Doping Effects on LPG Gas Sensing Properties of Spray Pyrolyzed ZnO:Cu/CuO Films

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Abstract

A spray pyrolysis system was used to obtain films of ZnO doped with different wt. % of $CuCl_2$ concentration on thoroughly cleaned glass substrates. The X-ray diffraction and scanning electron microscopy were used to study the phase and surface morphology of the films. The sensitivity of the films was studied for LPG gas at a fixed concentration of 1000 ppm. It is noted that, the spray pyrolysis (SP) technique offers an extremely easy way to prepare films with dopants, virtually any element in any proportion by merely adding it in a spray solution. The deposition rate and thickness of the film can easily be controlled for a wide range. It also offers an opportunity to have reactions at low temperatures (300 ^oC). In present work, the high sensitivity to LPG gas is found for ZnO films modified with 1 wt. % of $CuCl_2$.

Keywords: Zn ¸Cu, Metal oxide, spray pyrolysis

Introduction

Semiconductor inorganic thin/thick films play a central role in the development of the novel technology that modern society demands, mainly in the field of optic and electronic devices. The preparation of thin films of the size of a nanometer is important because of their potential applications in the various fields of science and technology, including the diverse fields of electronics, optics, space science, aircraft science, defense and other industries [1-4]. There are number of physical and chemical routes for preparing thin films, like pulsed laser deposition, ion beam sputtering, thermal evaporation, vacuum deposition, chemical vapor deposition, co-precipitation, sol-gel, chemical bath deposition etc. Owing to simplicity and inexpensiveness, the spray pyrolysis technique (SPT) is a better chemical method at a lower cost for the preparation of thin/thick films with a larger area. Also, it provides an easy way to dope any element in a ratio of required proportion through the solution medium. This method is convenient for preparing pinhole free, homogenous, smoother thin films with the required thickness [3]. During the last decade, a number of researchers have employed the spray pyrolysis technique for the preparation of different kinds of nanoparticles. Wei-Ning Wang et al. [4] prepared the Ni nanoparticle by using the low pressure SPT. These workers have studied the effect of pressure, the flow rate of carrier gas, the concentration of pressure and types of reducing agents on the size, morphology and crystalline nature of nanoparticles. Eslamian et al. [5] developed a mathematical model for the evaporation of the micro and nano size solution droplets. The model is used to predict whether the particles are fully filled or hollow. Kikuo Okuyama et al. [6] studied the preparation of regulated nanoparticles by means of spray drying process using a colloidal mixture as a precursor. In the SP technique, various parameters like air pressure, deposition rate, substrate temperature, distance between nozzles to substrate, cooling rate after deposition also affect the physical, electrical and optical properties of the thin films. The film properties are sensitive not only to their structure but also to many other parameters including thickness, surface states, morphology etc [7 - 9]. The SP technique has been found to be useful for the preparation of metallic oxides, semi-conducting oxides, binary and ternary chalcogenides and superconducting thin films of various materials [9 - 14].

In the present work, we have fabricated an SP technique instrument for the preparation of thin films. Using the above instrument, different wt. % $CuCl_2$ modified ZnO are prepared. The LPG gas sensing properties of these films are reported in present paper.

Experimental Work

Fabrication of Spray Pyrolysis System

Figure 1 shows the schematic diagram of a spray pyrolysis system. This contains a self designed spray gun, a thermal radiation control furnace for heating the substrate. A mechanical system includes moving spray gun platform, thermocouple, temperature controller and air compressor. To measure the flow of solution and air flow meters are used. The spraying system and furnace are kept inside airtight heat resistance asbestos of size 40 x 40 x 40 cm^3 and wooden chamber of size 60 x 60 x 60 cm^3. The outlet of the box is fitted with an exhaust fan to remove the toxic gases produced during the decomposition of the spray solution. The inner surface of the box is protected by using glass wool to reduce the heat loss through the surface as can be seen in figure below.

Kinetics involved in Spray Pyrolysis

The basic principle involved in spray pyrolysis is that when a droplet of the spray solution reaches the hot substrate, owing to the pyrolytic decomposition of the solution, well adherent film is deposited. In this process, the solution is pulverized by means of air and arrives on the substrate placed inside the furnace in the form of fine drops known as aerosols, which form a thin layer at the substrates. The phenomenon for the preparation of a metal oxide thin film depends on the surface hydrolysis of metal chloride on a heated substrate surface in accordance with the equation [8],

$$MCl_x + yH_2O \rightarrow MO_y + xHCl \qquad \text{--- (1)}$$

where, M is the host metal such as Zn, Cu, etc. of the oxide film. The spray nozzle with the help of the carrier gases (ambient air in the present system) accomplishes the atomization of the chemical solution into aerosols. The temperature of the substrate is maintained at a constant value by using a temperature controlled furnace or hot plate. In general, the films grown at a substrate temperature less than 200 ^{o}C are amorphous in nature. To get polycrystalline films, one needs to employ higher substrate temperature or post annealing treatment. The film formation depends upon the droplet leading to reaction and solvent evaporation, which relates to the droplet size. When the droplet approaches the substrate just before the solvent is completely removed, that is the ideal condition for the preparation of the film.

