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H_2S sensing characteristics of *Cu* doped *ZnO* thin film synthesized by SILAR

P.Mitra

Department of Physics, The University of Burdwan, Golapbag – 713104, West Bengal, (INDIA)

E-mail: mitrapartha1@rediffmail.com

ABSTRACT

Copper doped zinc oxide thin film (*Cu* : *ZnO*) was deposited on microscopic glass substrate following a chemical technique called successive ion layer adsorption and reaction (SILAR). Structural characterization by X-ray diffraction (XRD) revealed loss of preferred c-axis orientation and decrease in particle size due to copper incorporation. Morphology using SEM shows porous polycrystalline structure. Optical band gap measurement using UV-VIS spectrophotometer shows a decrease in band gap energy due to copper incorporation. Gas sensitivity in presence of 200 ppm (parts per million) H_2S was found to increase from ~40% for *ZnO* to ~60% for copper doped *ZnO*. Palladium surface sensitization was found to further enhance the sensitivity.

KEYWORDS

Cu : *ZnO* thin film;
SILAR;
H_2S sensitivity.

INTRODUCTION

Zinc oxide is a multifunctional material. Because of its high chemical stability, low dielectric constant, high luminous transmittance and catalytic activity in different gas environments, *ZnO* based materials finds applications in electronic and optoelectronic devices such as transparent conductors, solar cell windows, dielectric ceramics, and gas sensors[1,2]. *ZnO* is one of the earliest discovered gas sensing material and is sensitive to toxic and hazardous gases with satisfactory stability[3]. The sensing performance of the material can be improved by incorporating dopants and additives and *Cu* in *ZnO* may be useful for promoting sensing properties to LPG and H_2S[4]. Different physical and chemical techniques have been applied to prepare *Cu* doped *ZnO* thin films. The conventional physical techniques generally produce good quality transparent films. However they are very expensive and are difficult to carry out in the industrial level. Chemical techniques involving aqueous route, on the other hand, are relatively simpler and cost effective. Accordingly they can be easily scaled up for industrial applications. Since the last two decades, chemical techniques have come out to be a good alternative for material preparation in thin film form. In this study, *ZnO* and copper doped zinc oxide (*Cu* : *ZnO*) thin films were synthesized using a relative less used and less investigated chemical method called successive ionic layer adsorption and reaction (SILAR) technique.

The SILAR method, also known as modified version of chemical bath deposition, has a number of advantages apart from it being inexpensive, simple and convenient for large scale deposition: i) the process can be carried out on any kind of substrate, ii) It does not require vacuum at any stage, iii) the deposition rate and the thickness of the film can be easily controlled by changing the deposition cycles, iv) being a low temperature chemical method, doping of metal ions may be particularly suitable by this method. The SILAR method is basically a two-step chemical bath deposition technique in which a substrate is dipped in anionic and cationic precursors. Sequential reaction on the substrate surface under optimized conditions of concentration and pH of the reacting solutions results in the formation of the film. Preparation of *ZnO* thin film is performed using a zinc complex solution as first dip and a dip in hot water bath kept near boiling point as the second dip. Before deposition, the glass substrate is cleaned by chromic acid followed by cleaning with acetone. The well-cleaned substrate is immersed in the cationic zinc complex bath for a known standardized time followed by immersion in hot water for the same time for hydrogenation. The present study deals with the preparation and characterization of *ZnO* and *Cu*-doped *ZnO* thin films by SILAR and their gas sensing characterization in presence of H_2S. The concentration of *Cu* was intentionally chosen to be large (6 at. %) so that the effects of *Cu* (if incorporated in the *ZnO* lattice) can be easily detected.

EXPERIMENTAL

Pure zinc oxide films was deposited on glass substrates (microscope slides) by alternate dipping into 0.1M ammonium zincate [(NH_4) ZnO_2] bath kept at room temperature and hot water maintained near boiling point. The pre-cleaned substrate was tightly held in a holder so that only a requisite area for film deposition was exposed. Thus, the film deposition area could be easily varied by adjusting the holder arrangement. The ammonium zincate bath, used for deposition was prepared by adding ammonium hydroxide (~25% pure ammonia solution; Merck, Mol. Wt. 17.03 g/mol, density 0.91) to an aqueous solution of zinc sulphate [$ZnSO_4.7H_2O$]. The pH of the ammonium zincate solution was ~11.10. pH measurement was carried out in a systronics pH meter (Model 335). Copper doping was carried out by adding copper chloride ($CuCl_2.2H_2O$) in ammonium zincate bath.

