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RESEARCH ARTICLE

ETHANOL SENSING PROPERTIES OF FLUORINE DOPED ZINC OXIDE THIN FILMS BY SPRAY PYROLYSIS TECHNIQUE

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Abstract

Fluorine doped Zinc Oxide (F:ZnO) thin films were deposited on glass substrates by simple chemical spray pyrolysis technique. The effect of F doping (1 at% to 5 at %) on the ethanol gas sensing properties were studied. The Ethanol gas response is higher at the operating temperature 300 ^{O}C of the film and it is lower on either side of operating temperature. The response and recovery times of the F: ZnO films were enhanced significantly compared to those reported for ZnO films. The response of 4% F doped ZnO film to ethanol is certainly better than that others. For F doped ZnO film on exposure to 1000 ppm ethanol at 573 K, the response was increased to ethanol gas up to 4 at% while further increase in doping response was decreased.

Keywords: Spray pyrolysis, F-doped ZnO films, ethanol sensing properties, response time.

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 (Fay *et al.*, 2007; Minami *et al.*, 2006; Agashe *et al.*, 2004; Treharne and Durose 2010). A renewed interest in the study of zinc oxide thin films exists due to the simultaneous properties of low resistivity and high transmittance besides chemical stability under strong reducing environments. Despite the extensive investigations on this material, there are still some unknown points related with the effect of some dopants in the transport properties. The case of fluorine doped ZnO thin films is an example for this (Tsai *et al.*, 2009; Ku *et al.*, 2009; Treharne and Durose 2011).

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 (Guillen-Santiago *et al.*, 2008). Fluorine was expected to occupy the oxygen site in ZnO and hence promoting the conductivity of the film (Ratheesh Kumar 2007; El Hichou *et al.*, 2002; Rodriguez-Baez *et al.*, 2006; Lee *et al.*, 2004; Ellmer 2001; Ko *et al.*, 2000). We describe the effect of fluorine on the properties of ZnO thin films in this chapter.

Effective doping of fluorine can be performed with many fluorine compounds, which are highly soluble in aqueous solvents. Earlier, it was shown that hydrofluoric acid, [HF], could be used for highly conducting tin oxide or indium oxide thin films. But only very few reports were available regarding the usage of HF acid as dopant solution. One of the reasons for not using HF was the early precipitation of the solution, which occurred as soon as the HF was added to the starting solution. The corrosive character of HF might have been another important reason. Hence ammonium fluoride (NH_4F) was chosen as the doping solution for fluorine in the present study.

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 [$Zn(CH_3COO)_2.2H2O$] diluted in methanol and deionized water (3:1) was used for all the films, and ammonium fluoride (NH_4F) 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.

The sensing study was made on sensor setup in the lab.

Results and discussions

Ethanol sensing properties

(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

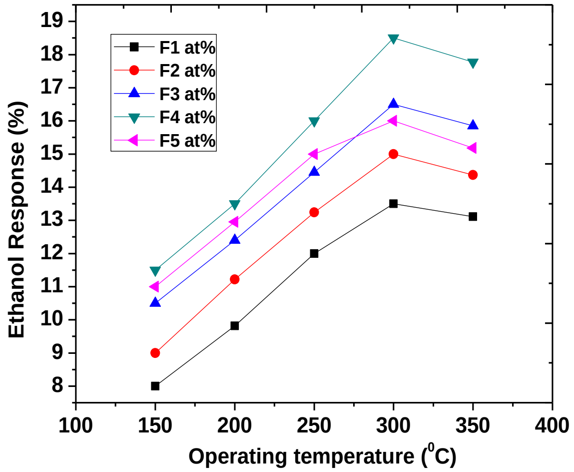

Figure 1: The variation of Ethanol response of F: ZnO film for different F at% to 1000 ppm Ethanol at different temperatures

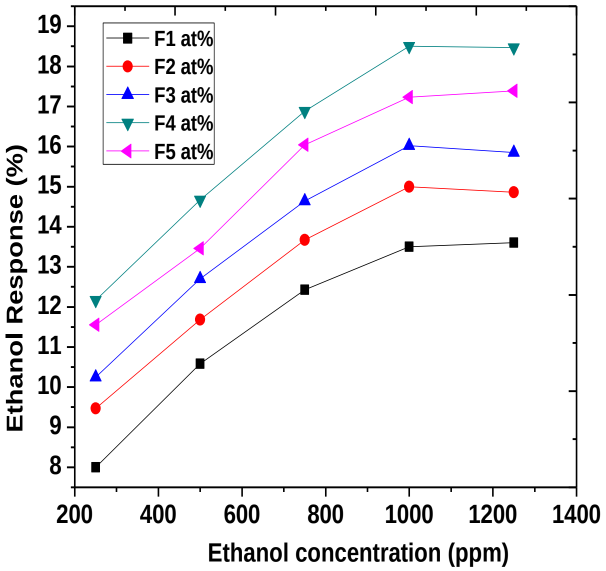

Figure 2: The variation of Ethanol response of F: ZnO film to different Ethanol concentrations

