www.sphinxsai.com

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.3, pp 2069-2072, May-June 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Novel Gas Sensor Using Nano Crystalline Zinc Oxide Matrix Deposited By Jet Nebulizer Spray Pyrolysis Technique

N.Manjula[1], G.Selvan[1]*, VS.Vidhya[2], M.Jayachandran[3]

[1]PG & Research Department of Physics, Thanthai Hans Roever College, Perambalur, India.
[2]Department of Chemistry, Chendhuran college of Engineering and Technology, Pudukottai, India.
[3]ECMS Division, Central Electrochemical Research Institute, Karaikudi, India.

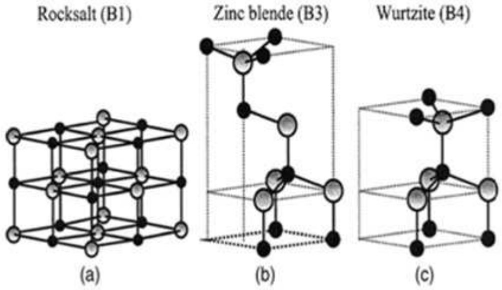
*Corres.author: selvan96@rediffmail.com

Abstract: Zinc oxide (ZnO) thin films have attracted in-depth research interest due to its large utility in a variety of optoelectronic devices. It finds importance due to its large exciton binding energy of 60 MeV and the existence of well developed epitaxial growth processes and is used as transparent electrodes in solar cells replacing expensive Indium Tin Oxide (ITO) electrodes. Nano grained ZnO films have been effectively used as effective gas sensor elements in various form. Because it is an n-type semiconductor normally crystallizing with hexagonal wurtzite structure in which lattice Zn atoms are tetrahedrally coordinated to four Oxygen atoms. For device development, preparation of nano crystalline and preferentially oriented films with uniform and large surface area morphology is essential to be prepared using a simple and low cost chemical route. Hence ZnO films were prepared by a novel and simple Jet Nebulizer Spray (JNS) Pyrolysis technique. The structural and morphological properties of these films were studied using which methanol gas sensing characteristics were recorded and the results are presented. Au/ZnO/Al structure was formed as the sensing gadget and the sensor shows good sensitivity to methanol gas. The minimum and maximum gas limits were recorded as 50 and 400 ppm respectively of methanol gas even when the sensor was operated at room temperature.
Keywords – Thin Films, Gas sensor, Jet Nebulizer Spray Pyrolysis technique.

Introduction and Experimental

ZnO is called a II-VI semiconductor because Zinc and Oxygen belong to the 2nd and 6th groups of the periodic table, respectively. This semiconductor has several favorable properties: good transparency, high electron mobility, wide band gap, strong room-temperature luminescence, etc. ZnO thin film presents investigating optical, acoustical and electrical properties which meet extent applications in the fields of electronics, optoelectronics and sensors as shown in the Figure 1 [1]. ZnO gas sensors have been fabricated in various forms such as single crystals, sintered pellets, thick films, thin films, hetero-junctions. Thin films of ZnO are expected to exhibit high degree of gas sensitivity, because of the fact that the sensing mechanism involves chemisorptions followed by charge transfer at the surface leading to change in resistance of the sensor element [2]. ZnO thin films are used as transparent electrodes in solar cells replacing expensive Indium Tin Oxide (ITO) electrodes. For device development, the preparation of nano crystalline and preferentially oriented films with uniform and large surface area morphology is essential to be prepared using a simple and low cost chemical route. So, ZnO films were prepared by a novel and simple Jet Nebulizer Spray (JNS) Pyrolysis technique. The structural and morphological properties of these films were studied using which methanol gas sensing characteristics are recorded and the results are presented using XRD and UV-Visible spectra analysis. ZnO thin films with nano grains were deposited on glass substrates at different temperatures under the optimized JNS Pyrolysis condition.

Physical Properties of ZnO	
Molar mass	81.408 g/mol
Density	5.606 g/cm^3
Solubility	Soluble in water
Melting point	1975 °C
Band gap	3.3 eV
Refractive index	2.0041
Exciton binding energy	60 meV
Lattice energy	964 kcal/mole



Stick and ball representation of ZnO crystal structures (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4)

Figure 1: Attractive Properties of ZnO

Results and Discussion

XRD Analysis

The XRD patterns of the deposited and annealed ZnO thin films are analyzed as shown in the Figure 2 [3]. The XRD pattern of the deposited and annealed at 300°C film shows amorphous nature whereas the all other annealed films show polycrystalline nature. All the annealed films show a preferential orientation along the (100) direction. As the annealing temperature increases, the crystalline quality of the films increases. At higher annealing temperatures, the grain growth is enhanced and re-crystallization effect is prominent resulting in better crystalline nature for the films. The structure and orientation of polycrystalline thin films depend on the processing parameters [4]. The improvement in structural features can also be due to the reduction in the Oxygen vacancies at higher annealing temperatures. The average sizes of the particles in the films are estimated by the Debye Scherrer equation [5].

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl}\cos(\theta_{hkl})} \longrightarrow (1)$$

, Where λ is the X-ray wavelength, θ_{hkl} is the Bragg diffraction angle and β_{hkl} is the full width at half- maximum (FWHM) in radian of the main peak in the X-ray diffraction pattern. The determination of the average size of the crystallites using the Scherrer equation shows that the size of the crystallites increases as the annealing temperature increases.

