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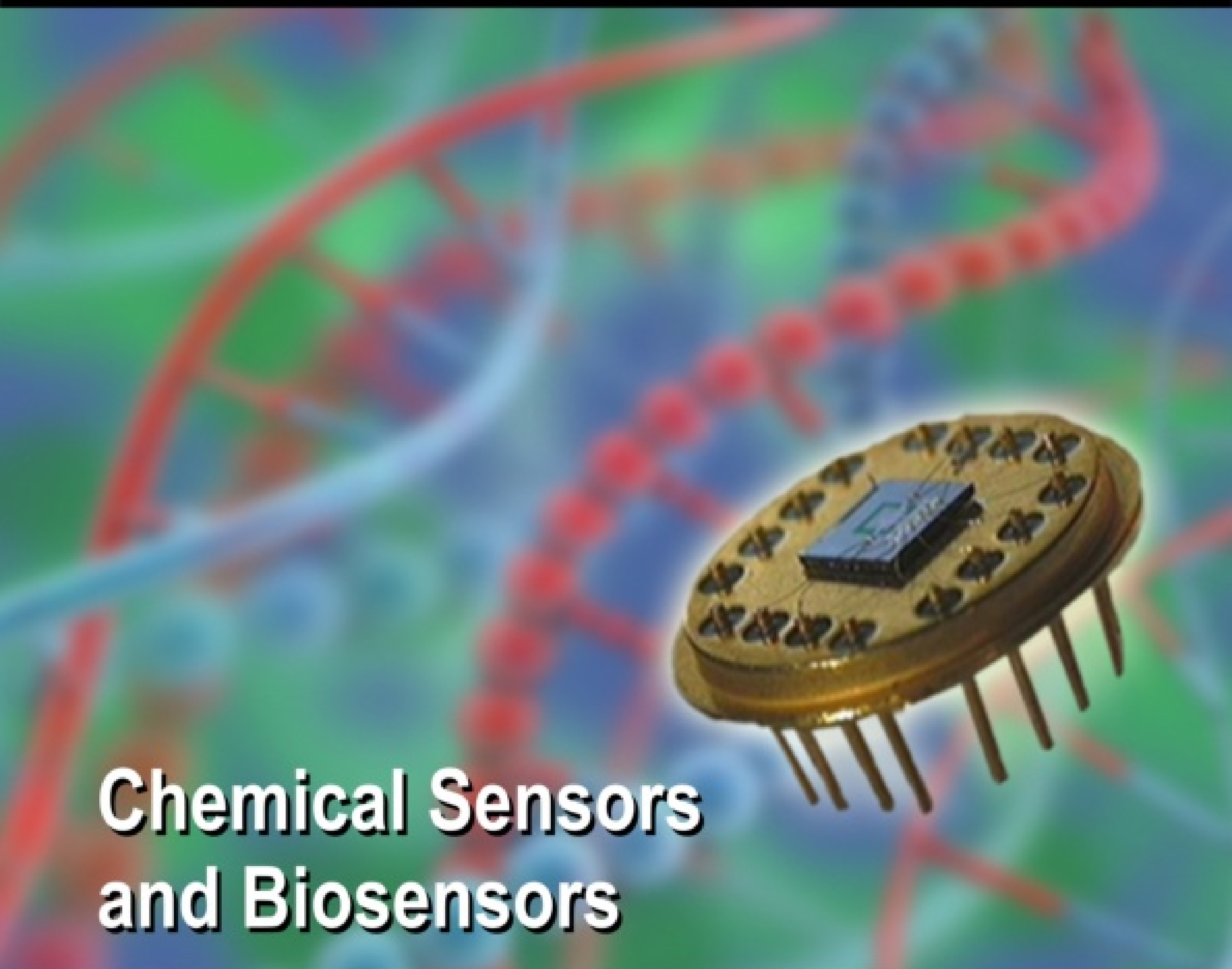

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Comparative Study of Irradiated and Annealed ZnO Thin Films for Room Temperature Ammonia Gas Sensing

