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Optical VOC sensing applications of Al-doped ZnO coated optical fiber

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Undoped and 1 at.% Al is prepared by sol gel method. Doped ZnO is coated on the optical fiber cores in order to sense various concentrations of methanol, ethanol, isopropanol and acetone vapour at room temperature. All the films have hexagonal wurtzite structure when analysed using the XRD spectra. The output power changes depending on the interaction between light propagation, coated fiber and the analyte. Output power ratio for 1 at.% Al-doped ZnO coated optical fiber reduces when the coated fiber is exposed to the tested vapour. Meanwhile for ethanol detection, the output power increases and has lower absorption than air. The time response of the vapour sensor is presented for undoped ZnO. Undoped ZnO has higher detection capability compared to Al-doped ZnO coated optical fiber due to the crystallite size.

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1. Introduction

Evanescent wave in fiber optics has attracted a wide measure of attention because of its potential applications in biochemical, biomedical and environmental sensors. These coated sensors have several advantages such as the possibility to operate under room temperature, low cost fabrication, applicable in explosive and electromagnetic environments. For tapered fiber preparation, the heat-pulling method still contains thick cladding while for fiber etching method, they tend to have only the core in the sensing region. By tapering, the evanescent field can be easily accessed and can interact with the examined analyte. Evanescent field mechanisms are used for sensor design detection by examining the interaction between light propagation in optical fibers and the target analytes. Metal oxide-based gas sensors have long been investigated as sensing materials for gasses. ZnO has attracted a wide measure of attention because of its potential applications in gas sensing applications [1], dye sensitized solar cell [2], optoelectronic devices and so on. Doping with different elements can improve and change the rate of gas adsorption. Zn^{2+} atoms is replaced by higher atom elements [1-3] which have high conductivities. ZnO thin film deposition techniques have been prepared by metalorganic chemical vapour deposition [4], electron beam evaporation [5], r.f. magnetron sputtering, [6] sol–gel process [3] and spray pyrolysis [1]. Recently, fiber optic gas sensor which is coated with metal oxides has been reported to operate with improved sensitivity at room temperature [7]. For the sensing mechanism, the oxygen molecule is adsorbed on the surface of ZnO as O^- and O^{2-}. Under the presence of a tested gas, the chemisorbed oxygen will react due to the sensing reaction and re-inject the free carrier thus reducing the ZnO resistance. The gas sensitivity depends on the concentration of the adsorbed oxygen ions on the surface of the metal oxide [1]. In this paper, we report the detection of volatile organic compound (VOC) of methanol, ethanol, isopropanol and acetone vapour at room temperature using undoped ZnO and Al-doped ZnO coated on the optical fiber core. The doped ZnO on unclad fiber optic for gas sensing application have been rarely reported.

2. Methodology

For material preparation, undoped ZnO and 1 at. % Al-doped ZnO were prepared using a simple and low cost sol gel technique. Zinc acetate dehydrate and the aluminium nitrate were dissolved in a solvent of 2-methoxyethanol and monoethanolamine (MEA) was added as a stabilizer. The solution was stirred for several hours as to obtain a clear and homogenous sol. The films were coated using spin coating technique and the solvents were evaporated in order to remove any organic residuals. The films were annealed for one hour in air for crystallization. The crystallographic structure can be determined by analysing the X-ray Diffraction (XRD) spectra and the morphological features were studied using field emission scanning electron microscope (FESEM). The optical properties of the films were characterised by examining the data from UV-Vis spectrometer. Meanwhile, for optical fiber preparation, glass-clad silica fibers were used as the sensing probe. The jacket is removed and the cladding is etched using hydrofluoric (HF) acid solution in room temperature. The optical fiber reacts with HF and the rate of etching depends on the area of exposed length, temperature and acid concentration [8] that causes dissolution. The vapour sensor is constructed using a bent U-shaped optical fiber. The surface of the fiber core is coated with undoped ZnO or 1 at.% Al-doped ZnO using dip-coating techniques. The experimental setup is done under dark surrounding at room temperature with normal atmospheric pressure conditions. A bent fiber has higher detection capabilities compared to a straight fiber. Laser source at a wavelength of 1550 nm was used as the light source for sensing and was detected using EXFO optical power meter. Various concentrations of acetone, isopropanol, methanol and ethanol were prepared and injected directly using a syringe into the gas chamber through a gas inlet without disturbing the coated fiber. The liquid is allowed to vaporise for several minutes and the measurement is taken by observing the changes on the power meter. Fig. 1 shows the experiment setup for alcohol vapour detection using coated fiber with ZnO and Al-doped ZnO.

