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Tungston Doped ZnO Thin film Prepared by Spray Pyrolysis for enhanced Hydrogen Sensing

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Abstract : Spray pyrolysis technique has been used for the manufacture ofW doped Zinc oxide (ZnO) thin films. The influence of concentration of W on ZnO thin film on the structural, optical and photoluminescence properties of the films have been investigated. XRD patterns reveal the growth of preferentially oriented(002) c-axis ZnO with hexagonal wurtzite structure. The PL peak shifts towards lower wavelength and the blue shift in the PL peak confirms the possibility for quantum confinement effect. Hydrogen sensing measurements indicated that W doped ZnO on glass substrate showed better response. The sensor response of 5 % W doped ZnO thin film exhibit highest response of 152 towards 500 ppm H_2 gas at the operating temperature of 200 ^{0}C.

Introduction

Hydrogen with its non polluting nature and high energy density proves to be one of the most efficient energy carriers with a flammability range of 4-75% by volume in air. The lower limit of hydrogen concentration to cause explosion is 4.65 % which is detected using a sensor[1.] Metal oxide semiconductor gas sensors draws researchers because of it low power consumption reproducibility, low operating temperature and ability to detect large no of gases. The sensing properties are highly depends on the preparation condition and it can be increased by processes such as doping or using metal catalyst.

ZnO nanomaterials has a wide band gap of 3.31ev and binding energy of 60 mev with high electrochemical stability, non toxicity and suitability to doping. It is highly sensitive towards flammable material or toxic gases. However ZnO sensors design at room temperature is demanding and to regulate its properties ZnO and tungsten trioxide (WO_3)[2.] has been used to provide good sensitivity and selectivity towards hydrogen nitrogen and CO and O_3. The addition of W into ZnO is favourded due to the valance difference between W^{6+} and Zn2$^+$ and it is of utmost importance. It also has several advantages as less lattice mismatch, controllable band gap and good crystal quality. The investigation of structural, optical and gas sensing properties of W:ZnO films is new and also, it has many excellent properties like good conductivity, high optical transparency, low resistivity and low work function. Presently several methods are used for coating thin films. In this work, we use pyrolytic deposition route with specially designed spray nozzle. This paper investigated the W doped ZnO films varying concentrations of hydrogen better sensing performance.

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Experimental Condition

The deposition of W doped ZnO thin film involved decomposition of aqueous solution of high purity zinc acetated dehydrate and tungsten chloride dissolved in ethanol and with deionized water as solvent. The deposition rate was kept constant at about 7ml/1 min. a specially designed spray nozzle is used and the precursor solution plays a major role. The solution was atomized using compressed pure air. The nozzle distances were maintained at 25 cm. The resultant solution is sprayed on glass substrate at temperature of 300 ^{0}C. The concentration is varied from 3-5% and the chemical real is as follows

$Zn(CH_3COO)_2.2H_2O \rightarrow ZnO + CO_2 + CH_4$

$Wcl_6 + 3/2\ O_2 \rightarrow WO_3 + 3cl_2$

$(1\text{-}X)\ ZnO + WO_x \rightarrow Zn_{(I\text{-}x)}\ W_xO_{(Substrate)}$

The optical, photoluminescence and structural properties of the deposited films were examined. The resultant film were used to fabricate to detect hydrogen sensing.

Results and Discussion

Structural Properties

The results of addition of W on the crystal phase are studied using X-ray diffraction patterns. The (002) orientation led to the formation of a strong peak at 34.44^0. The patterns exhibit hexagonal wurtzite structure and the diffraction peaks were sharp, indicating crystallization of the product. W doping increases peak intensities and the (002) peak at half maximum does not change much and intensity increases with crystalline quality whereas there is no change in structure. Metallic W characteristic peaks and peaks owing to the existence of separate doping metal phase were not detected. The crystallite size of (002) peak of W doped ZnOfilms on glass substrate for different concentration is calculated using Debye –Scherrer formula[3] .

$$D = \frac{k\lambda}{\beta\cos\theta} \quad \text{--------------} \ (1)$$

where k is the shape factor of the average crystallite (0.91), λ is the wavelength of the incident X-ray (λ = 1.5418 Å), β is the full width at half-maximum (FWHM) in radians and θ is the Bragg angle. The average crystallite size of W doped ZnO was found to be 26.5 and 24 nm for 3-5 %, respectively which plays a significant role in the hydrogen sensing performance.