The details of pure ZnO film deposition process from ammonium or sodium zincate bath have been reported earlier[5-7]. Briefly, a pre-cleaned substrate (microscopic glass slide) was alternatively dipped in zinc complex solution (zincate bath) kept at room temperature and hot water bath maintained at ~95-98°C. One set of dipping involved dipping in zincate bath for two (2) seconds and two (2) seconds in hot water bath. 50 dipping were performed for the present experiment. Copper concentration was varied upto 6% in the bath solution. Further addition of $CuCl_2$ resulted in precipitation in the zincate solution. The phase identification and crystalline properties of the films were studied by the X-ray diffraction (XRD) method employing a Philips PW 1830 x-ray diffractometer with CuK_a radiation (λ=1.5418 Å). The 2θ variation was employed with a 0.05 degrees step and a time step of 1 second. The experimental peak positions were compared with the standard JCPDS files and the Miller indices were indexed to the peaks. Scanning electron microscopy (SEM, Model S530, Hitachi, Japan) was used to study the surface morphology and to illustrate the formation of crystallites on the film surface.

Spectrophotometric measurements were performed by using a UV-VIS spectrophotometer (Shimadzu, UV-1800). Optical measurements were carried out at room temperature. The spectra were recorded by using a similar glass as a reference and hence the absorption due to the film only was obtained. The optical absorbance spectrum was measured within the wavelength range of 200–500 nm. The band gap of the films has been calculated from the absorption edge of the spectrum using Tauc formula for direct band gap material.

The electrical resistance of the films was measured before and after exposure to 200 ppm H_2S using a Keithley System Electrometer (Model 6514). Approximately 5 mm long silver (Ag) contacts, separated by 2 mm, were made on the films for electrical measurements. The dimension of the film was 6 mm× 6 mm. The width of the electrodes was approximately 1 mm. The film was mounted on a home-made two-probe assembly placed into a ceramic tube which was inserted coaxially inside a resistance-heated furnace. The conducting silver (Ag) paste was cured at 200°C. Commercially available calibrated mixture of hydrogen sulphide (H_2S) in air (Spancan, USA) was used. Before exposing to target gas, the film was allowed to equilibrate at the operating temperature for 30 minutes. The sensing characteristics were measured by measuring the resistance change with respect to time. Palladium surface sensitization of the film was carried out using chemical dipping technique.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of *ZnO* and Figure 2 shows the XRD pattern of *Cu* : *ZnO* film. Intensity in arbitrary units is plotted against 2θ in Figure 1. It is seen from Figure 1 that peaks appear at 31.75°, 34.4°, 36.2°, 47.45°, 56.45° and 62.8°. The diffractogram of the sample reveals that all the peaks are in good agreement with the Joint committee on powder diffraction standard (JCPDS) data belonging to hexagonal *ZnO* structure[8]. The corresponding reflecting planes are (100), (002), (101), (102), (110) and (103) respectively. The (002) peak appears with maximum intensity in pure and *Cu* doped films indicating all the samples have high preferred c-axis orientation. However copper incorporation results in loss of relative intensity of (002) peak compared to other peak. This

