RESEARCH PAPER

Synthesis and Study of ZnO Thin Films Using CVD Technique For Waveguide Sensor Applications

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ABSTRACT

Zinc oxide was deposited on the glass substrate as a waveguide sensor by chemical vapor deposition technique. The structure, surface morphology and optical properties of ZnO thin films are characterized using X-ray diffraction, binding energy SEM , UV-spectrophotometer, Raman spectroscope and Photoluminescence (PL). The results show that the waveguide sensor of ZnO offers a good response to detect different concentrations of glucose solution. The maximum sensitivity has been determined as 1.09 dB at 560 nm thickness of ZnO layer, while the minimum sensitivity was found to be 0.79 dB, 0.87 dB and 0.96 dB at thickness 213 nm, 315 nm and 435 nm respectively. It is believed that the ZnO material has a great potential to be utilized as a sensing layer in real world applications for the detection of chemicals leakage. In this work, the ZnO was deposited on the glass substrate as waveguide sensor by CVD method. Different thickness of ZnO layers are deposited on the glass substrate. The waveguide sensor was combined with laser source and photo-detector to detect different concentrations of glucose. it was showed a good response toward the change of the glucose concentration, which will be used to detect the chemical leakage in fuel station, wells and pipeline oil.

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INTRODUCTION

ZnO thin film is an optical transparent semiconducting material . Recently, Zinc oxide thin films have been studied extensively due to their potential applications such as, piezoelectric transducers , optical waveguides , surface acoustic wave devices , conductive gas sensors [1,2]. New days, ZnO is an emerging material that has many advantages over its competitors such as, inexpensive , relatively abundant , nontoxic and chemically stable [3]. ZnO has a hexagonal structure and it is characterized by a wide direct band-gap of 3.37eV. Zinc oxide is one of the most encouraging materials for improvement of chemical probes [4]. This is due to the availability of the variety of synthesis means and the diversity of topologies that can be grown by thin films and nano rods . In addition, Zinc oxide has a good carrier mobility and a broad spectrum absorption. There are many techniques to synthesis of high quality ZnO thin film on glass substrates. These techniques are reactive evaporation, chemical vapor deposition (CVD) [5], plasma enhanced

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chemical vapor deposition (PECVD) [6] ,sputter coater [7], spray pyrolysis [8] and sol-gel [9]. Comparing to the other methods, the chemical vapor deposition CVD method offers many benefits. These benefits are inexpensive, simple and good efficiency to synthesis of ZnO in powder form as the catalysts material [10]. Additionally, the performance of the CVD method makes the ZnO thin film an effective and homogenous layer which is required in many applications [11]. Thus, we considered that CVD method in this work. ZnO exhibits sensitivity to a broad range of external media such as, organic vapors, gases and chemical liquids and this is attributed to its high absorbance [12]. There are many studies which have been reported about the synthesis ZnO with different substrates as a sensing material [13,14]. In such applications, waveguide sensors are used in a wide range like detection of malignant gases [15,16] monitoring pollutants and other liquid compounds[17], pH detection [18], and detection of liquid chemical concentrations [19]. In this case, some sensitive materials coated the planar or channel waveguides which were used in such application of sensitivity. In one class of commonly used planer waveguide chemical sensor, an analytic (the measured concentration of solution) is placed in the evanescent field of the waveguide. On the other word, the measured change in the output light through the waveguide can be used to determine the change in the refractive index of the analyte. In this work, the ZnO was deposited on the glass substrate as waveguide sensor by CVD method. Different thickness of ZnO layers are deposited on the glass substrate. The waveguide sensor was combined with laser source and photo-detector to detect different concentrations of glucose. it was showed a good response toward the change of the glucose concentration, which will be used to detect the chemical leakage in fuel station, wells and pipeline oil.

MATERIALS AND METHODS

Chemical Vapor Deposition technique

Fig. 1 shows a schematic description for CVD technique involved many transport mechanisms. Firstly, the glass substrates have been cleaned before to their use. Diethylzinc (DEZ), dimethylzinc (DMZ) and zinc acetylacetonate have been used in this process. DEZ is the commonly used in this work. It has a high vapor pressure and it can be reacted with either oxygen or water to form zinc oxide by the following equation 1 and 2 [20].

$$(C_2H_5)_2Zn + 7O_2 \longrightarrow ZnO+4CO_2+5H_2O \quad (1)$$

$$(C_2H_5)_2Zn+H_2O \longrightarrow ZnO+2C_2H_6 \quad (2)$$

A pressure has been used about 2 mbar . The process was beginning by opening the gas valves as well as discharge DEZ vapor and water into the chamber. The partial pressures have controlled by manually checking the opening of needle valves of the sources, which regulates the precursor flow rate. After finishing of the deposition time, the DEZ flow was stopped, while preserving the water flow for ten minutes to clean the reactor. Furthermore, nitrogen gas was used within ten minutes in order to purge chamber before the pressure was lifted and the substrates were removed from the reactor. ZnO films with different thicknesses have been deposited on the glass substrates and the thickness was calculated by the gravimetric method as the following equation[21]:

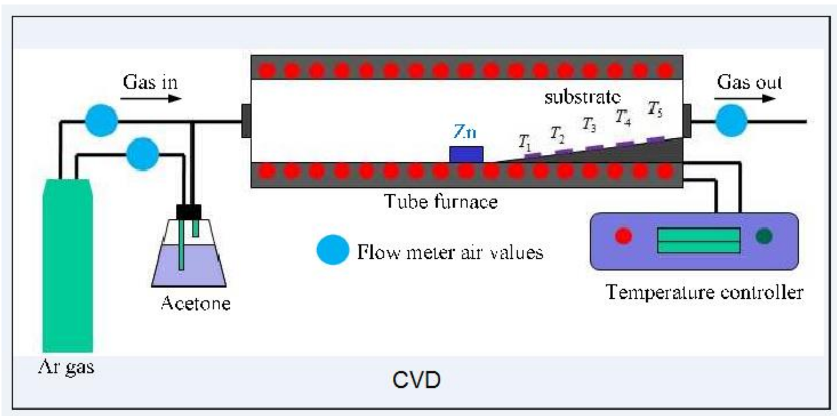

Fig. 1. Experimental setup of CVD technique

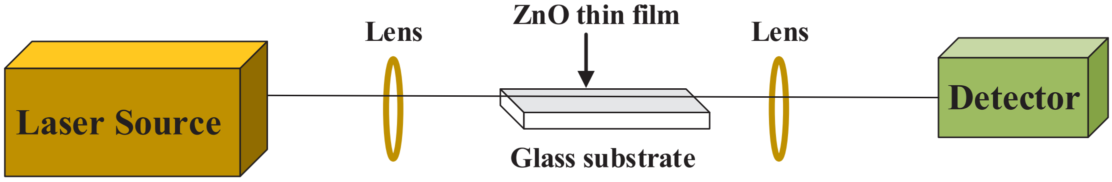

Fig. 2. Experimental setup of waveguide sensor .

$$t = \frac{m2 - m1}{A.\rho} \quad (3)$$

Where ρ is the density of zinc oxide (5.59 gm/cm^3) , t is the layer thickness of zinc oxide , A is the substrate area , m_1 and m_2 are the weight of substrates before and after deposition respectively.

Optical waveguide sensor preparation

The schematic setup of the waveguide sensor coated with ZnO is shown in Fig. 2. It consists of a semiconductor laser source (HOLMARC-OPTO-MECHATRONIC PVT.LTD) with emission wavelengths 650 nm and a highly sensitive photo-detector (HOLMARC-OPTO-MECHATRONIC PVT. LTD). The experimental setup of proposed waveguide sensor coated with different ZnO thickness was used to detect different glucose concentration. The signal from the laser source is incident on the waveguide sensor after exposing of different concentrations of the glucose solution and the transmitted signal is detected by photo-detector. The lenses , laser source, waveguide sensor and photo-detector were whole arranged together by 3D to obtain the strong signal received using the photo-detector. The waveguide coated with ZnO was placed in a container filled with the glucose solution and the light source was passed through the container and the output lights were sent into the photo-detector.

The optical properties depend on the materials that are used by the waveguide sensors in order to reach a specific measurement in the concentration. It readout system can then detect a change in refractive index and absorption of this material. The waveguide sensor is a channel that consists of at least two types of layers. In this study, the two-dimensional waveguide (2 x 2 cm) is a silica substrate. Such a waveguide, is made by depositing ZnO layer on the fused silica substrate to increase the sensitivity to change the concentrations of glucose solution. Nevertheless, at each transition between two adjacent layers of waveguide sensor, light is coupled from the ZnO layer into the glucose solution. Additionally, the propagating light in the optical waveguide is attenuated according to the absorption of the glucose solution. Therefore, the transmission of propagated light is decreasing and the losses increase. In Fig. 3 , it has been shown a photograph of the optical waveguide sensor.

RESULTS AND DISCUSSION

Structure properties

The structure properties for different thicknesses of ZnO layers deposited on glass substrates have been studied using XRD patterns. The typical XRD spectra of the ZnO layers have been illustrated in Fig. 4 . Zinc oxide film has crystallized in the wurtzite phase of hexagonal structure and presents a preferential orientation along the c-axis [22]. It is clear that the strong peak