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

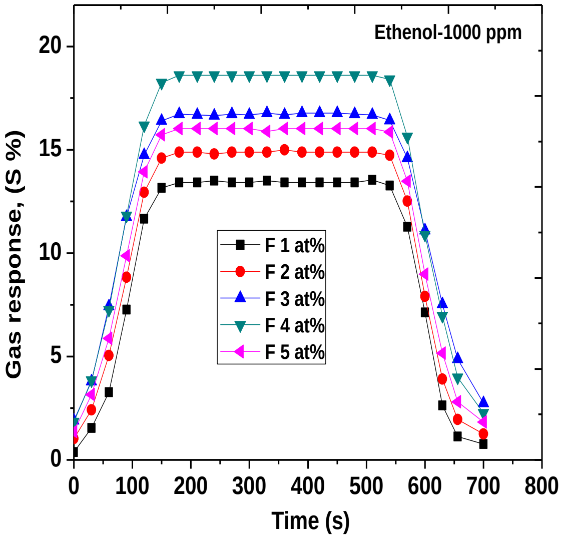

Figure 3: Dynamic Ethanol transient response of ZnO films for different F at% exposed to 1000 ppm Ethanol at an operating temperature of 573 K.

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.

(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.

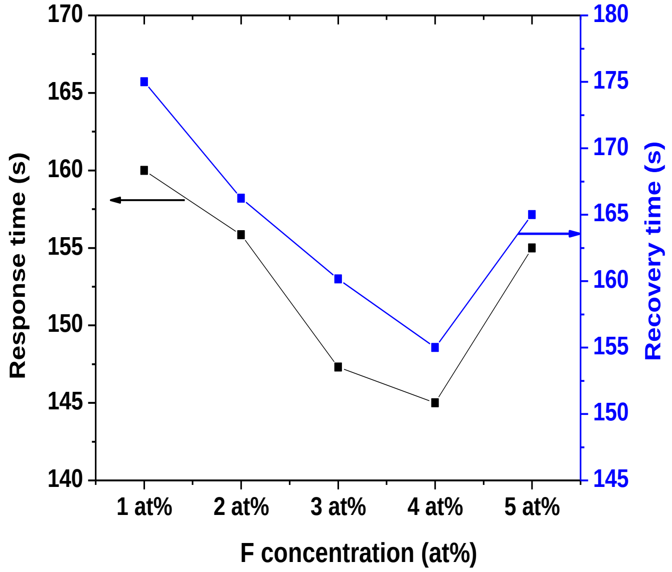

Figure 4: The variation of response and recovery time periods of ZnO films for different F at% upon exposure of 1000 ppm Ethanol.

Conclusion

The effect of F doping (1 at% to 5 at%) on the ethanol gas sensing properties were studied. The sensors response gradually increases up to the 1000 ppm ethanol concentration and then starts to saturate above 1000 ppm. The response and recovery times of the F: ZnO films were enhanced significantly compared to those reported for ZnO films. The response time of 145 s and corresponding recovery time is 155 s is observed for 4% F doped ZnO thin film.

Reference

1. Fay, S., Steinhauser, J. Oliveira, N. Vallat-Sauvain, E and Ballif, C. (2007). Thin Solid Films 515, 8558.
2. Minami, T., Miyata, T. Ohtani, Y and Mochizuki, Y. (2006). Jpn. J. Appl. Phys. 45, 409.
3. Agashe, C., Kluth, O. Hupkes, J. Zastrow, U. Rech, B and Wuttig, M. (2004)). J. Appl. Phys. 95 (2004) 1911.
4. Treharne, R.E and Durose, K. (2010). Thin Solid Films, doi:10.1016/j.tsf.2010.12.126.
5. Tsai, Y., Wang, N and Tsai, C. (2009). Mater. Lett.1621.
6. Ku, D., Kim, Y. Lee, K. Lee, T. Cheong, B. Seong, T. Kim,W. (2009). J. Electroceram. 23. 415.
7. Treharne, R.E and Durose, K. (2011). Thin Solid Films 520, 1313.
8. Guillen-Santiago, A., M de la L. Olvera, Maldonado, A. Asomoza, R and Acosta, D. R. (2004). Phys. Stat (a), Sol. 201,952.
9. Ratheesh Kumar, P. M., Ph. D. thesis. (2007). Cochin University of Science and Technology Cochin, January 2007.
10. El Hichou, A., Bougrine, A. Bubendorff, J.L. Ebothe, J. Addou, M and Troyon, M. (2002). Semicond. Sci. Technol. 17,607.
11. Rodriguez-Baez, J., Maldonado, A. Torres-Delgado, G. Castanedo-Perez, R. De la, M. Olvera, L. (2006). Mater. Lett. 60,1594.
12. Lee, J.H., Yeo, B. W., B.O. Park, Thin Solid Films 457 (2004) 333.
13. Ellmer, K. (2001). J. Phys. D Appl. Phys. 34, 3097.
14. Ko, H.J., Chen, Y.F. Hong, S.K. Wenisch, H. Yao, T. (2000). Appl. Phys. Lett. 77, 3761.

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