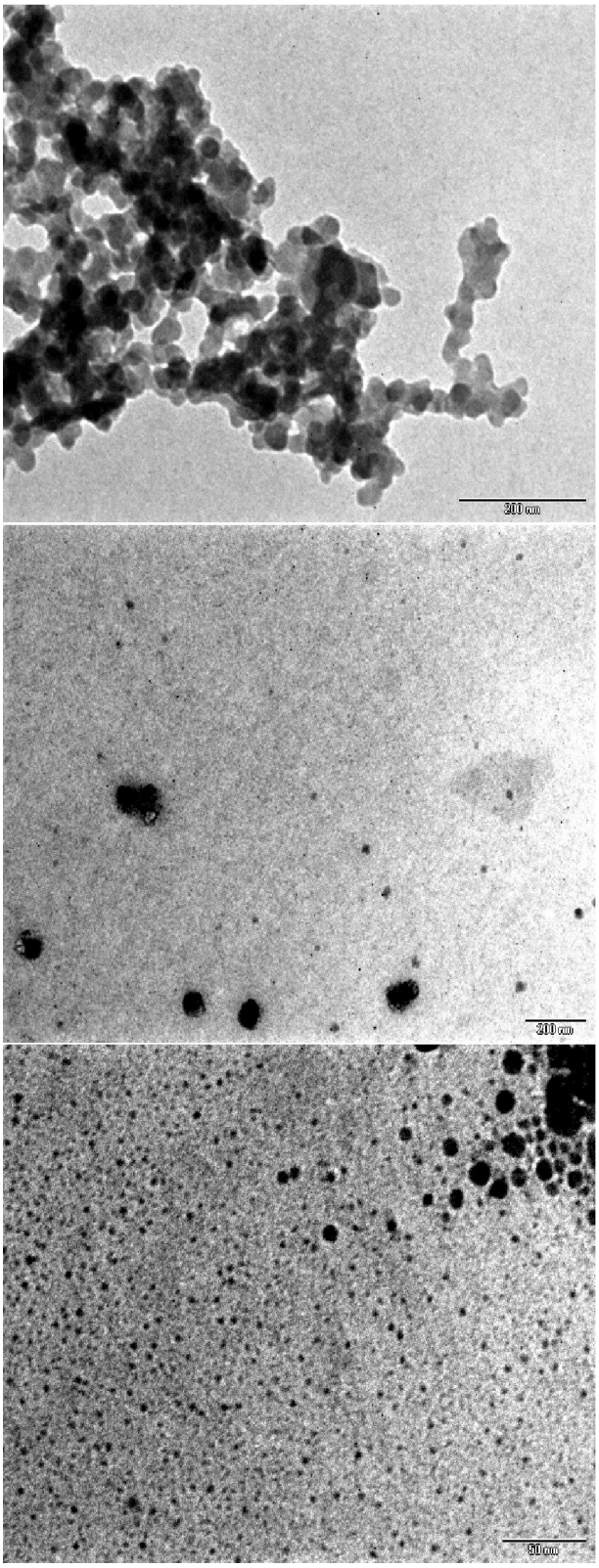

Figure 2: TEM images of zinc-tin composite oxides annealed at 400^{o}C (top), 600^{o}C (middle), and 800^{o}C (bottom).

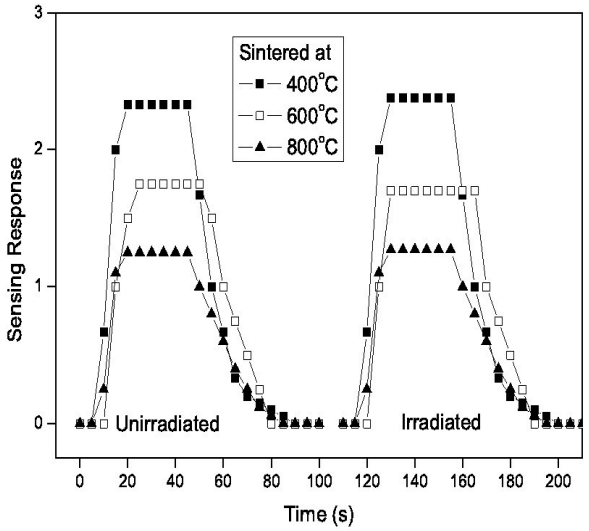

Figure 3: Sensing response of zinc-tin composite oxides.

have reduced which may be attributed to particle size increase, moreover the composite oxides Zn_2SnO_4 and $ZnSnO_3$ have also appeared as observed in XRD graph. Figure 2(c) represents powder annealed at 800^{o}C, the particles are spherical in shape and uniform in size, this may be the fact that zinc particles have diffused with tin oxide and moreover a temperature of 800^{o}C may have provided sufficient energy for Ostwald ripening to come into play and hence thermally stable phases of Zn_2SnO_4 and $ZnSnO_3$ have appeared and particles are uniform in size. Figure 3 represents the sensing response of synthesized powders to 250 ppm of ethanol at optimum operating temperatures of 375^{o}C. We observe that sample annealed at 800^{o}C has low sensing response than samples treated at 600 and 400^{o}C. This behaviour is due to the fact that annealing has promoted the grain growth, which in turn led to decrease in the sensing response. The sensing response of these sensors to ethanol vapours were investigated before and after irradiation. From Figure 3 one can note that the sensing response of sensors for 250 ppm of ethanol remained same before and after irradiation. This observation hints at the inference that the synthesized Zn-Sn composite oxide materials are not at all damaged by the O^{7+} irradiation. In one of our works [17] we have reported that with the passage of ions through ZnO, the lattice or crystals are not damaged at all. It is known that ZnO bonds exhibit a high degree of ionicity, and therefore an easier recovery than covalent bonds [18, 19]. It is also mentioned in the literature that ZnO is radiation hard material [20]. As discussed earlier that Zn-Sn composite oxide has grown on the expense of ZnO, so ZnO could have owed the high degree of ionicity to the bonds in composite oxide resulting in the easier recovery after the damage caused by the irradiation. As sensing is predominantly dependent upon the material structure and surface morphology therefore unchanged sensing response of Zn-Sn composite oxide sensors even after O^{7+} irradiation interprets that no structural modification have been induced by irradiation. Though it is too early conclude, but it seems that Zn-Sn composite oxide is immune to the swift heavy ion irradiation damage.

4 Conclusions

In conclusion, using the simple co-precipitation technique nano sized composite oxides of zinc and tin have been synthesized. Under the influence of annealing the phases of Zn_2SnO_4 and $ZnSnO_3$ have grown at the expense of zinc, and at 800^{o}C these phases constituent the major portion of the powder. The results showed that sensing response remained same before and after irradiation indicating that Zn-Sn composite oxide is radiation prone material.

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