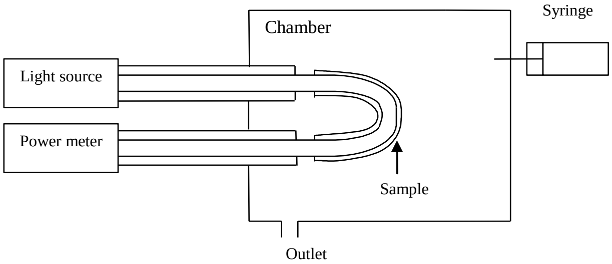


Fig. 1. Experiment setup for alcohol vapour detection using ZnO coated optical fiber.

3. Results and discussion

3.1 Structural and optical analysis

The XRD spectra as shown in Fig. 2 can be used to determine the crystallographic structure of the thin films. Al-doped ZnO film has peaks with high intensities at planes (100), (002), (101) and peaks with lower intensities at (102) and (110). It shows that doped ZnO form a hexagonal with wurtzite structure that have nanosized particles. Scherrer's formula as shown in equation (1) [9] is used to determine the estimated crystallite size.

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the wavelength of CuKα radiation, β represents FWHM of the peak and θ is the Bragg's angle. The crystallite size for undoped ZnO and 1 at.% Al-doped ZnO are 61.4 Å and 67.5 Å respectively. The diffraction peak for (002) increases by doping ZnO with Al which indicates an improvement in the crystallinity of the films.

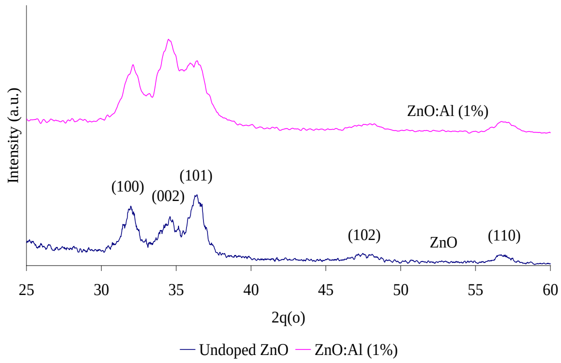


Fig. 2. XRD spectra of undoped ZnO and 1 at.% Al-doped ZnO thin films.

Fig. 3 shows FESEM images of undoped ZnO and 1 at.% Al-doped ZnO films that were deposited on glass substrates. The nanoparticle sizes for undoped ZnO and 1 at.% Al-doped ZnO were almost the same which is approximately around 25 nm to 35 nm. It can be seen that the surface to volume ratio of nanocrystalline ZnO thin film increases and became denser when doped with Al.