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Abstract: Ceramic based thin film sensors are well known for gas sensing applications. These sensors are operated at elevated temperature for good sensitivity. ZnO thin film sensors operated at high temperature are used in ammonia sensing application. But to the best of author's knowledge no room temperature ZnO (Zinc Oxide) thin film sensors are reported. The deposited ZnO films are found to be highly unstable with respect to resistance of the films at room temperature. To increase the stability two different techniques viz. annealing and irradiation are tried. Comparative study of annealed and irradiated ZnO films for stability in resistance is done. Further the performance of these films as ammonia (NH_3) gas sensor at room temperature has been studied. The results obtained are reported in this paper and analyzed. *Copyright © 2008 IFSA.*

Keywords: Sensor, ZnO, Zinc Oxide, Ammonia, Irradiation

1. Introduction

Recently, the use of ammonia gas sensor has greatly increased in many fields of technological importance, such as food technology, chemical engineering, firepower plant, medical diagnosis, environmental protection, and industrial processes. The importance of Zinc Oxide (ZnO) for inflammable gases applications was demonstrated way back in 1962 [1] and is still being used for sensing various other gases including ammonia (NH_3) gas. ZnO gas sensors are fabricated in various forms, such as, single crystals [2], sintered pellets [3], thick films [4], thin films [5] and heterojunctions [6]. Thin films of ZnO are expected to exhibit high degree of gas sensitivity. This is mainly because of their polycrystalline nature and in turn more exposed surface area. The sensing mechanism involves chemisorptions followed by charge transfer at the surface leading to change in resistance of the sensor element.

Different methods have been used to obtain ZnO thin films, e.g., thermal oxidation [7], chemical deposition [8], electron beam evaporation [9], activated reactive evaporation [10], spray pyrolysis [11], low pressure metal organic chemical vapour deposition (MOCVD) [12] and RF / DC magnetron sputtering [13]. In the present work magnetron-sputtering technique is used for deposition of ZnO films. As deposited ZnO films are found to be unstable with respect to resistance of the films at room temperature. Annealing and irradiation are two methods tried to stabilize the resistance. However the resistance of the films may vary over a period. As deposited, annealed and irradiated ZnO films are characterized for NH_3 sensing. The results obtained on resistance stability and NH_3 sensing is discussed in this paper.

2. Experimentation

ZnO thin films were prepared by using DC magnetron sputtering system. A ZnO target of 99.99 % purity was used for deposition. The distance between the substrate and target was kept fixed at 5 cm. Argon (Ar) and Argon + oxygen (O_2) were used as sputtering gases. Base pressure obtained for deposition was 6 x 10^{-5}mbar and deposition pressure was kept at 0.04 mbar. ZnO was deposited at a voltage 320 Volts and a current of 50mA (negative terminal connected to target), for 50 min. The films were deposited on glass and alumina substrate. The film thickness was measured by Fitzeau fringes method. Aluminum was then deposited for making electrical contact. The deposited film resistance was not stable. It varied between hundreds of Kilo-ohm to tens of Mega-ohm. For attaining stability of ZnO films a few deposited films were annealed. Annealing was done in different annealing environments (O_2 atmosphere and air atmosphere) and different annealing temperatures (100^0C to 350^0C) for different annealing time (15 min to 90 min). Irradiation by High-energy Ion was explored for possible increase in stability and sensitivity of ZnO based sensors. Irradiation of ZnO thin films was carried out by 100 MeV Si^{8+}ions. The dose of 10^6ions/cm^2 was given at ≈ 10^{-6} mbar vacuum pressure. The irradiation experiments was done in Inter University Accelerator Centre (IUAC) (Previously known as Nuclear Science Center), New Delhi.

Annealed and irradiated ZnO films were characterized using Energy Dispersive X-Ray Analysis (Philips XL 30) and Reflection mode UV-visible spectroscopy. These films were also characterized for NH_3 gas sensing. In house gas testing system as shown in Fig. 1 was designed and developed.