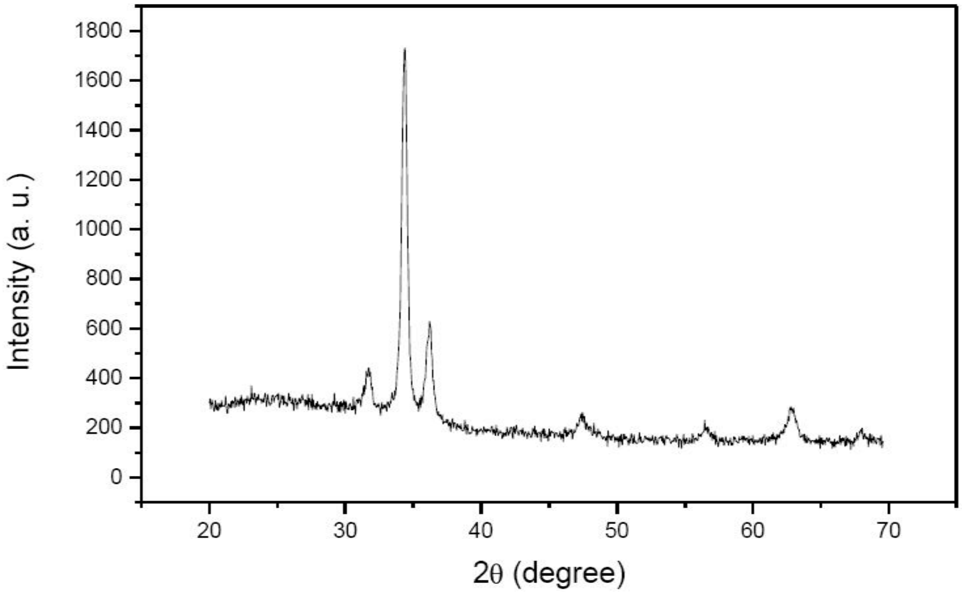

Figure 1 : XRD pattern of *ZnO*

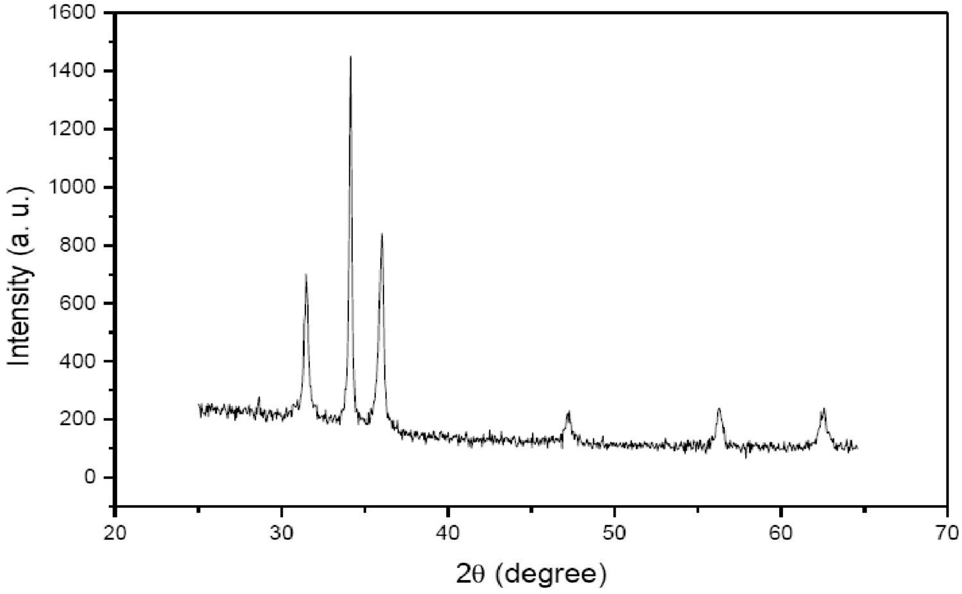

Figure 2 : XRD pattern of *Cu* : *ZnO*

suggests enhanced polycrystallinity of *Cu* : *ZnO* compared to *ZnO*. Apart from *ZnO* characteristic peaks, no peaks that correspond to either copper, zinc or their complex oxides could be detected. This observation suggests that the films do not have any phase segregation or secondary phase formation as well as *Cu* incorporation into *ZnO* lattice. Particle size evaluated using Scherrer's formula and utilizing MARQ2 computer software[9,10] gives ~ 25nm for *ZnO* and ~19.5 nm for *Cu* : *ZnO* indicating lowering of particle size due to *Cu* doping.

