Studies on Al-doped zinc oxide thin film based LPG sensors

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ABSTRACT

Al-doped ZnO thin films were prepared by chemical spray pyrolysis technique. The dopant concentration (Al/Zn at.%) was varied from 0 to 1.5 at.%. Structural analyses of the films reveal that all the films are polycrystalline in nature with (002) preferred orientation. The lattice constants calculated from the most prominent peaks are found to be in good agreement with ICDD Reference Pattern: Zinc Oxide, 01-080-0074 (a = 3.2535 Å and c = 5.2151 Å). It is observed that compared to undoped ZnO film, Al-doped films show high sensitivity to LPG. Among all the doped films studied, 0.5 at.% Al-doped ZnO film shows the maximum sensitivity (~ 89 %) at 325 ^{0}C to 1 vol.% concentration of LPG in air. Further, the response and recovery of the films to LPG are found to be fast at higher operating temperatures.

Keywords: Zinc oxide films, spray pyrolysis, LPG sensors

1. INTRODUCTION

Zinc oxide (ZnO) is a promising material for gas sensor applications. Thin films of ZnO (doped and undoped) have been investigated by many researchers for detection of toxic pollutant gases, combustible gases and organic vapours which is a subject of growing importance in both domestic and industrial environments. Mitra et al [1, 2] have studied the LPG sensing properties of zinc oxide thin film sensitized with Pd layer. They reported a sensitivity of 88% for 1.6 vol.% of LPG in air at 250 ^{0}C. Shinde et al [3] have examined the effect of molarity of precursor solution on the LPG sensing properties of spray deposited ZnO films and observed the maximum sensitivity of 43% for 0.4 vol.% of LPG at the operating temperature of 400 ^{0}C. ZnO thin film ammonia gas sensors were investigated by Nanto et al [4]. Sahay et al [5, 6] have studied the sprayed ZnO thin films for detection of ethanol and acetone vapour. Influence of Al, In, Cu, Fe and Sn dopants on the response of ZnO thin film gas sensor to ethanol vapour has been studied by Paraguay et al [7]. In the work reported here, the structural characteristics of the Al-doped films and their gas sensing properties to LPG have been discussed.

2. EXPERIMENTAL

The films were deposited on clean glass substrates by spray pyrolysis technique which involved the decomposition of an aqueous solution of high purity zinc acetate (Merck, India). Aluminium chloride was used as the source of dopant. The dopant concentration (Al/Zn at.%) was varied from 0 to 1.5 at.%. The atomization of the solution into a spray of fine droplets was carried out by the spray nozzle, with the help of compressed air as carrier gas. The detailed description of the spray system has been reported elsewhere [8]. Substrate temperature was found to be the most important process parameter in regards to film preparation for gas sensor applications. During the course of spray, the substrate was kept at a constant temperature of (410 ± 10) ^{0}C. Film thickness was determined by the weight-difference method using an electronic high precision balance (Citizen, Model: CY 204).

Structural analysis of the sprayed films was carried out using PANalytical X'Pert Pro X-ray Diffractometer with CuKα radiation (λ = 1.5418 Å) as X-ray source at 40 kV and 30 mA in the scanning angle (2θ) from 30^0 to 80^0 with scan speed 0.02 ^{0}/s. High conducting silver paste was used to make ohmic contacts on both the ends of the films to carry out electrical measurements on them. The film was mounted on a home-made two-probe assembly placed into a silica tube which was inserted coaxially inside a resistance-heated furnace. The electrical resistance of the films was measured

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before and after exposure to LPG using a Keithley System Electrometer (Model: 6514). The sensitivity of the film was determined at different operating temperatures in the range 275-400 ^{0}C for various volume concentrations of LPG in air. Before exposing to LPG, the film was allowed to equilibrate at each operating temperature for about 15 minutes.