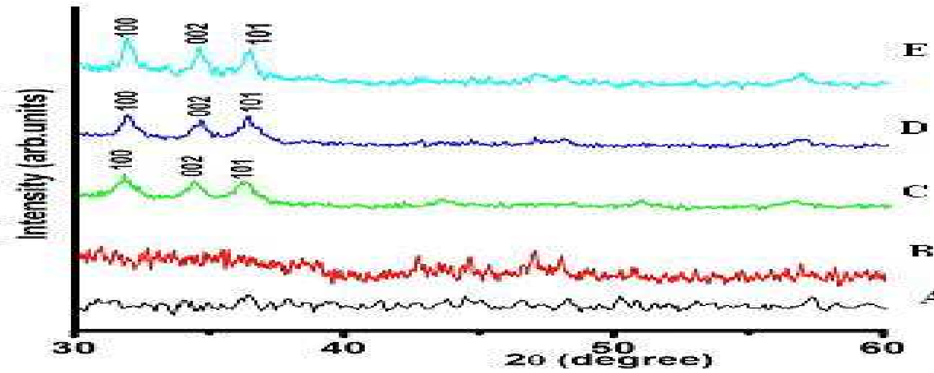


Figure 2 XRD spectra of ZnO thin films (A) as deposited (B) annealed at 350, (C) 400, (D) 450 and (E) 500^{0}C

UV-Visible Spectra Analysis

The optical transmission spectra for a wavelength range of 350- 900 nm for the deposited and annealed films are shown in as shown in the Figure 3. The high transmittance shown by the films is an indication that the films are highly crystalline and have high degree of stoichiometry [6]. The sharp reduction in optical transmittance around 350 nm corresponds to the intrinsic band edge of ZnO [7]. The sharp decrease in transmittance near the band edge is observed for all the films and is an indication of the high crystalline quality of the films as envisaged by the XRD.

$(\alpha h\nu) = A(h\nu - E_g)^n \longrightarrow (2)$, Where, E_g is the band gap corresponding to a particular transition occurring in the film, A is a band edge constant, ν is the transition frequency and the exponent n characterizes the nature of band transition, n=1/2 and 3/2 corresponds to direct allowed and direct forbidden transitions and n=2 and 3 corresponds to indirect allowed and indirect forbidden transitions, respectively [8]. The optical band gap E_g can then be obtained from the intercept of $(\alpha h\nu)^2$ vs. $h\nu$ for direct transitions. It is observed that for all the films, the best straight line is obtained for n = 1/2, which is expected for direct allowed transition. The calculated band gap values are in good agreement with the reported values as shown in the Table 1.

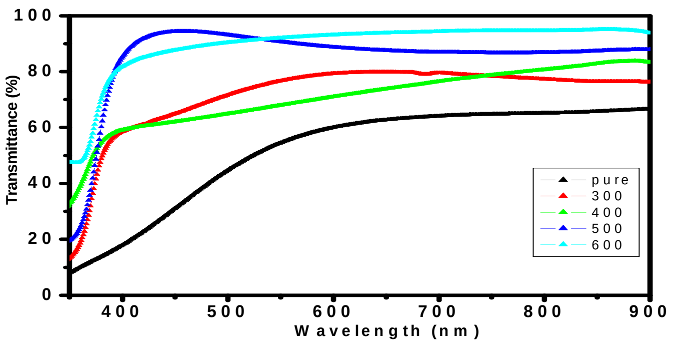


Figure 3 Transmittance spectra of as deposited and annealed ZnO films

Table 1 Structural and Optical Parameters of ZnO Thin Films

Annealing temperature (K)	Thickness (nm)	RMS roughness (nm)	Band gap (eV)	Average transmittance (%)
As-deposited	198	-	2.92	57
573	175	-	3.19	76
673	160	15.0	3.20	74
773	159	11	3.23	87
873	149	8.0	3.25	92

Conclusions

ZnO thin films with nano grains were deposited on glass substrates at different temperatures under the optimized JNS Pyrolysis condition. Films deposited at 350°C, 400°C and 450°C revealed good crystallinity with hexagonal structure as observed from the XRD results. All the films showed three intense peaks corresponding to (100), (002) and (101) planes. Interestingly the ZnO films deposited at 400°C were highly preferentially oriented along the (002) plane. Presence of this triplet confirmed the formation of hexagonal structured ZnO films and the broad nature of the peaks reveals the presence of nano grained morphology, which is also confirmed by the surface morphological studies carried out by scanning electron microscopy. Using these nano structured ZnO film matrix, a novel ZnO based methanol gas sensor was fabricated. Au/ZnO/Al structure was formed as the sensing gadget and the sensor shows good sensitivity to methanol gas. The minimum and maximum gas limits were recorded as 50 and 400 ppm respectively of methanol gas even when the sensor was operated at room temperature.

References

1. C . Klingshirn.phys.Status.solidi B, 71, 1975, 547.
2. Zhou.J, et al, Adv. Mater, 18, 2006, 2432.
3. A. Kasis, M.Saad, Sol.Ener. Mater. Sol. Cell. 80, 2003, 491.
4. Nizamoglu, S.; Ozel, T.; Sari, E.; Demir, H. V. Nanotechnology, 2007, 18 (6), No. 065709.
5. U. Ozgur, I.Ya, C.Alivov, A. Liu, M.A. Teke, S. Reshchikov, V.Dogan, S.J. Avrutin, H. Cho, Morkoc, j. Applied Physics. 98, 2005, 041301
6. Manolache, S.A.; Isac, L.; Purghel (Ienei), E.; Duta, A. Three dimensional solar cell Proceedings of the 23th European Photovoltaic Solar Energy Conference, 2008, 1, 563-566.
7. Slocik, J. M.; Tam, F.; Halas, N. J.; Naik, R. R. Nano Lett., 2007, 7 (4), 1054–1058.
8. Zin, M. T.; Leong, K.; Wong, N. Y.; Ma, H.; Sarikaya, M.; Jen, A. K. Nanotechnology, 2009, 20 (1), No. 015305.

*****