Figures 3 and 4 shows the SEM micrograph of pure *ZnO* film while Figures 5 and 6 shows the SEM images of copper doped *ZnO* film. Figure 3 shows SEM image at normal incidence with magnification ×5000 while Figure 4 shows the SEM image of the same film with magnification ×20000. Figure 5 shows the SEM image of *Cu* : *ZnO* film with magnification ×3000 and Figure 6 shows that with magnification×20000. It is evident that the microstructure consists of many nearly round shaped grains covering the substrate surface more or less uniformly. The grains get clearly defined at higher magnifications. There is agglomeration in certain regions for copper doped film. Porous microstructure is also clearly evident from images at high magnification indicating low density of the films.

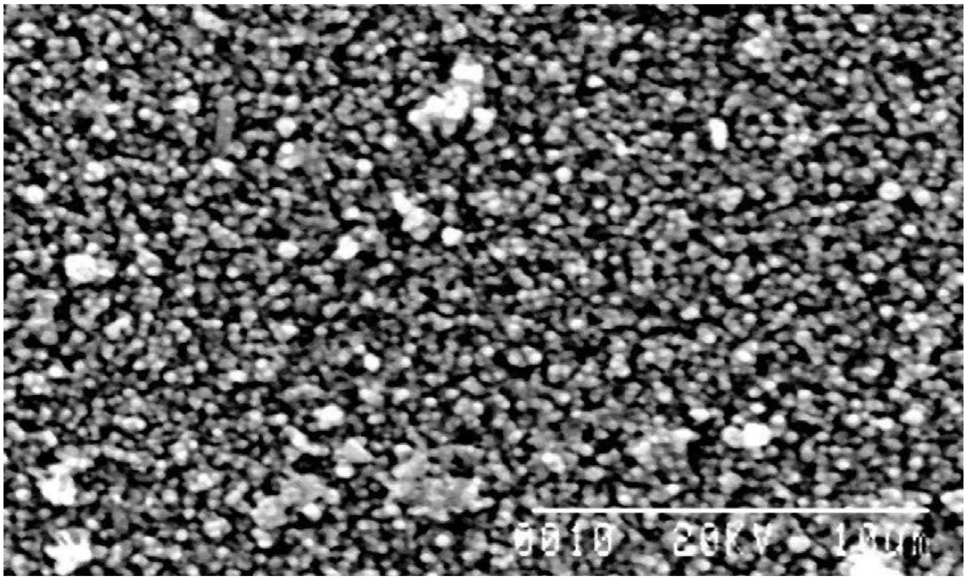

Figure 3 : SEM of *ZnO* (mag.×5000)

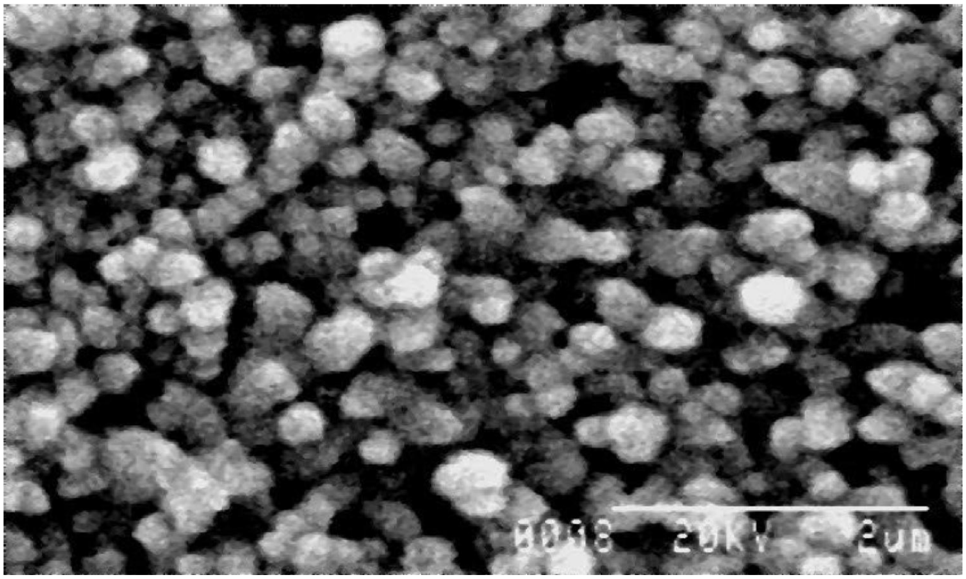

Figure 4 : SEM of *ZnO* (mag.×20000)