3. RESULTS AND DISCUSSION

3.1 ZnO film formation

When aerosol droplets arrived close to the heated glass substrates, a pyrolytic process took place and a highly adherent film of ZnO formed on the substrates. Possible reaction mechanisms are as follows [9]:

$$Zn(CH_3COO)_2 \text{ [solid near substrate]} \xrightarrow{\text{Heat}} 4\ Zn(CH_3COO)_2 \text{ [gas near substrate]} + H_2O$$

$$\xrightarrow{\text{Adsorption}} Zn_4O(CH_3COO)_6 \text{ [adsorbed/ substrate]} + 2\ CH_3COOH \text{ [gas near substrate]} \uparrow$$

and

$$Zn_4O(CH_3COO)_6 \text{ [adsorbed/substrate]} + 3H_2O \longrightarrow 4\ ZnO \text{ [film/substrate]} + 6\ CH_3COOH \text{ [gas]}\uparrow$$

The films thus prepared were almost clear and transparent in physical appearance, and undergone for structural analysis.

3.2 Structural analysis

Fig. 1 shows the X-ray diffraction patterns of the typical Al-doped films. The observed XRD patterns are found to

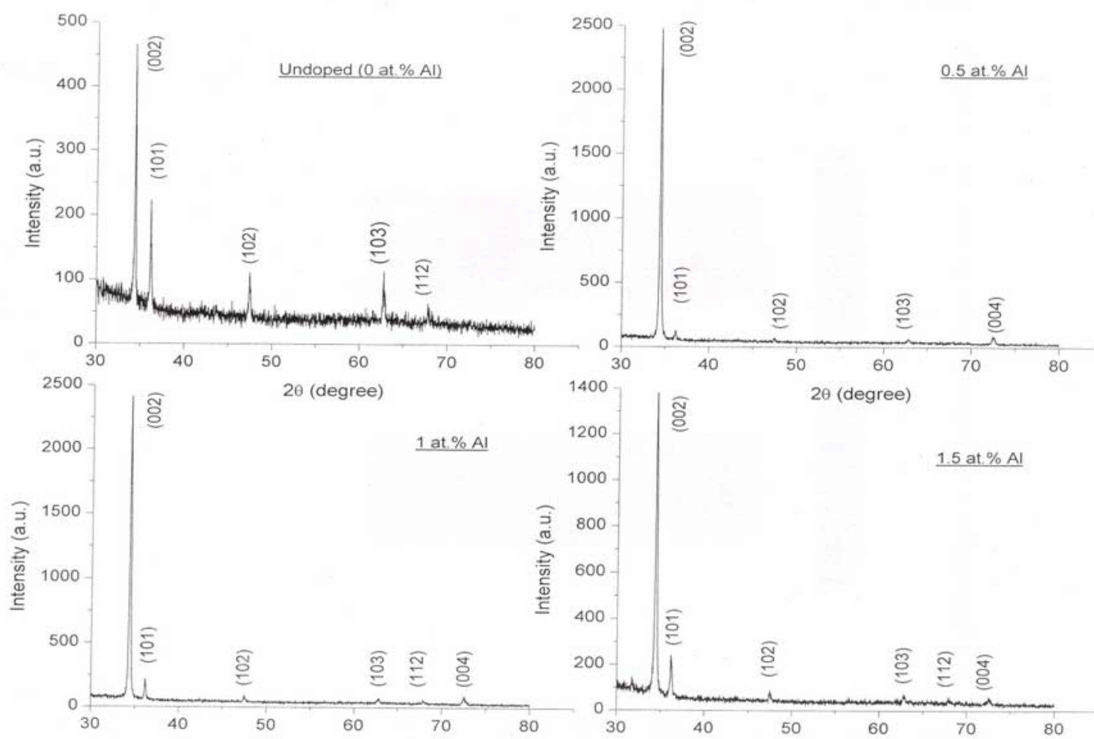

Fig.1: XRD patterns of the typical Al-doped ZnO thin films.

match with the ICDD Reference Pattern: Zinc Oxide, 01-080-0074, using X'Pert HighScore software. All the films are found to be polycrystalline in nature, possessing hexagonal wurtzite structure. No phase corresponding to aluminium or other aluminium compound is observed in the XRD patterns. It is seen in the figure that all the films exhibit a strong orientation along c-axis (002) perpendicular to the substrate surface. With increasing aluminium concentration, the positions of the measured peaks do not change significantly but the intensity of (002) peak improves. For all the films, other peaks corresponding to (101), (102), (103), (112) planes etc. are present with low relative intensities. Similar results for the spray deposited ZnO films have been reported by other researchers [9 - 11].