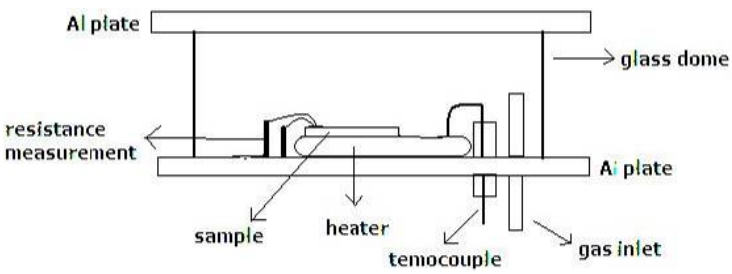


Fig. 1. Gas testing system.

The gas testing system has volume of approximately 2.5 litres. Ammonia gas at different ppm levels could be inserted through syringe. The resistance of the film was measured using half bridge method. The testing of ZnO samples for 400-ppm ammonia gas was carried out.

3. Result and Discussion

Experiments for deposition of ZnO films by magnetron sputtering were carried out initially with only Ar as a carrier gas and at other deposition condition same as mentioned in the experimental above. When observed visually the films looked metallic and were non-uniform. The film resistance was found to be lying between 500KΩ to 13 MΩ. The film thickness measured by Fitzeau fringes method was found to be of the order of 1500 Å. The resistance obtained is low as compared to the insulator behavior of ZnO. The reason may be attributed to the decomposition of ZnO and vacuum drag of O_2 in argon plasma during deposition.

This problem has been discussed by Naota Tsuji [14]. They report that to compensate the dragged O_2during deposition one can simultaneously introduce O_2 with argon as a carrier gas. The paper also reveals the thin film ZnO resistance to be in the range of M-ohms to Few G-ohms after O_2 introduction. Following the same in present work O_2 gas was introduced simultaneously with Ar at an optimized ratio of 3:1 with necessary changes in system. This gave high resistance ≈ few G-ohms. ZnO thin films obtained are found to be highly unstable. Their resistance randomly varies in the range 0.1 GΩ - 10 GΩ at an instant. ZnO thin films are known to be unstable as they continuously absorb and desorbs oxygen and moisture [14]. Annealing is one of the solutions to overcome the instability. Attempt is also made to stabilize the film resistance by irradiating the film with high-energy ions.

Annealing was done in different annealing environment (O_2 atmosphere and air atmosphere) and different annealing temperatures (100^0C to 350^0C) for different annealing time (10 min-90 min). Stability was also found to be dependent on substrate material. Deposition and annealing on both glass and Alumina substrates was carried out. Samples on glass at 300^0C for 30 minutes gave comparatively stable films. It was found that ZnO films on glass annealed at 300^0C for 30 minutes were more stable than that on alumina. The possible reason behind this may be due to high roughness and porosity of alumina. Therefore deposited films on alumina were not used further. Literature survey reveals that higher the temperature of annealing more crystalline ZnO is formed. But we could not go beyond 300^0 C due to soda lime glass.