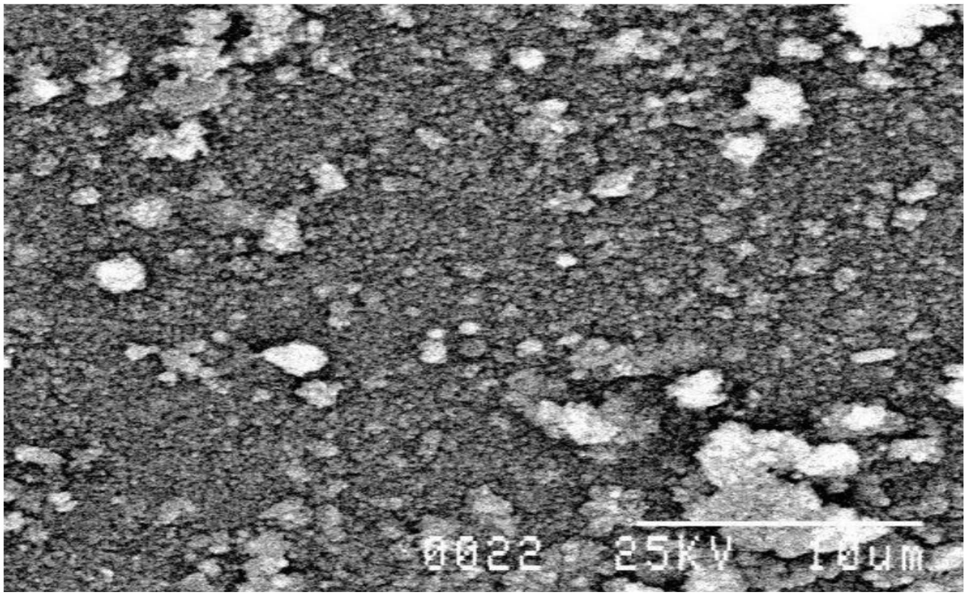

Figure 5 : SEM of $Cu : ZnO$ (mag.×3000)

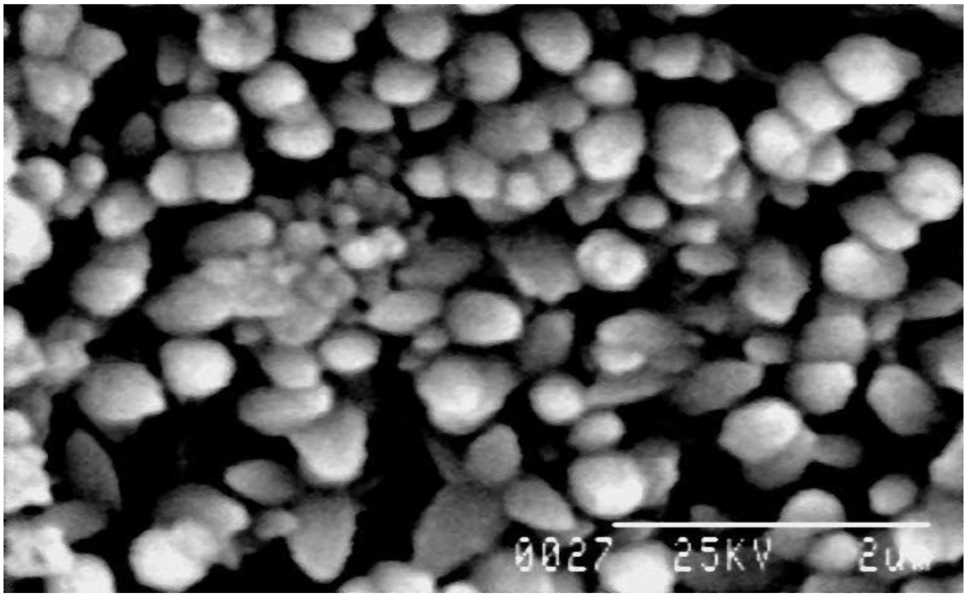

Figure 6 : SEM of $Cu : ZnO$ (mag.×20000)