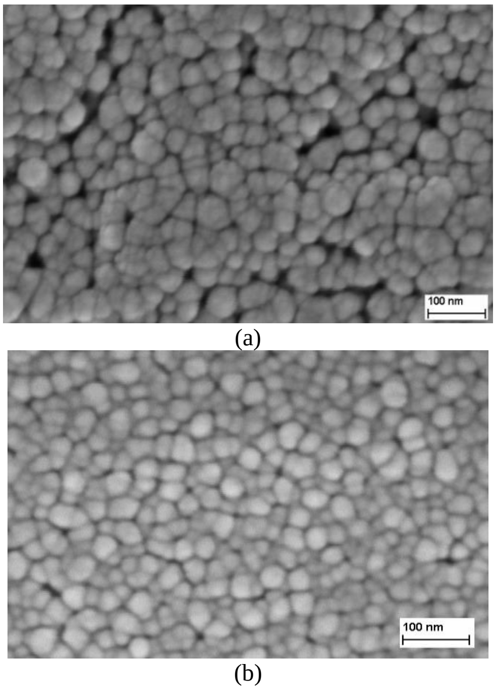
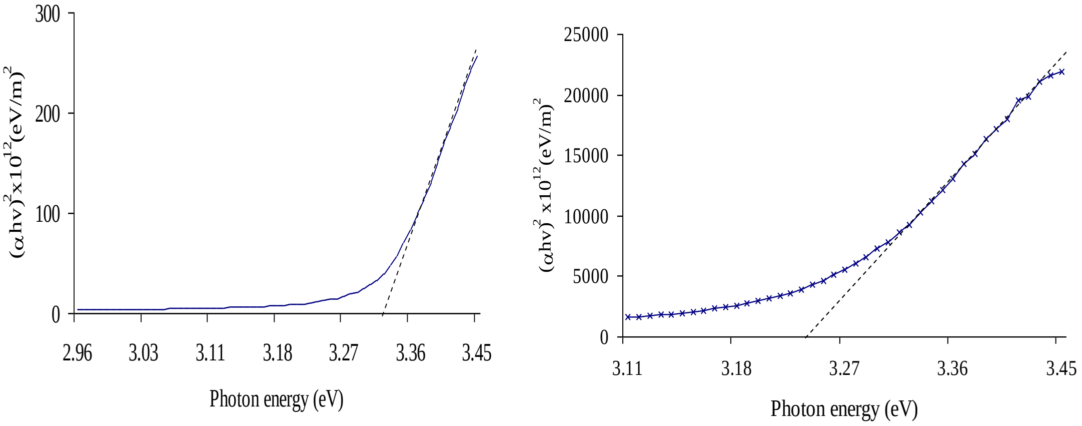


Fig. 3. FESEM images of (a) Undoped ZnO and (b) 1 at.% Al-doped ZnO.

The optical properties of the thin film describe the nature of the band gap and can be evaluated from Fig. 4 by extrapolating the linear line part of the curves. The direct band gap of the films were calculated using the relationship as equation (2) [10],

$$\alpha hv = A(hv - E_g)^n \tag{2}$$

where α is the absorption coefficient, A is a constant, $h\nu$ is the photon energy, n is a constant determining the type of optical transition and E_g is the energy band gap. The band gap value of ZnO and 1 at.% Al-doped ZnO is 3.312 eV and 3.24 eV respectively. The band gap reduces when doped with Al which may be due to the band shrinkage effect due to increasing carrier concentration [11].



(a) (b)

Fig. 4. $(\alpha h\nu)^2$ versus hν plots of (a) ZnO and (b)1 at.% Al-doped ZnO.

3.2 Gas sensing mechanism

3.2.1 The transmission ratio for coated quartz slide under alcohol vapour

Gas sensing mechanisms in metal oxide is related to the change in resistance of material due to the interaction between gas vapour and the adsorbed oxygen species on the surface of ZnO. The photoconductivity increment may be due to the free electrons during the photodesorption process. Experimental setup with 1550 nm laser source and spectrometer HR4000 as a detector was used to measure the transmission ratio of ZnO-coated quartz slides under air, methanol, ethanol, acetone and isopropanol vapour. This measurement is done in order to determine the changes of transmission ratio (P_o/P_i) where P_o represents the power intensity under alcohol vapour while P_i is the power intensity without alcohol vapour. Fig. 5 shows the measurement setup for the quartz substrate of doped ZnO. The coating did not make any contact with the solution and is allowed to vaporise. Blank substrate without coating is used as a reference. The magnitude of the transmission spectra for each dopant is showed in Fig. 6. From Fig. 6(a), the light intensity reduces when isopropanol, acetone and methanol is injected inside the chamber but for ethanol, the laser intensity increases. It shows that for undoped ZnO substrates, the absorption of ethanol vapour is lower than the absorption in air and other alcohol vapours. Meanwhile, from Figure 6(b), the Al-doped ZnO substrates show higher absorption of the surrounding alcohol vapours as compared to a purely air ambience which results in the output power reduction with time. This film transmission ratio results may be used as a reference in order to determine the variation of output power ratio based on coated optical fiber. Therefore, usage of undoped-ZnO coating on optical fibers as gas sensors will increase the alcohol vapour absorption and hence improve the transmission ratio and sensitivity of the gas sensor.