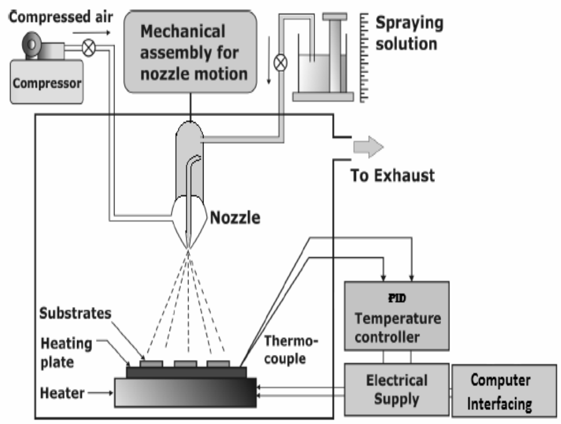

Figure 1. Schematic diagram of home-built spray pyrolysis system

Deposition of films

For the deposition of Cu/CuO doped films (ZnO:Cu/CuO films), a above mentioned home-built spray pyrolysis system consisting of spray gun, heating element with insulating pad and chromel-alumel thermocouple for temperature monitoring was used. One mole solution of $ZnCl_2$ was prepared in double distilled water to which different percentage (i.e. 1, 2, 3, 4, 5 wt. %) of $CuCl_2.4H_2O$ solution prepared in distilled water was added. The resultant mixture solution was further added to 70 % ethanol carrier concentration. The glass substrates were cleaned by using soap solution followed by boiling in dilute hydrochloric for 30 min. and finally ultrasonically rinsing in double distilled water for 15 min. The thoroughly cleaned glass substrates were used for the deposition of ZnO:Cu/CuO films. The resultant mixture solution in ethanol with known wt. % of $CuCl_2$ was sprayed with a flow rate of ~ 9 ml per minute on to the substrate maintained at 300 ^{o}C as a deposition temperature.

The ZnO:Cu/CuO films were deposited at different wt. % of $CuCl_2$ on thoroughly cleaned glass substrates by using process parameters: (i) spray gun nozzle - substrate distance = 30 cm, (ii) carrier gas (compressed air) flow rate = 20 lpm, (iii) deposition time = 5 min., (iv) solution flow rate = 9 ml/min. and (v) substrate temperature (T_s) = 300 ^{0}C. After each deposition, the films were cooled naturally to the room temperature (RT).

The resultant ZnO:Cu/CuO films were characterized by using the different physical techniques.

The structural analysis of films was done by using X-ray diffraction patterns recorded with Bruker D8 Advance (filtered CuK_α radiation, $\lambda = 1.5406$ Å) machine. The surface morphological analysis of films was done by using scanning electron microscope (JEOL JSM-6360-LA and Philips XL - 30).

The sensing properties of the resultant ZnO:Cu/CuO film were studied by recording the change in the resistance of the film when exposed to LPG and ambient. For the resistance measurement, the input circuit voltage was applied across half bridge of sample (R_s) and reference resistance (R_f). The resistance of the film sample was obtained by measuring the voltage across the R_f when exposed to LPG and ambient. The resistance variation was measured at various temperatures and the sensitivity factor (S.F.) was calculated by using the relation,

$$S.F. = \frac{R_g}{R_a} x\,100 \qquad \text{--- (2)}$$

where, R_a is the resistance of sensor in air and R_g is the resistance of sensor in LPG.

Results and Discussions

Figure 1 shows the XRD pattern of typical 1 wt. % $CuCl_2$ modified ZnO film. It is shown that, compared with the standard PDF card (JCPDS 36 - 1451), single strong peak can be ascribed to ZnO characteristic diffraction peak with a hexagonal wurtzite structure. The single strong (002) diffraction peak of ZnO:Cu/CuO film indicates that ZnO growth orientation of the c-axis is taken place.

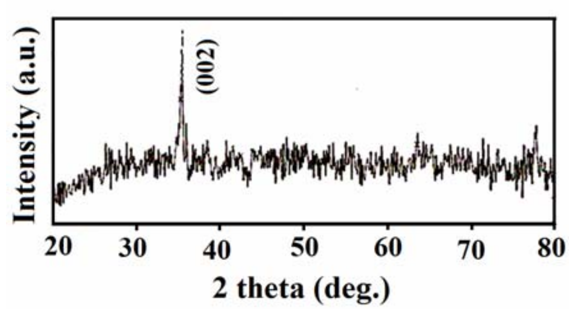

Figure 2. XRD pattern for 1 % wt. of $CuCl_2$ modified ZnO film

The morphological analysis and with particle sizes identification of the films is done by using the scanning electron microscopy (SEM) technique. Figure 3 show the SEM image of 1 % wt. $CuCl_2$ modified ZnO film. The SEM image shows the mixed -morphology spherical and rod shaped. It shows the crystallization of ZnO particles with the rod shape. The spherical particles may be due to the crystallization of CuO. The size ZnO rods is 1 μm in diameter and 6 - 8 μm in length. The size of spherical particles is 20 - 50 nm. Qualitatively, the surface roughness is high, whereas surface densification is low for a given resultant film.

