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Ethanol Sensing Properties of F Doped ZnO Thin Films by Spray Pyrolysis

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Abstract:-**The F doped ZnO thin films were deposited on preheated amorphous glass substrates using spray pyrolysis technique. Among all the deposited thin films, the 4 at% F-doped ZnO film shows the maximum response (~20.5%) at 300 °C to 1000 ppm of Ethanol in air. The response time of 145 s and corresponding recovery time is 155 s is observed for 4% F doped ZnO thin film.**

Keywords: ZnO thin films, recovery time, response time

1. INTRODUCTION

Doped ZnO films offer a promising alternative to indium tin oxide (ITO) as a transparent conducting front contact layer in CdTe/CdS solar cells. The substitutional doping of ZnO films with group III metals such as Al, B and Ga has been widely reported [1–5], however out-diffusion of the electrically active metal dopants during subsequent cell fabrication procedures can lead to detrimental effects on device performance. It has been shown, using reactive RF sputtering, that ZnO films can instead be doped with fluorine and maintain comparable electrical and optical properties to those of the group III doped films [6-9]. Such films should be better suited for maintaining stability in CdTe/CdS solar cells where the diffusion of F out of the layer during subsequent high temperature fabrication of CdS and CdTe layers is unlikely to cause a significant degradation in device performance [10-12]. Apart from the academic interest, the fluorine doping has several potential advantages over the well-known and successful In-doping, such as low cost and abundance. More over fluorine does not introduce significant perturbation into the conduction band, due to the size compatibility of the oxygen and fluorine atoms [13-14]. Fluorine was expected to occupy the oxygen site in ZnO and hence promoting the conductivity of the film [15].

2. EXPERIMENTAL DETAILS

The F-doped ZnO films were deposited onto amorphous glass substrates, chemically cleaned, using spray pyrolysis method at 450 ^{0}C substrate temperature. 0.5M solution of zinc acetate dehydrate [$Zn(CH_3COO)_2.2H_2O$] diluted in methanol and deionized water (3:1) was used for all the films, and ammonium fluoride (FNH_4) was added to starting solution for fluorine-doping. Zinc acetate dehydrated and ammonium fluoride solutions were mixed together in different volume proportions ranging from 1 at% to 5 at% in steps of 1%. Air was used as the carrier gas, pressure at 0.2 bar. The ultrasonic nozzle to substrate distance was 28 cm and during deposition, solution flow rate was held constant at 3 ml/min.

3. RESULTS AND DISCUSSIONS

(a) Effect of temperature and Ethanol concentration

Fig. 1 represents the sensing characteristics of the F-doped ZnO films as a function of the operating temperature for 1000 ppm concentrations of Ethanol in air. It is observed that F dopant enhances the response of the films to Ethanol. Among all the films, the 4 at% F-doped ZnO film shows the maximum response (~20.5%) at 300 °C to 1000 ppm of Ethanol in air.

Fig. 2 represents the sensing characteristics of the F doped ZnO film as a function of Ethanol concentration in air at different F at%. It is observed in the figure that F concentration increased, the response increases rapidly in the lower concentration region of Ethanol, while it increases gradually at higher concentrations of Ethanol. For a low concentration (250 ppm), there is a smaller surface coverage of Ethanol molecules on the film and hence the surface reaction proceeds slowly. On an increase in gas concentration to 1000 ppm the surface reaction increases due to a larger surface coverage of Ethanol molecules, resulting in a rapid increase in response. On a further increase in gas concentration to 1250 ppm, the surface coverage of Ethanol molecules on the film begins to decrease which leads to a gradual decrease in response.