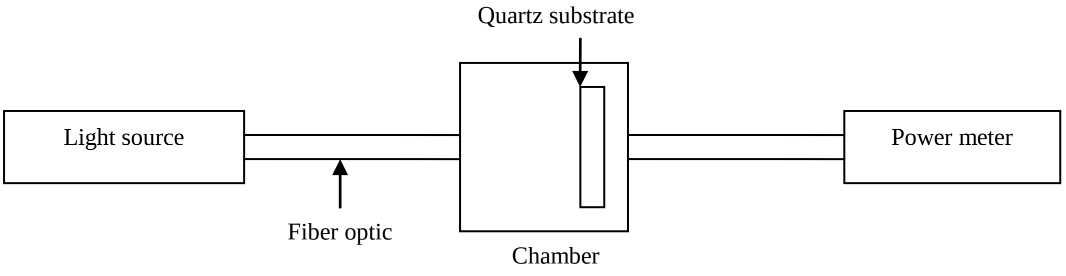
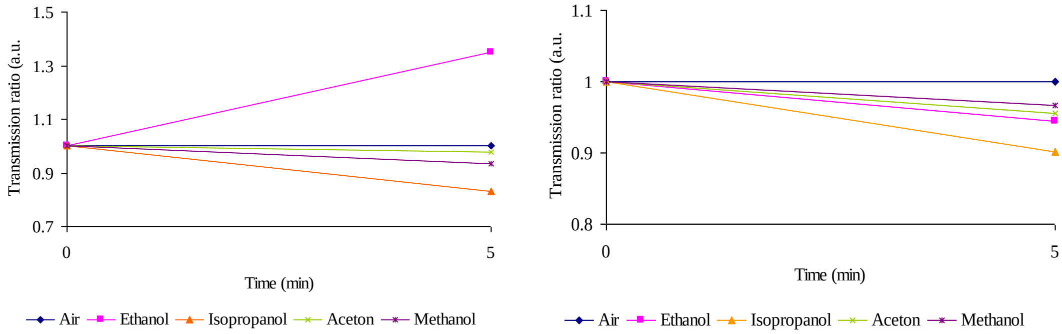


Fig. 5. Transmission setup for coated quartz substrate of doped ZnO under alcohol vapour.



(a) (b)

Fig. 6. Transmission ratio of coated quartz substrate with (a) Undoped ZnO, (b) Al-doped ZnO.

3.2.2 The reaction of coated fiber optic with alcohol vapour

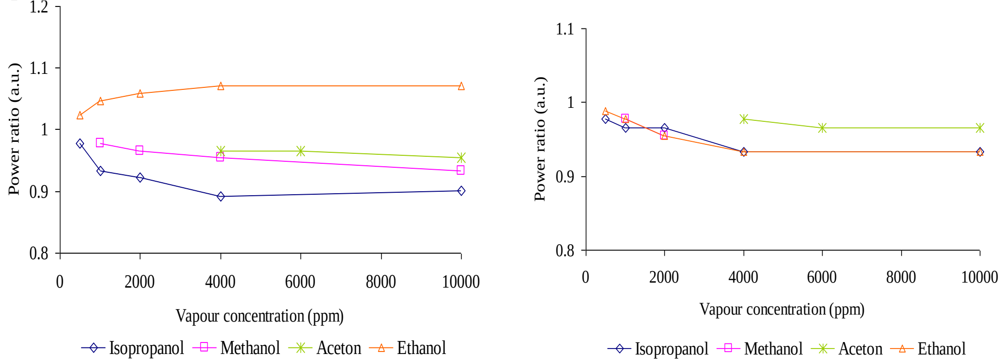
The penetration depth of the evanescent field on unclad U-shaped part of an optical fiber is significantly increased compared to purely straight fiber. The penetration depth, d_p is given by equation (3) [12],

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\cos^2\theta - \left(\frac{n_2}{n_1}\right)^2}} \tag{3}$$

where λ is the wavelength of light source, θ is the incidence angle at the interface of core and cladding. n_1 and n_2 is the refractive index of the core and cladding respectively. The light enters the modified cladding and the occurrence of the total internal reflection or leaking depends upon the changes at the outer medium of refractive index, the modified probe geometry and the incident angle [13, 14].