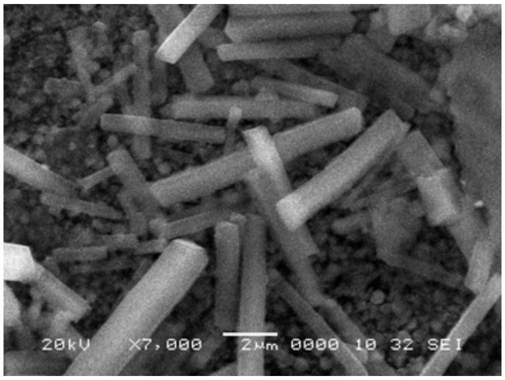

Figure 3. Scanning electron microphotograph of 1 % wt. of $CuCl_2$ modified ZnO film

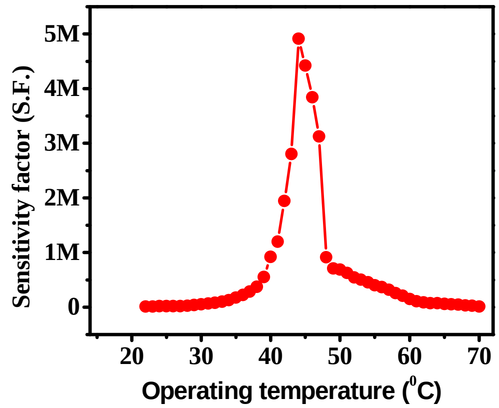

Figure 4. Variation of sensitivity factor with operating temperature for 1 % wt. of $CuCl_2$ modified ZnO film at 1000 ppm of LPG gas concentration

Figure 4 shows the variation of sensitivity factor with operating temperature for 1 % wt. $CuCl_2$ modified ZnO film at 1000 ppm of LPG gas. From Figure 4, sensitivity factor is found to be very high (S.F. = 5×10^6) with operating temperature of 44 ^{0}C for 1 % wt. $CuCl_2$ modified ZnO film at 1000 ppm of LPG gas. Figure 5 shows the Variation of sensitivity factor (S.F.) with wt. % of $CuCl_2$ in ZnO:Cu/CuO films at 1000 ppm of LPG gas concentration. The sensitivity factor (S.F.) is found to be very high for ZnO:Cu/CuO film with 1 wt. % of $CuCl_2$ as compared to ZnO:Cu/CuO films prepared with 2, 3, 4, 5, and 6 wt. % of $CuCl_2$. Further, ZnO:Cu/CuO films prepared with 4 wt. % of $CuCl_2$ also shows the noticeable sensitivity (S.F. = 230) as compared to ZnO:Cu/CuO films prepared with 0, 2, 3 and 5 wt. % of $CuCl_2$. In comparison with More et al. [1, 2], the increase LPG sensitivity properties of samples prepared by spray pyrolysis technique may be due to the smaller surface area leading to the higher sensitivity. The higher sensitivity of samples prepared in present work may be due to better microstructure and smaller grain size.

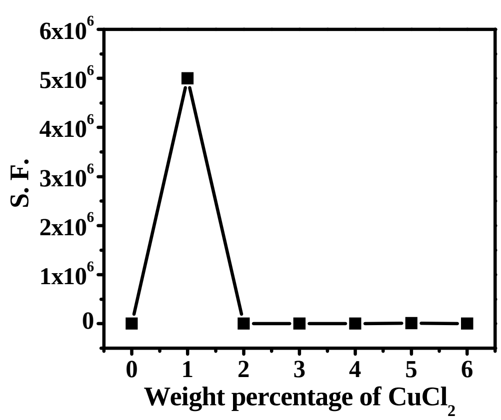

Figure 5. Variation of sensitivity factor with wt. % of $CuCl_2$ in ZnO:Cu/CuO films at 1000 ppm of LPG gas concentration

Conclusions

The versatility of the home-made spray pyrolysis unit is demonstrated by way of preparing reasonably good quality films of ZnO:Cu/CuO. The films thus prepared have high homogeneity over large areas, a single phase as ascertained by XRD and a reasonable systematic in thickness. Worth mentioning is the drop in resistivity of $CuCl_2$ doped ZnO by about 5 orders of magnitude, quite reasonable for possible sensing applications.

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