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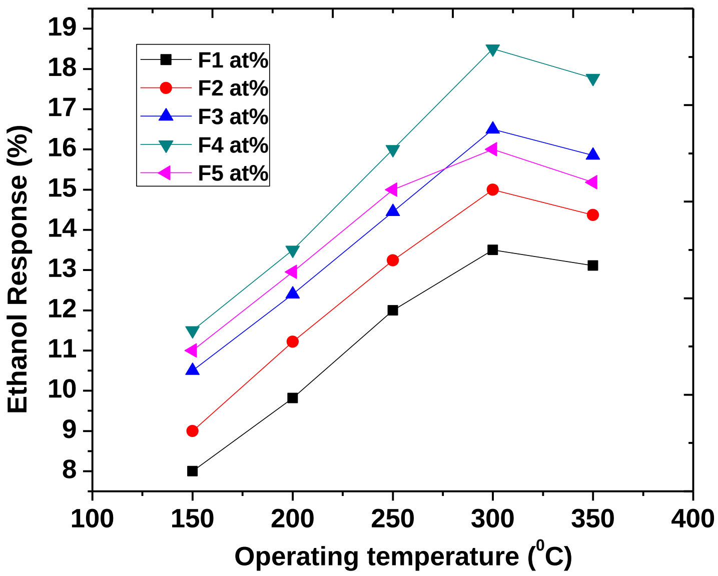

Figure 1: The variation of Ethanol response of F: ZnO film for different F at% to 1000 ppm Ethanol at different temperatures

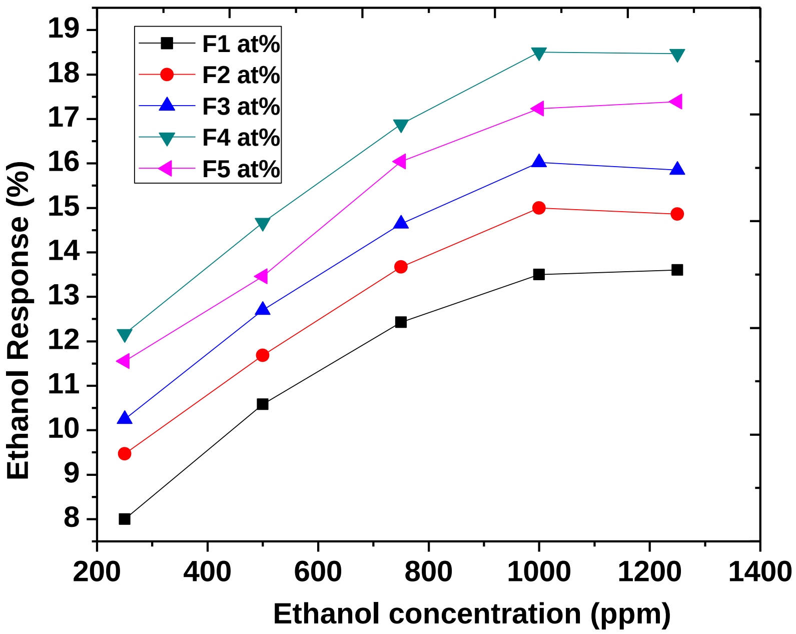

Figure 2: The variation of Ethanol response of F: ZnO film to different Ethanol concentrations

(b) Dynamic gas response transients of F: ZnO film to Ethanol

Fig. 3 represents the transient response characteristics of the F doped ZnO films to 1000 ppm of Ethanol vapor in air at 300 ˚C. It is found that in case of the 4 at% F-doped film, the response time to attain the maximum response value is almost the same (~20.5%) as that of the 1% F doped ZnO film. But in other F-doped films, the corresponding recovery time increases. On the other hand, the response time of the doped films is observed to decrease with an increase in F-dopant concentration.

