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LPG sensing Properties of Ga doped ZnO Thin Films by Spray Pyrolysis Technique

M. A. Barote,E. U. Masumdar

Department of Physics, Azad Mahavidyalaya, Ausa-413520, Maharashtra, India.

Abstract: The Ga:ZnO films were deposited onto glass substrates by spray pyrolysisat optimized temperature of 450 ^{0}C by varying the gallium concentration form 1 to 5 at%.It was observed that the response of the films increased till 573 K and decreased beyond 573 K in the presence of LPG.The Ga:ZnO thin films exhibited good sensitivity and rapid response–recovery characteristics to LPG

1. Introduction

Transparent conducting oxides (TCOs) have been widely applied to the optoelectronic devices such as solar cells, flat panel displays and flexible displays [1,2]. Among the various TCOs, indium tin oxide (ITO) has been widely used in display applications because of its high optical transmittance and high electrical conductivity. However, other TCOs materials such as ZnO, SnO_2, and TiO_2 have been steadily investigated as an substituent for the expensive ITO. In particular, ZnO is one of the most interesting materials having the optimum electrical and optical properties as well as economic values. Recently, the Ga-doped ZnO has been spotlighted as a promising TCO material because of an improved conductivity [3-4].

Ga-doped ZnO (GZO) has drawn attentions recently because it has some advantages over AZO. Whereas AZO and GZO TCOs have comparable electrical properties [5], Ga dopant is less reactive with oxygen compared with Al dopant meaning that it can function as better dopant within ZnO [6]. In addition, the Ga- O covalent bond length of 1.92A˚, which is smaller than that of Zn–O (1.97A˚), is expected to cause smaller deformation of ZnO lattice when Ga3+ ions substitute Zn2+ site in case of high doping concentration [6]. Concerning the use of Ga as the dopant to enhance electrical properties, it has been reported that resistivity of GZO films decreased with increasing film thickness whereas the transmittance of films decreased as the film thickness increased [7]. On the

practical side, increasing the thickness of the GZO TCO film would result in rising cost and reduced throughput. Further, as in the case of the AZO films, it would be possible to improve the electrical properties of GZO films by post-annealing treatment in hydrogen atmosphere [8-12].

2. Experimental details

In this investigation, the ZnO:Ga thin films were deposited on preheated amorphous glass substrates using P C controlled spray pyrolysis technique supplied by Holmark (Cochin, India). A solution of zinc acetate in a mixed solvent of 75% methanol and 25% double distilled water was used as a precursor. Compressed air was used as the carrier gas. The GZO films were deposited at optimized temperature of 450 ^{0}C by varying the gallium concentration form 1 to 5 at%. The precursor solution was atomized into the fine droplets and carried to the preheated glass substrates.

LPG sensing properties of ZnO:Ga thin films were studied for various parameters.

3. Results and discussion

LPG sensing properties

(a) Effect of temperature and LPG concentration

The gas response depends on factors, such as morphology, dopants and their concentrations, thickness of film and operating temperatures. Fig. 1 shows the response as a function of operating temperature for Ga: ZnO thin films obtained by spraying zinc acetate solutions of different Ga concentrations upon exposure to 1000 ppm LPG.

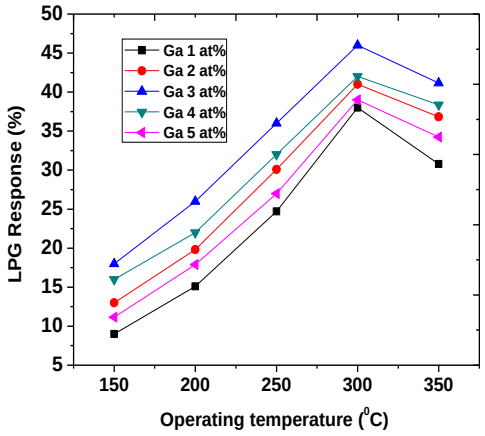

Figure 1: The variation of LPG response of Ga: ZnO film for different Ga at% to 1000 ppm LPG at different temperatures.

It was observed that the response of the films increased till 573 K and decreased beyond 573 K in the presence of LPG. This trend is attributed to the fact that at lower operating temperatures (below 573 K) the LPG molecules did not have enough thermal energy to react with the chemisorbed oxygen species. But at higher operating temperatures (above 573 K) the thermal energy obtained is high enough to overcome the space–charge region, which leads to a significant increase in the electron concentration on the surface and hence increased response. Further, response of the sensor element depends on the rate of the chemical reaction on the surface and the diffusion on the surface. On the other hand, at a temperature of 573 K, both the rate of the chemical reaction and diffusion becomes equal, allowing the sensor to attain a maximum response [13-15]. Hence 573 K was

fixed as the operating temperature throughout the sensing studies.