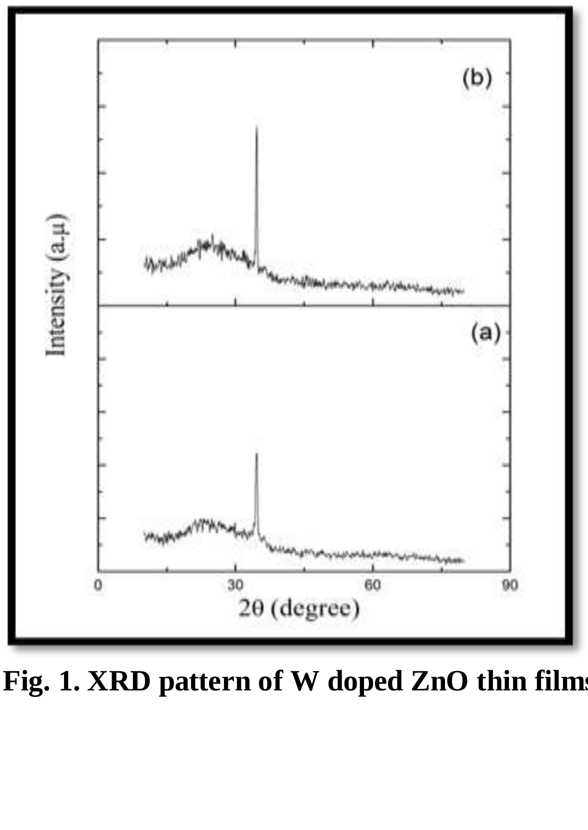

Fig. 1. XRD pattern of W doped ZnO thin films with the dopant concentration of W (a) 3% and (b) 5%.

Optical and Luminscence Properties

The transmittance of W:ZnO films is greater than 70% in visible region which indicates good quality of the deposited films. The concentration of3 to 5 % increases the transmittance from300-700nm and also enhances optical properties. Films with 5% W show80% average transparency which is greater than films with3% W. This accounts for the improvement in structural homogeneity and crystal quality of the resultant films and reduces. This scattering effect owes to the ejection of organic species and point defects in W doped ZnO[4]. The quality and purity of the materials is preferably analyzed with the help of luminescence property. It is illustrious that the origination of UV emission peak is due to the recombination of free excitons through an exciton-exciton collision process which corresponds to near band edge (NBE) emission of wide band gap ZnO. This property is closely related with crystallinity of the film and the defects

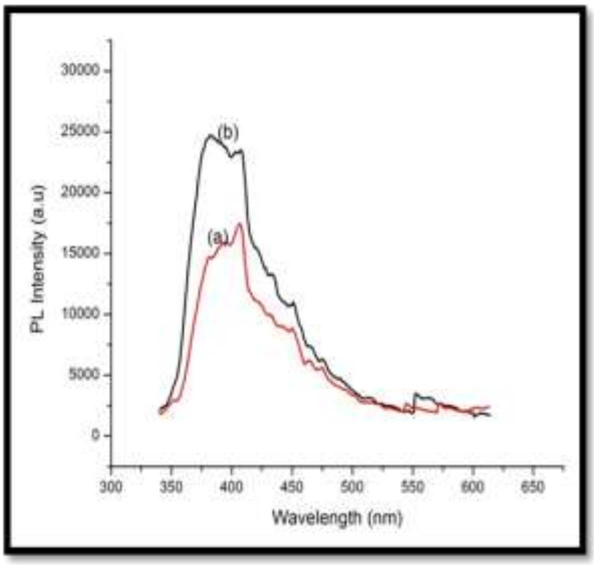

Fig. 2. PL spectra of W doped ZnO thin films with the dopant concentration of W (a) 3% and (b) 5%.

decrease with crystallinty. A strong UV-emission peak at ~380 nm and the near band emission (NBE) at 380nm (3.265eV) is examined due to recombination of exciton through exciton-exciton process. The increase in W dopant concentration from 3% to 5% increases intensity and this signifies the development of crystallinity of the film. This case shows absence ofdefect emission for both the samples. XRD result implies the formation of ZnO nanostructures due to the incorporation of W. Absence of defect emission in W doped ZnO films makes it an excellent material for optoelectronic device applications especially in sensing performance[5].