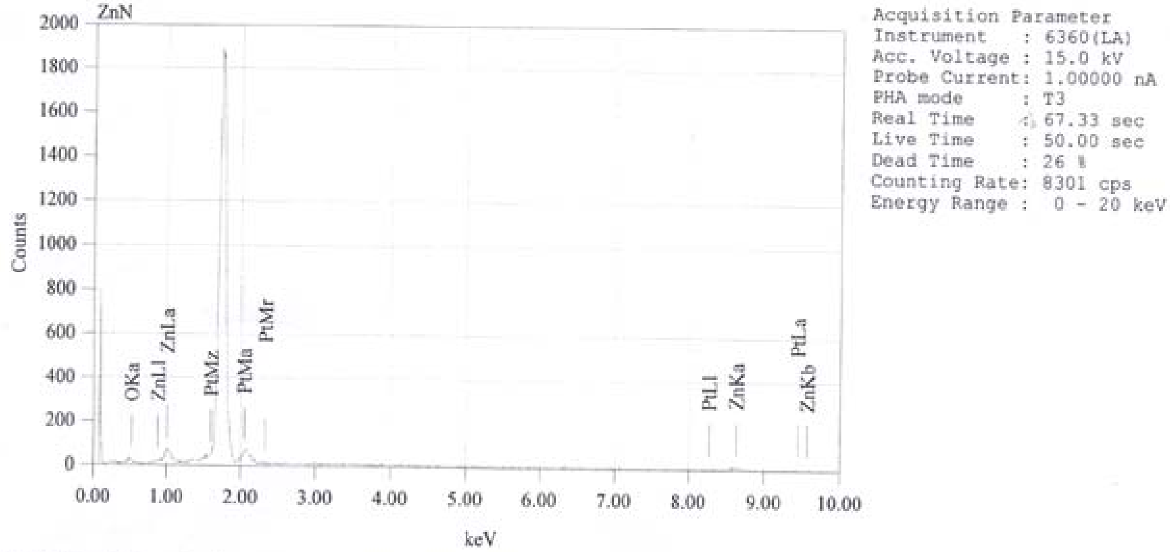
3.1. Structural Characterization

3.1.1. UV- Visible Spectroscopy

ZnO films on glass substrates annealed at 300^0 C for 30 min and irradiated ZnO films were subjected to UV-visible spectroscopy. The standard band gap of ZnO in bulk is 3.10 eV. For annealed films the gap was observed at 3.06 eV, while for irradiated films the same was seen at 2.92 eV. Large reduction in the band gap energy in case of irradiated films may be attributed to the possible irradiation induced defect levels in the band gap.

3.1.2. SEM / EDAX

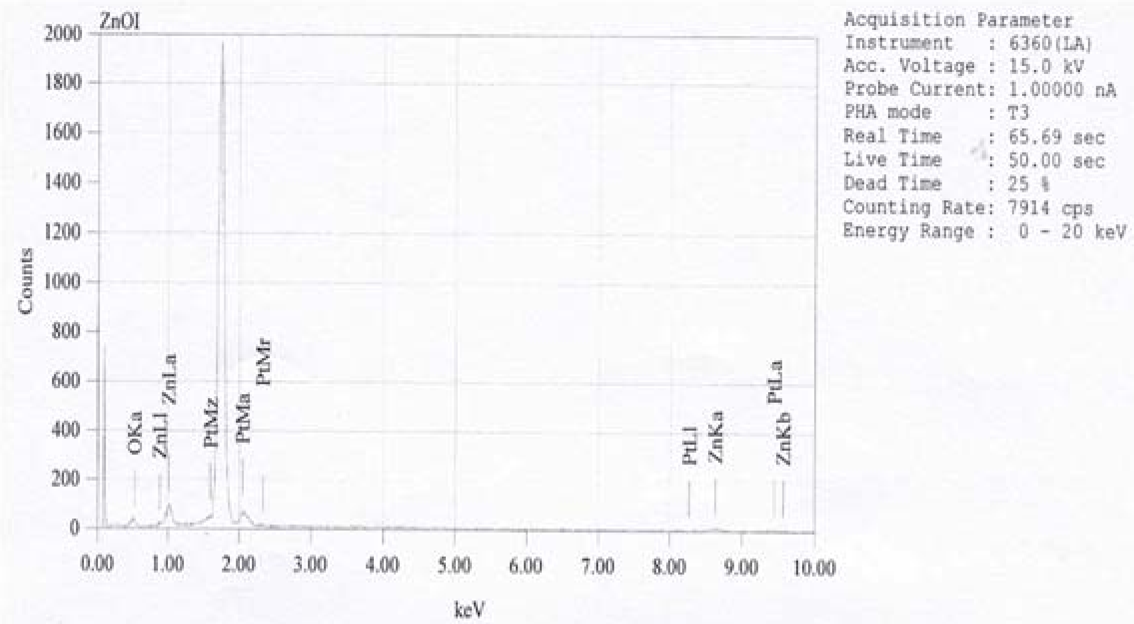
Fig. 2 and Fig. 3 exhibit the energy dispersive x-ray analysis spectra for annealed and irradiated ZnO films respectively. It can be observed that there are no impurities in the films. The large peak, which is unnamed, is of Si substrate. The atomic percentage ratio of Zn:O calculated from the data of annealed films is 65.36**:**23.23 and that of irradiated films is 49.34**:**42.65. It is observed that oxygen atomic percentage in irradiated samples was 42.65% and that for annealed films was 23.23 %. Irradiation gave rise to change in chemical stoichometry of the thin film and thus doubled the oxygen content than in annealed sample. This possibility gave rise to more stable film.