When the refractive index of modified cladding is lesser than the core (n_1>n_2), internal reflections occurs at the interface and increase the intensity of light propagation. Meanwhile, when the refractive index of modified cladding is higher than the core (n_2>n_1), some of the light is reflected at the interface and enter the modified refractive index which is called the leaky mode.

A small amount of solution was injected inside the chamber using a micrometer syringe and the alcohol was allowed to vaporise. ZnO which act as a modified refractive index has a higher refractive index which is 1.709 [15] compared to the fiber core which is 1.4446. The sensor operates in a leaky mode as some of the light enters the modified cladding of the doped ZnO region. The changes on the refractive index value depends on the tested vapours. Fig. 7(a) shows that the output intensity ratio decreases as the ZnO coated fiber is exposed to isopropanol, methanol and acetone vapours. Meanwhile for ethanol vapour detection, the output power for ZnO coated fiber will increase as the ethanol absorption is lower compared to air. Refractive index of ZnO is assumed to decrease from 1.709 and become lower than core. Undoped ZnO has higher detection on isopropanol vapours compared to other vapours. Fig. 7(b) shows that the output power reduces when exposed to the tested vapours. The magnitude of absorption is higher compared to air as a reference. Gas sensitivity of the sensor depends on the changes on peak intensity with concentration. The variation in the output power is due to the evanescent wave absorption. When the coated fiber sense and react with the examined analyte, the refractive index of the sample is changing and affect the output power. Smaller crystallite size leads to a larger surface area of the film, which gives higher oxygen adsorption. Gas sensitivity is effected by amount of adsorbed oxygen ions on the surface [16] of the materials. For the same amount of vapour concentration, undoped ZnO substrates give better power ratios for alcohol vapour absorption hence better sensitivity compared to Al-doped ZnO substates.



(a) (b)

Fig. 7. Power output ratio versus vapour concentration for coated fiber optic with (a) undoped ZnO (b) Al-doped ZnO.

Undoped ZnO substrates has the highest detection for ethanol vapours. Fig. 8 shows the performance of fiber coated with ZnO under ethanol vapours at room temperature. The repeatable sensing performance can be observed by monitoring the power ratio with a pulse width of 15 minutes. The output power is reduced by time until it reaches a saturated point. When the vapour is removed, the output power in increases and recovers back to its original state. The power could be reversibly modulated due to the reversible photoinduced changing of the ZnO refractive index.

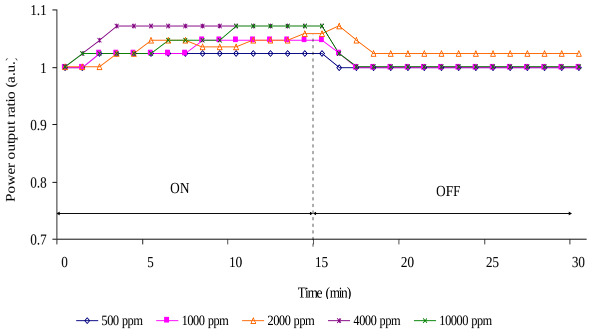


Fig. 8. The ratio of output power with a series of ethanol vapour pulse width of 15 min for undoped ZnO.

4. Conclusions

Undoped and Al-doped ZnO (1 at.%) have a hexagonal wurtzite structure. Undoped ZnO has a smaller crystallite size compared to 1 at.% Al-doped ZnO which affects the magnitude of alcohol vapour detection. For fiber coated with 1 at.% Al-doped ZnO, the output power is reduced with tested vapour concentrations. Meanwhile the output power is increased when undoped ZnO is exposed to ethanol vapours. Undoped ZnO has a higher detection capability compared to 1 at.% Al-doped ZnO.

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