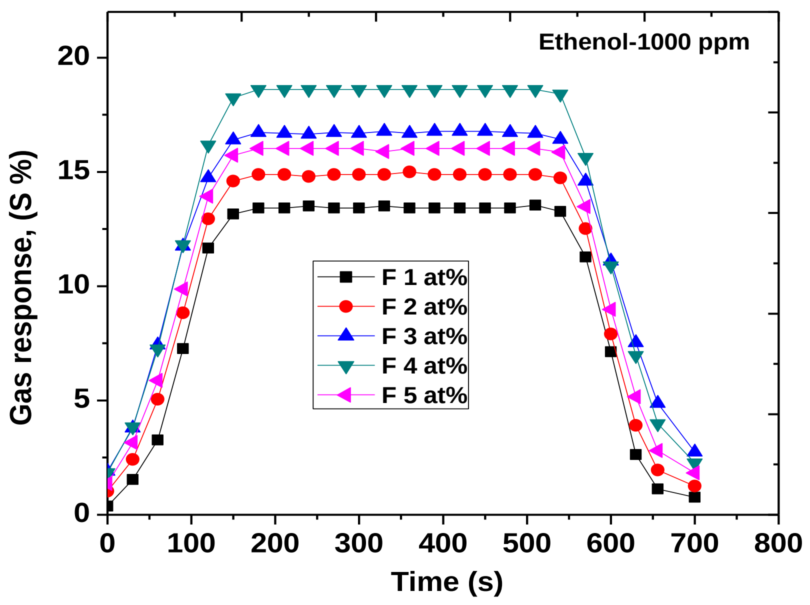

Figure 3: Dynamic Ethanol transient response of ZnO films for different F at% exposed to 1000 ppm Ethanol at an operating temperature of 573 K.

(c) Response and recovery time periods for Ethanol

From the Fig. 4, the response time of 145 s and corresponding recovery time is 155 s is observed for 4% F doped ZnO thin film. from the Figure it is found that as F concentration increases in ZnO lattice response and recovery time decreases up to 4 at% and further increase in F concentration to 5 at% both response and recovery time increased.

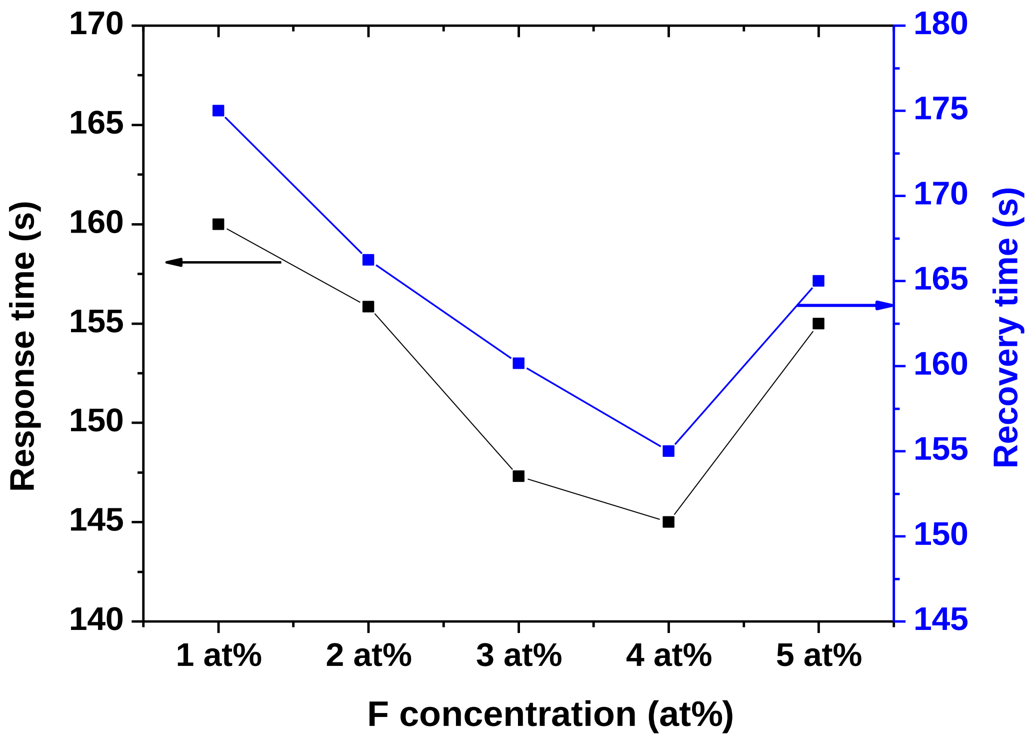

Figure 4: The variation of response and recovery time periods of ZnO films for different F at% upon exposure of 1000 ppm Ethanol.

CONCLUSION

The ZnO and F doped ZnO thin films were deposited by simple spray pyrolysis technique. As we increase the gas concentration to 1000 ppm the surface reaction increases due to a larger surface coverage of Ethanol molecules, resulting in a rapid increase in response. On a further increase in gas concentration to 1250 ppm, the surface coverage of Ethanol molecules on the film begins to decrease which leads to a gradual decrease in response. The response time of 145 s and corresponding recovery time is 155 s is observed for 4% F doped ZnO thin film.

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