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.9669

Element	(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
O K	0.525	5.41	9.61	23.23				5.7379
Zn K	8.630	62.19	157.22	65.36				71.4357
Pt M	2.048	32.40	37.62	11.41				22.8264
Total		100.00		100.00				

Fig. 2. EDAX of Annealed sample.



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.9567

Element	(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
O K	0.525	12.48	10.64	42.65				13.5516
Zn K	8.630	58.96	181.61	49.34				66.4386
Pt M	2.048	28.57	42.89	8.01				20.0098
Total		100.00		100.00				

Fig. 3. EDAX of Irradiated sample.

3.1.3. X-Ray Diffraction

Fig. 4 and Fig. 5 show grazing angle XRD patterns of annealed and irradiated ZnO films respectively. The peaks at 31^0, 34^0, 36^0, 47^0, 56^0, and 62^0 were observed. Comparing these peaks with standard ASTM data, it was found that ZnO has the hexagonal structure with a density of 5.680g/cm^3. The peak at 34^0 shows a (104) hkl plane and at 56^0 shows a (110) hkl plane. Further analysis shows that the irradiated sample peak at ~ 56^0 has increased by a factor of 4 and the peak at 34^0 has increased by a factor of 2 than that at annealed sample peaks. Observed increase in the peak intensity may be due to structural change in ZnO, due to which large orientation of (110) plane on the surface followed by (104) planes are formed. Particle sizes for annealed and irradiation samples were calculated from (110) peak of XRD. The sizes come out to be 12.41nm and 20-86nm respectively. This increase in particle size may be due to local heating by irradiated ions i.e. conversion of kinetic energy into heat energy.

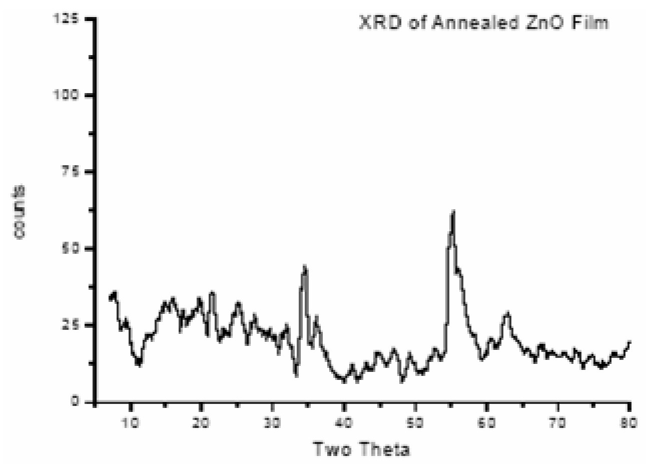


Fig. 4. XRD of Annealed ZnO Film.

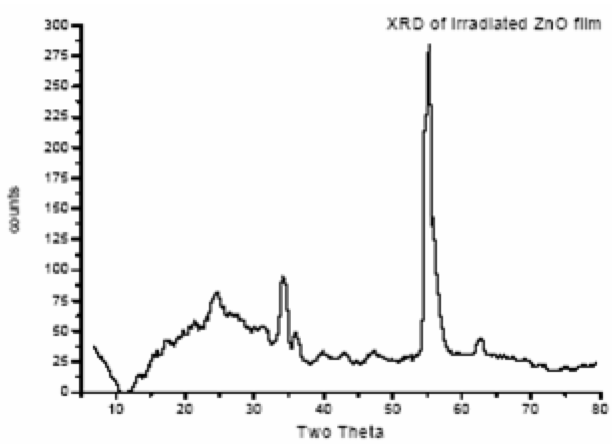


Fig. 5. XRD of Irradiated ZnO Film.