Further, Fig. 2 shows the gas response as a function of LPG concentration at 573 K. The figure reveals that the response increased from 10 to 46% as the LPG concentration increased from 250 to 1000 ppm. However, at higher LPG concentrations the increase in gas response value was gradual and saturated for LPG concentrations more than 1000 ppm. The response of a sensor depends on removal of adsorbed oxygen molecules by reaction with a target gas and generation of electrons. For a small concentration of gas exposed on a fixed surface area of a sample, there is a lower coverage of gas molecules on the surface and hence lower surface reaction occurred. An increase in gas concentration increases the surface reaction due to a larger surface coverage. A further increase in surface reaction will be gradual when the saturation point on the coverage of molecules is reached. The LPG-sensing mechanism of the ZnO films may be explained as follows. The adsorption of atmospheric oxygen on the ZnO film surface forms ionic species such as O_2^- and O^- which acquire electrons from the conduction band [16-18].

(b) Dynamic gas response transients of Ga: ZnO film

Fig. 3 shows the dynamic gas response transients of Ga: ZnO films of different Ga concentrations upon exposure to 1000 ppm of LPG at 573 K. It is observed from the above Fig. 3 that as Ga % is increase the LPG response increased up to 3 at % and further increase in doping level gas response decreased. The maximum response was obtained with film Ga 3 at%. The grain size and porosity of the film played an important role [14]. For film Ga 3 at% non-spherical grains were observed. As exposure area of film Ga 3 at% increased, the response was gradually increased.

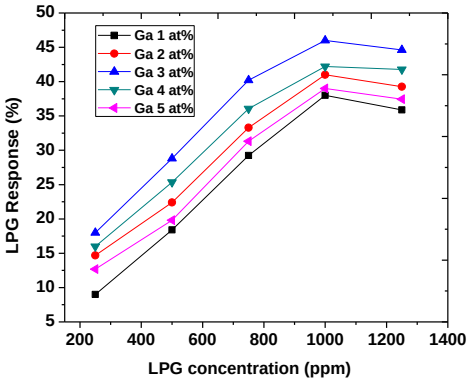

Figure 2: The variation of LPG response of Ga: ZnO film to LPG of different gas concentrations

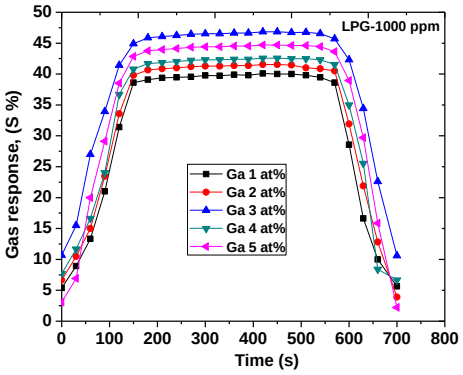

Figure 3: Dynamic LPG transient response of ZnO films for different In at% upon exposure of 1000 ppm LPG at an operating temperature of 573 K.

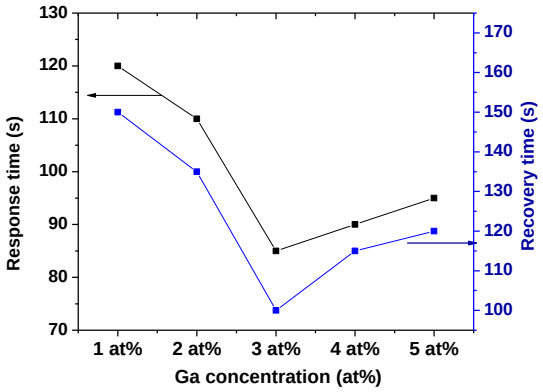

Figure 4: The variation of response and recovery time periods of ZnO films for different Ga at% upon exposure of 1000 ppm LPG.

(c) Response and recovery time periods

Fig. 4 shows the variation of response and recovery time with film having different Ga at% at 573 K. It is observed that both the response and recovery times decrease first with increasing Ga percentage and again increase with the further increase in Ga concentration. The smallest response time of 75 s and the recovery time of 100 s obtained for sample with 3 at% might be due to nano-sized grains which is not able to trap gas molecules.The response–recovery times of the 3 at% Ga doped ZnO sensor are shorter than the other one, which may be caused from the special doping structure and the different ability of electronic conduction, and which is shorter than the most reported results of doping sensors. This seems to show that 3 at% Ga doped ZnO are more suitable to be used as LPG sensor.

4. Conclusions

The effect of Ga doping on the LPG sensing characteristics of ZnO films preparedby spray pyrolysis was studied. It is found that response of the sensor element depends on the rate of the chemical reaction on the surface and the diffusion on the surface.The response increased from 10 to 46% as the LPG concentration increased from 250 to 1000 ppm.. The smallest response time of 75 s and the recovery time of 100 s obtained for sample with 3 at%. It is observed that the Ga doped ZnO are more suitable to be used as LPG sensor

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