Gas Sensing Properties

The resistance of the films in dry air and in test gas is measured by the analysis of hydrogen sensing property. The gas sensing response was given by R_a/R_g, where R_a and R_g are the resistance of the sensors before and after exposure in the test gas, respectively[6]. Fig. 3 shows the variation in response of W doped ZnO films prepared at different concentration with the operating temperature, towards 50 0 ppm H_2 gas. Combination of chemisorbed H_2 and absorbed oxygen results in the origination of sensing mechanism. The interaction between hydrogen and preadsorbed oxygen ions on the ZnO surface takes place when ZnO film is exposed to hydrogen gas. The reactions are defined by the equations.

$$H_{(2)ads} + O^{-}_{(abs)} \longrightarrow H_2O + e^{-} \quad (2)$$

$$H_{(2)ads} + O^{2-}_{(abs)} \longrightarrow H_2O + e^{-} \quad (3)$$

Depending on the following two factors, the response of the sensors are altered (i) the rapidity of chemical reaction on the surface of grains at low temperatures (ii) the rate of diffusion of gas molecules in the surface at high temperatures. The rate of above two processes will become equal at some intermittent temperature

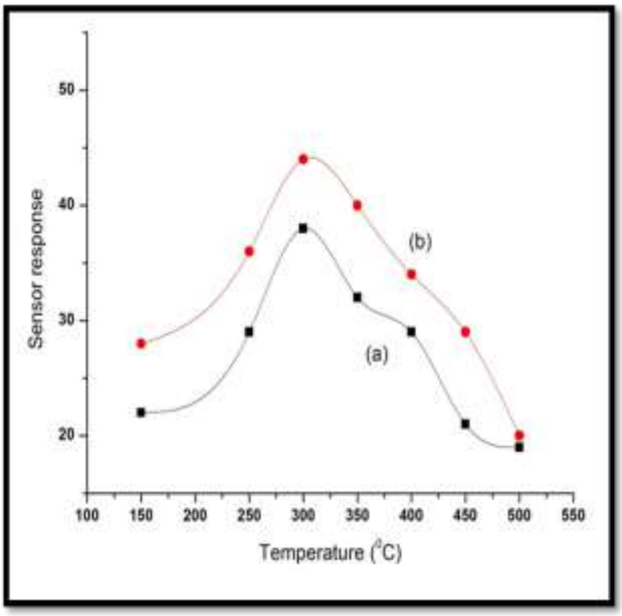

Fig. 3. Gas sensor response of W doped ZnO thin films with the dopant concentration of W (a) 3% and (b) 5%.

value, resulting in maximum sensor response at that point. This infers the fact that there is specific temperature for every gas sensor at which the sensor response reaches its maximum value[7]. It is observed from Fig. 7 that the gas response increases with increase in the operating temperature, and the maximum response is received at the operating temperature of 300 ^{0}C for all the samples. Higher gas response is achieved by the high surface activity and decreased particle size. The decrease in the crystallite size with concentration, reveled by XRD, supports our results of enhancement in gas response.

Conclusion:

The H_2 sensing characteristics of W activated ZnO films were investigated and the structural, optical and photoluminescence properties were studied. XRD patterns revealed high crystallinity of W doped ZnO and the formation texture of ZnO. The crytallite size reduced from 26.5 nm to 24 nm with increasing concentration from 3% to 5%. The concentration of W dopant provides direct control over the properties with gas sensors fabricated using W activated ZnOhas better sensitivity and response under ambient conditions. The conclusion is that 5%W doped ZnO films shows high and fast sensor response towards H_2.

References

1. Adamyan A.Z., Adamyan Z.N., Aroutiounian V.M., Arakelyan A.H., Tourayan K.J., Turner J.A., Sol-gel derived thin film semiconductor hydrogen gas sensor, Int. J. Hydrogen Energy., 2007,32, 4101-4108.
2. Sukon Phanichphant, Semiconductor Metal Oxides as Hydrogen Gas Sensors, Procedia Engineering, 2014, 87, 795-802
3. Al. Salamn S.H., Abdullah M.J., Naif Al-Hardan, ZnO thin films nanostructures for hydrogen sensing applications, Ceram.Int. 2013, 39, S447-S450.
4. Sofian Kanan M., Oussama El-Kadri M., Imad Abu-Yousef A., and Marsha Kanan C., Semiconducting Metal Oxide Based Sensors for Selective Gas Pollutant Detection, Sensors., 2009, 9, 8158-8196.
5. Dhahri R., Hjiri M., El Mir L., Bonavita A., Iannazzo D., Latino M., Donato N., Leonardi S.G., Neri G., Gas sensing properties of Al-doped ZnO for UV-activated CO detection, Journal of Physics D: Applied Physics, 2016, 49, 13.
6. Liu Y., Hang T., Xie Y., Bao Z., Song J., Zhang H., Xie E., Effect of Mg doping on the hydrogen sensing characteristics of Zno thin film, sens.Actuat B. 2011, 160-270 .

7. Rothschild A., Komem Y., The effect of grain size on the sensitivity of nanocrystalline metal- oxide gas sensors. J. Appl. Phys. 2004, 95, 6374-6380.3.

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