3.2. Results of Gas Testing

As deposited ZnO thin films have large resistance fluctuations as mentioned before, which makes it difficult to use it as a sensor and therefore not tested for gas sensitivity. ZnO thin films, annealed and irradiated, were tested for sensing of 400ppm of NH_3 gas at room temperature. The sensitivity is defined as S= [(R_{air} - R_{gas}) / R_{air}] * 100 %, where R_{air}= resistance of ZnO samples in air and R_{gas} = resistance of ZnO films in NH_3 gas. Approximately 25 samples were annealed at 300^0C for 30 min. All the samples were tested for ammonia gas sensing at room temperature and representative curve for sensitivity versus time is shown in Fig. 6. The response time for all samples is in the range of 60 to 240 sec (1-4 minutes) and that of recovery time is in the range of 420 to 900 sec (7-15 minutes).A general trend was also observed that faster the response time, slower recovery time.

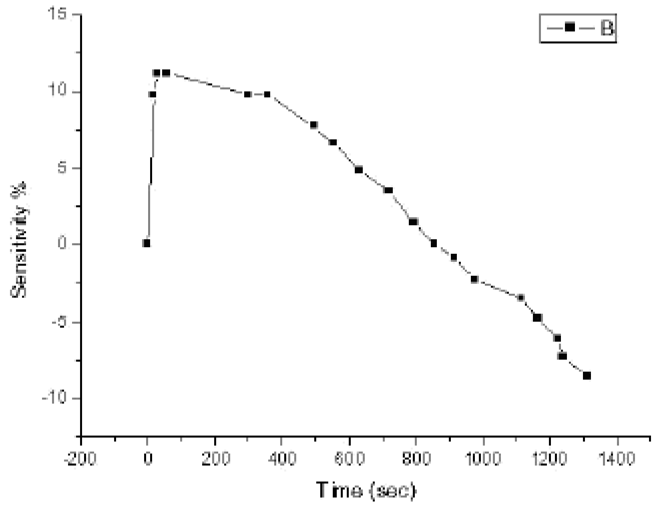


Fig. 6. Sensitivity curve for Annealed sample at room temperature for 400 ppm of NH_3.

Approximately 25 samples irradiated with 100 MeV Si ions were tested for ammonia gas sensing at room temperature. The representative curve for sensitivity versus time is shown in Fig. 7. The curve exhibited a response time in the range of 120 to 180 sec (2-3 minutes) and recovery time in the range of 600 to 1200 sec (10-20 minutes).

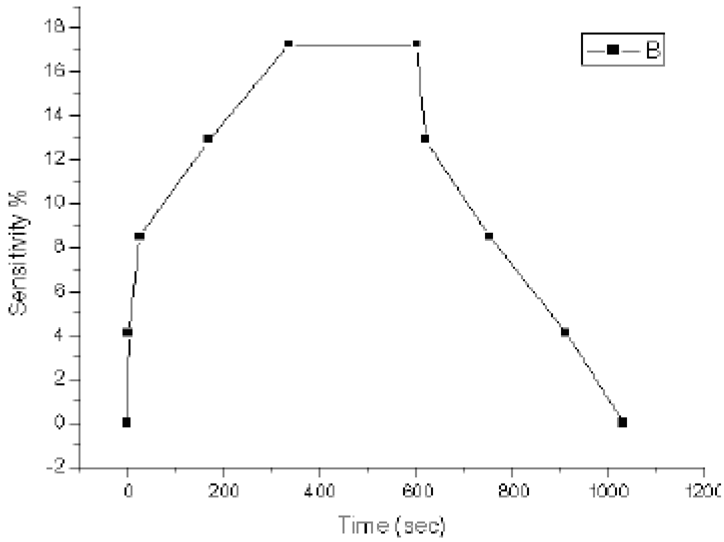


Fig. 7. Sensitivity curve for Irradiated sample at room temp for 400ppm of NH_3.

A general trend was observed that faster the response time, faster the recovery time and slower the response time, slower the recovery time. Comparing the sensitivity of annealed and irradiated ZnO films shows that irradiated ZnO has more sensitivity (~17%) than annealed ZnO (~10.5%). The increased sensitivity of irradiated films for NH_3 sensing can be attributed to radiation enhanced reactivity of these films.