The crystallite size D is calculated using the Scherrer formula [12]

$$D = 0.9 \lambda / (\beta \cos\theta) \qquad \ldots\ldots \qquad \ldots\ldots \qquad \ldots\ldots \qquad \ldots\ldots (1)$$

where λ is wavelength of the incident x-ray (λ = 1.5418 Å), β is the full width at half maximum (FWHM), in radians, of the maximum intensity peak and θ is the angle at which the maximum peak occurs. It is observed that compared to undoped film, the crystallite size in the doped films decreases.

3.3 LPG sensing properties

It is observed that compared to undoped ZnO film, Al-doping enhances the sensitivity of the films to LPG. Among all the films, 0.5 at.% Al-doped ZnO film shows the maximum sensitivity (~ 89 %) at 325 ^{0}C to 1 vol.% concentration of LPG in air. Fig. 2 represents the sensitivity characteristics of this particular film as a function of the operating temperatures for three different volume concentrations namely, 0.5, 0.75 and 1 % of LPG in air. At low operating temperature of 275 ^{0}C, the sensitivity of the films to LPG is restricted by the speed of the chemical reaction because the gas molecules do not have enough thermal energy to react with the surface adsorbed oxygen species. In fact, during adsorption of atmospheric oxygen on the film surface, a potential barrier to charge transport is developed. At higher operating temperatures the thermal energy

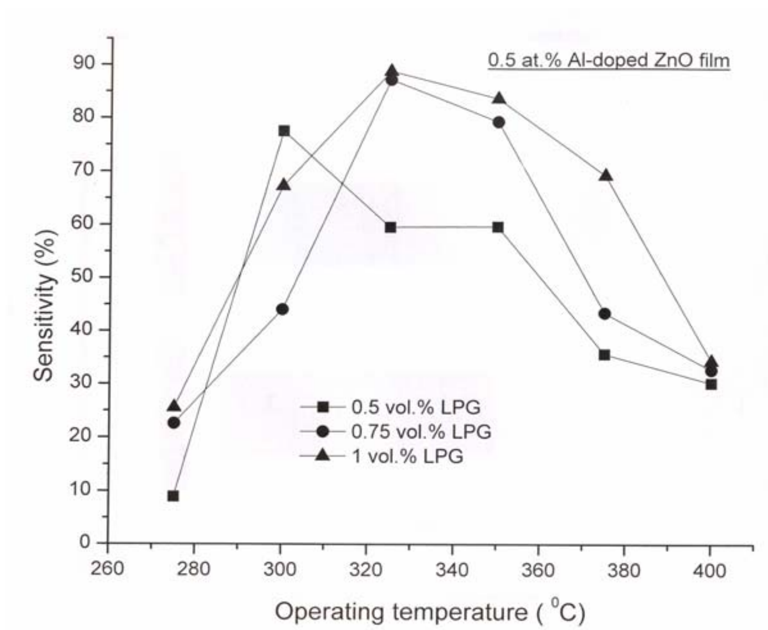

Fig. 2: Sensitivity vs. operating temperatures

obtained is high enough to overcome the potential barrier and thus the electron concentration increases significantly due to sensing reaction. This, in turn, leads to increase in sensitivity of the films.

LPG-sensing mechanism of the films may be explained as follows: The adsorption of atmospheric oxygen on the film surface forms ionic species such as O_2^- and O^- which acquire electrons from the conduction band. The reaction kinematics is as follows [3, 5]:

$$O_2\,(gas) \leftrightarrow O_2\,(ads)$$
$$O_2\,(ads) + e^- \leftrightarrow O_2^-\,(ads)$$
$$O_2^-\,(ads) + e^- \leftrightarrow 2\,O^-\,(ads)$$

It is well known that LPG consists of hydrocarbons like CH_4, C_3H_8, C_4H_{10}, etc. Although reaction mechanism for LPG is quite complex and proceeds through several intermediates, but the overall reaction of LPG molecules with adsorbed oxygen species may be explained as follows [3]:

$$C_nH_{2n+2} + 2O^- \leftrightarrow H_2O + C_nH_{2n} - O + e^-$$

where C_nH_{2n+2} represents the CH_4, C_3H_8 and C_4H_{10}. Thus, during oxidation LPG liberates electrons into the conduction band, thereby decreasing the resistance of the film upon exposure to LPG.

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