ZnO is a direct band gap materials and the energy gap (E_g) was estimated using Tauc formula

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where A is a function of index of refraction and hole/electron effective masses, α is the absorption coefficient and $h\nu$ represents the photon energy. The direct band gap is determined using this equation when straight portion of the $(\alpha h\nu)^2$ against $h\nu$ plot is extrapolated to intersect the energy axis at $\alpha = 0$. Plot of $(\alpha h\nu)^2$ against $h\nu$ for ZnO and $Cu : ZnO$ are shown in Figures 7 and 8 respectively. Figure 7 shows the spectrum of pure ZnO while Figure 8 shows the spectrum of $Cu : ZnO$ thin film. It is seen that copper doping results in a decrease in the value of the fundamental absorption edge. The values are ~3.17 eV for ZnO and 3.02 eV for $Cu : ZnO$. This decrease can be accounted for the large difference in E_g values of ZnO and CuO. Also Cu incorporation increases film resistance by forming deep acceptor states within the band gap of ZnO[11,12]. Such decrease in donor levels may also gives rise to increased band gap[13].

Figure 9 shows the plot of resistance ratio R_{gas}/R_{air} against time in minutes at an operating temperature of

300°C. Here R_{air} and R_{gas} represents the equilibrium sample resistance in ambient air and under test gas (200 ppm H_2S) respectively. The sensitivity has been defined in different ways in the literature[14-17]. It has been defined as R_{gas}/R_{air} [14,15], in which case it is a quantity less than one (1), since for reducing gases since resistance of sensor material decreases in presence of a reducing gas. Sensitivity has also been defined as percent reduction of sensor resistance[16,17]. The percent sensitivity (or the percent reduction of sensor resistance in presence of test gas) can be expressed as

$$S\% = \frac{R_{air} - R_{gas}}{R_{air}} \times 100.$$

In the present work, the sensing characteristic was carried out for a fixed concentration of target gas and we have used the above equation for calculation of sensitivity. All the sensing measurements were carried out at 300°C. The percent sensitivity of ZnO and Cu doped ZnO are ~ 40% and ~ 60% respectively indicating that Cu incorporation enhances sensitivity to H_2S. Such enhancement in H_2S sensitivity due to Cu doping has been attributed to increased material resistance[18] (decrease in donor density observed in our present work). The surface of the thin films was sensitized with palladium (Pd) by a dipping technique. The process involved multiple dipping of the film in a 50 cc solution of 1 wt. % palladium chloride ($PdCl_2$) in ethyl alcohol (C_2H_5OH). After each dipping the film was withdrawn