4. Conclusion

ZnO thin films deposited by DC magnetron sputtering can be used for ammonia sensing at room temperature. Instability of ZnO thin films can be reduced using irradiation and by annealing of the samples. Considering the characterizations carried out for annealed and irradiated samples of ZnO films and sensing behavior of these films, it can be said that both annealing and heavy ion irradiation stabilize the initial resistance of ZnO films, stability might be due to increased oxygen content of the films. It is clearly seen that the irradiated ZnO films show higher oxygen content, which might be due to radiatively increased reactivity of these films. Similarly it was found from UV-Visible spectroscopy that irradiated film show a transition at lower energy as compared to un-irradiated annealed films. This is the consequence of radiation induced defect levels in the samples. The increased sensitivity of irradiated films for NH_3 sensing can be attributed to radiation enhanced reactivity.

References

[1]. T. Seiyama, A. Kato, K. Fujiishi and M. Nagatani, A new detector for gaseous components using semiconductive thin films, *Anal. Chem.*, Vol. 34, October 1962, pp. 1502-1503.

[2]. A. Jones, T. A. Jones, B. Mann And J. G. Firth, The effect of the physical form of the oxide on the conductivity changes produced by CH4, CO and H_2O on ZnO, *Sensors And Actuators*, Vol. 5, April 1984, pp. 75-88.

[3]. G. Uozumi, M. Miyayama And H. Yanagida, Fabrication of a CuO-infiltrated ZnO composite and its gas sensing properties, *J. Mater. Sci.*, Vol. 32, June 1997, pp. 2991- 2996.

[4]. S. Pizzini, N. Butta, D. Narducci and M. Palladino, Thick Film ZnO Resistive Gas Sensors, *Journal of Electrochem. Soc.*, Vol. 136, July 1989, pp. 1945-1948.

[5]. T. Yamazaki, S. Wada, T. Noma and T. Suzuki, Gassensing properties of ultrathin zinc oxide films, *Sensors And Actuators B*, Vol. 13/14, June1993, pp. 594-595.

[6]. S. Basu and A. Datta, Modified metal-insulator-metal (M-I-M) hydrogen gas sensors based on zinc oxide, *Journal of Material Science*, Vol. 6, December 1995, pp. 415-418.

[7]. P. Bonasewicz, W. Hirschwald and G. Neumann, Conductivity-controlled preparation of ZnO films with high electrical resistance, *Thin Solid Films*, Vol. 142, August 1986, pp. 77-82.

[8]. M. Ristov, G. J. Sinadinovski, I. Grozdanov and M. Mitreski, *Ibid.,* 149, 1987, p. 65.

[9]. A. Kuroyanagi, Properties of Aluminum-Doped ZnO Thin Films Grown by Electron Beam Evaporation, *Jpn. J. Appl. Phys,* Vol. 28, February1989, pp. 219-222.

[10].H. Gopalaswamy and P. J. Reddy, Preparation of ZnO films by activated reactive evaporation, *Semicond. Sci. Technol*, Vol. 5, Issue. 9, September 1990, pp. 980-981.

[11].A. Ghosh And S. Basu, Spray/CVD deposition and characterization of surface modified zinc oxide thick films for gas sensor, *Mater. Chem. Phys.*, Vol. 27, January 1991, pp. 45-54.

[12].J. S. Kim, H. A. Marzouk, P. J. Reucroft and C. E. Hamrin, Jr., Characterization of high quality c axis oriented ZnO thin films grown by metal organic chemical vapor deposition using zinc acetate as source material, *Thin Solid Films*, Vol. 217, September 1992, pp. 133-137.

[13].M. Peneza, C. Martucci, V. I. Anisimkin and L. Vasanelli, Deposition of Doped and Undoped ZnO Thin Films for Gas Sensors, *Mater. Sci. Forum*, Vol. 203, 1996, p. 137.

[14].Naota Tsuji et al., Growth Mechanism of ZnO Film by Reactive Sputtering Method–Significance of Thermodynamics in a Plasma System, *Jpn. J. App. Phys.*, Vol. 29, No 5, May 1990, pp. 835-841.

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