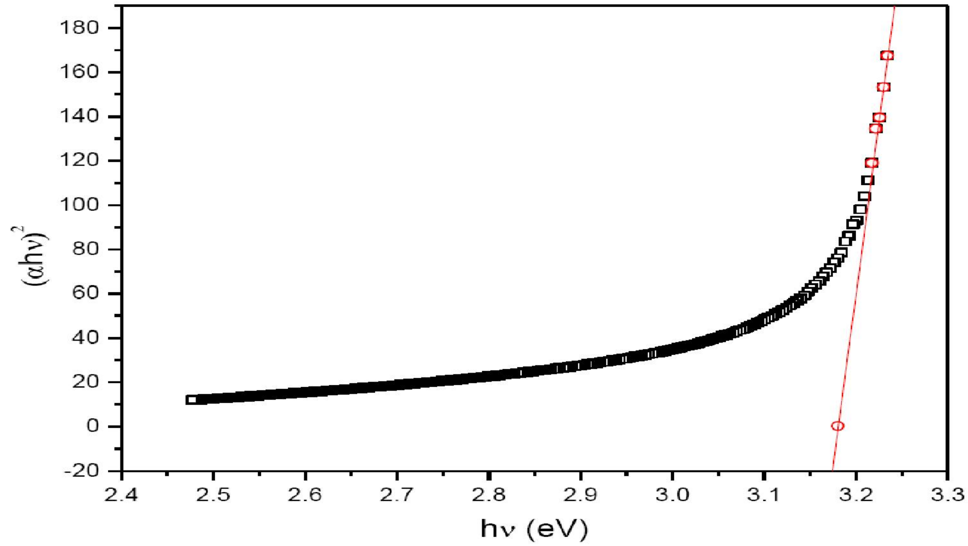

Figure 7 : Plot of $(\alpha h\nu)^2$ vs photon energy (in eV) of ZnO

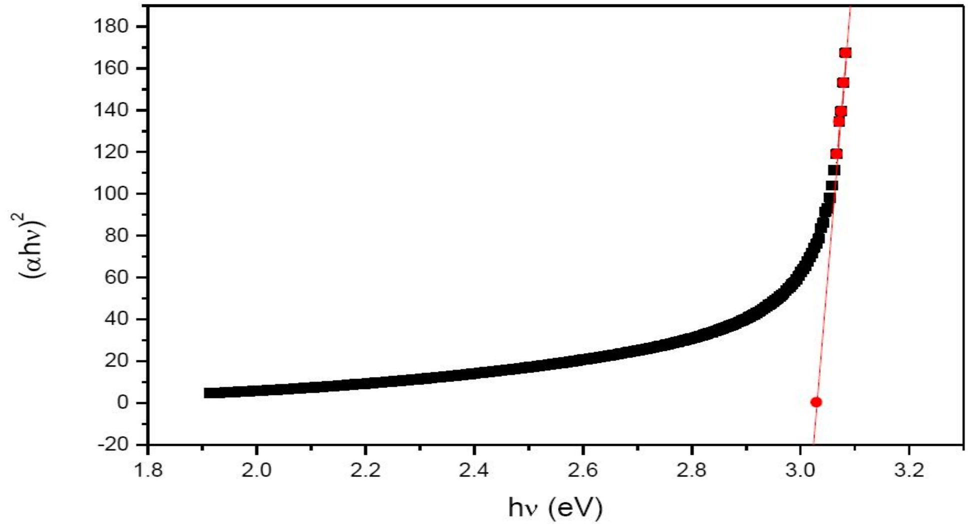

Figure 8 : Plot of $(\alpha h\nu)^2$ vs photon energy (in eV) of $Cu : ZnO$

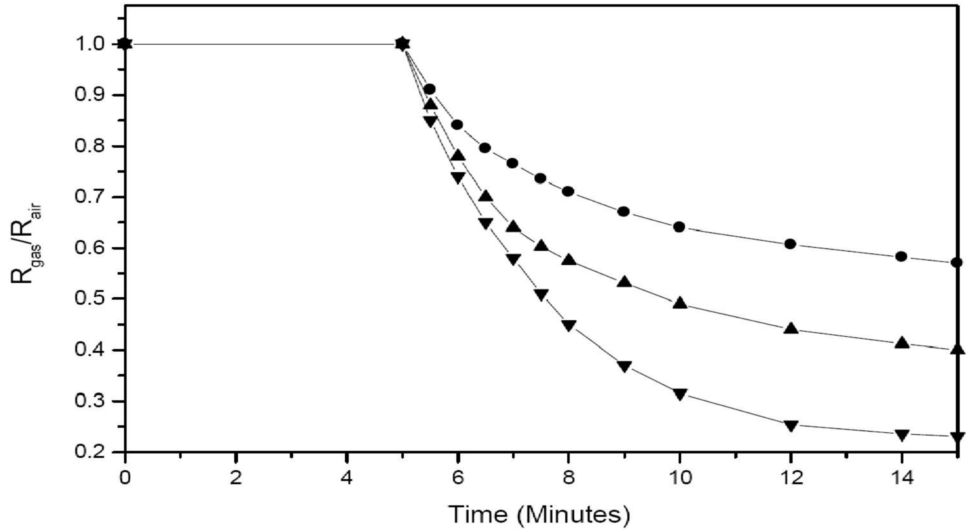

Figure 9 : Sensing characteristics in presence of 200 ppm H_2S in air at 300°C for (●) *ZnO*, (▲) *Cu* : *ZnO* and (▼) *Pd* Pd sensitized *Cu* : *ZnO*

form the solution and the volatile solvent (alcohol) was allowed to evaporate leaving behind a coating of $PdCl_2$. The dipping time was 2–3 seconds each time in alcohol medium. The *Pd* loaded films were subsequently heat treated at 250°C for 1 hr. to remove chlorine. Such surface sensitization with palladium increases the sensitivity to ~ 77% which clearly shows catalytic activity of palladium.

The gas sensing mechanism normally accepted for semiconductor sensors assume that the oxygen adsorbed on the surface of the oxide traps some of the conduction electrons and thus decreases the material's conductivity[10]. The surface adsorbed oxygen species thus becomes negatively charged chemisorbed species (O_2^- or O^-) and acts as reaction centers for gas molecules. At temperatures high than 200°C, O^- is the dominant species. When reduction gas molecules come into contact with this surface, they may interact with this chemisorbed oxygen species, leading to an inverse charge transference[20]. Upon the return of the electrons to the conduction band, conductivity increases. The reaction mechanism for H_2S with surface adsorbed species leading to the final products SO_2 and H_2O may be represented as

$$H_2S + 3O^- \rightarrow H_2O + SO_2 + e^-$$

The released electron decreases the resistance (sensing action).

Enhancement in sensitivity due to palladium incorporation has been explained by the fact that the palladium treatment increases the density of adsorbed oxygen species. This means increase of reaction centers for gas molecules. Thus the *Pd* layer enhances the sensitivity by increasing the availability of chemisorbed species required for the gas molecules to react.

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REFERENCES

[1] S.H.Jeong, B.N.Park, D.G.Yoo, J.H.Boo; Journal of the Korean Phys.Soc., **50**, 622 **(2007)**.
[2] K.V.Gurav, V.J.Fulari, U.M.Patil, C.D.Lokhande, O.Joo; Appl.Surf.Sci., **256**, 2680 **(2010)**.
[3] R.A.Michaels; Environ.Health Perspat., **107**, 617 **(1999)**.
[4] M.Batzill, U.Diebold; Phys.Chem.Chem.Phys., **9**, 2307 **(2007)**.
[5] P.Mitra; Mat.Sc.Res.India, **8**, 197 **(2011)**.
[6] P.Mitra, J.Khan; **98**, 279 **(2006)**.
[7] S.Mondal, P.Mitra; Bull.Mat.Sc., **35**, 751 **(2012)**.
[8] Joint Committee on Powder Diffraction standards; Inorganic Vol., B.Post, S.Weissmann, H.F.McMurdie, (Eds); Card No. 36-1451, International Centre for Diffraction Data, Swarthmore, PA, **(1990)**.
[9] X.Jumin, J.Wang; Matt.Lett., **49**, 318 **(2001)**.
[10] P.Sharma; Nat.Mater., **2**, 673 **(2003)**.

[11] A.Furukawa, N.Ogasawara, R.Yokozawa, T.Tokunaga; Jpn.J.Appl.Phys., **47**, 8799 **(2008)**.

[12] J.Leea, H.Leea, S.Seob, J.Parka; Thin Solid Films, **398-399**, 641 **(2001)**.

[13] R.Cebulla, K.Wendt, K.Elmer; J.Appl.Phys., **83**, 1087 **(1998)**.

[14] N.S.Baik, G.Sakai, K.Shimanoe, N.Miura, N.Yamazoe; Sensors and Actuators B, **65**, 97 **(2000)**.

[15] J.H.Yu, G.M.Choi; Sensors and Actuators, **75**, 56 **(2001)**.

[16] D.Lee, H.Jung, S.Ban, J.Huh, D.Lee; Sensors & Actuators B, **71**, 90 **(2000)**.

[17] L.Jianping, W.Yue, G.Xiaoguang, M.Qing, W.Li, H.Jinghong; Sensors & Actuators, **65**, 111 **(2000)**.

[18] P.S.Shewale, V.B.Patil, S.W.Shin, J.H.Kim, M.D.Uplane; Sensors & Actuators, **186**, 226 **(2013)**.

[19] S.M.Chou, L.G.Teoh, W.H.Lai, Y.H.Su, M.H.Hon; Sensors, **6**, 1420 **(2006)**.

[20] S.S.Kale, R.S.Mane, H.M.Pathan, A.V.Shaikh, O.S.Joo, S.H.Han; Appl.Surf.Sc., **253**, 4335 **(2007)**.