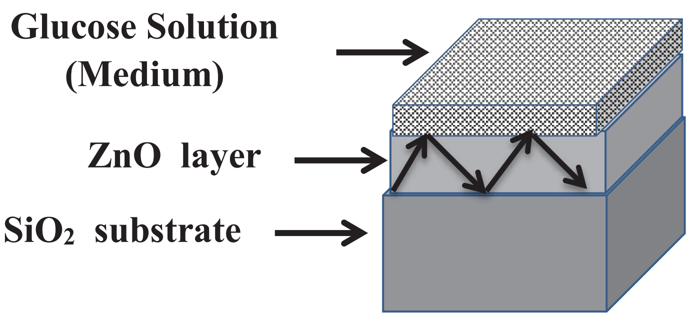

Fig. 3. Schematic view of optical waveguide sensor. structure

(101) observed at 2θ = 36.4° and other small peaks (100) , (002) , (102) , (110) , (103), (200), (112) and (201) corresponding at 32.87° and 34.43° , 47.73° , 57.88° , 63.53° , 67.23° , 68.33° , 69.53° respectively. Additionally, it was founded that the peak of intensity increases with increasing the thickness of the ZnO layer[23].

XPS analysis was investigated of the high resolution of the ZnO thin films for different thicknesses .It can be seen the state of 1s electrons of oxygen was existence at 531 nm and the peak intensity increases with thickness layer as Fig. 5 [24].

Surface properties

Zinc oxide films have been investigated by scanning electron Microscope (SEM). Fig. 6 shows the nanostructure of distribution particles of ZnO layer [25]. The uniform surface structure was observed for all thicknesses of ZnO layers .Moreover, it was founded that the deposited ZnO covered all the surface of substrate .However the surface roughness was increased with increasing of ZnO thickness due to the particles size is associated with the film thickness[26] as shown in Fig. 6 (a,b,c and c) respectively.

Optical properties

UV-Spectrophotometer

The optical properties of the Zinc oxide films have been studied by UV-Vis spectroscopy which equal that the thicknesses 213 nm, 315, 435 nm and 560. Fig. 7 illustrates the relationship between transmittance and wavelength of the ZnO layers. It can be seen that the transmittance spectrum decreases with increasing the wavelength of all thickness. However, the transmittance spectra decrease with increasing ZnO thickness. The samples exhibit high transmittance at minimum thickness of ZnO layers <80 [27] . Figs. 8 and 9 indicate that reflectance and refractive index respectively. It can be seen that both of reflectance and refractive index decrease with increasing the wavelength of range (300 nm- 900 nm). Also, it has been found that all spectra increased when the thickness of ZnO layers were increased. This increase is due to increase in the reflectance with the layer thickness, this process leads to increase in the refractive index. Furthermore , larger crystalline size leads to the higher value of n [28], which is turn increases the optical reflection. Thus, when the thickness increased , the optical transmittance was decreasing . it may be attributed to the larger crystalline size . The optical energy gap of ZnO layers of all thickness are shown in the Fig. 10. It is clear that the energy gap decreases

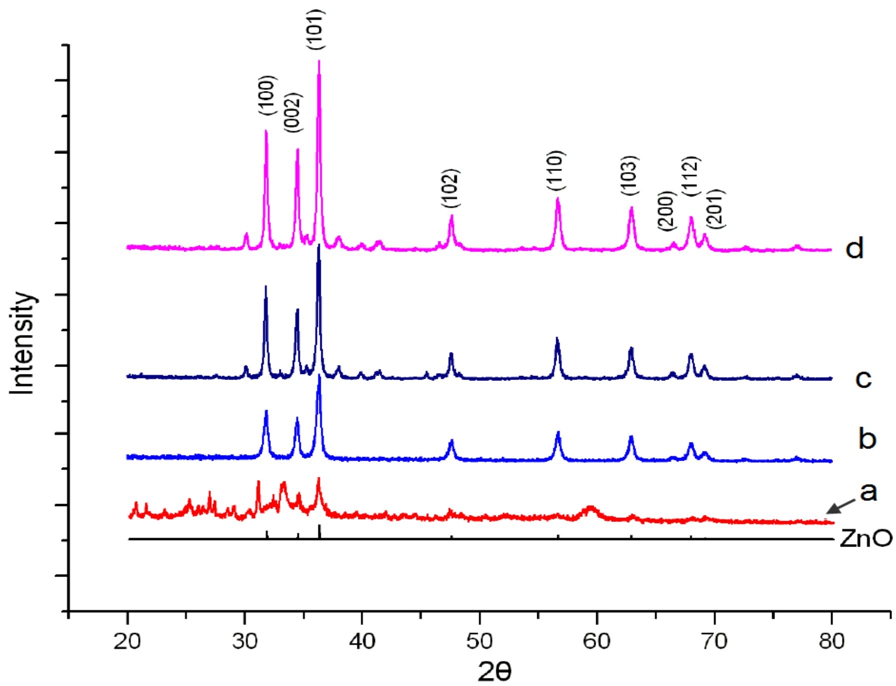

Fig. 4. XRD pattern of ZnO thin film with thickness (a) (213nm), (b) (315 nm), (c) (435 nm), (d) (560 nm) .

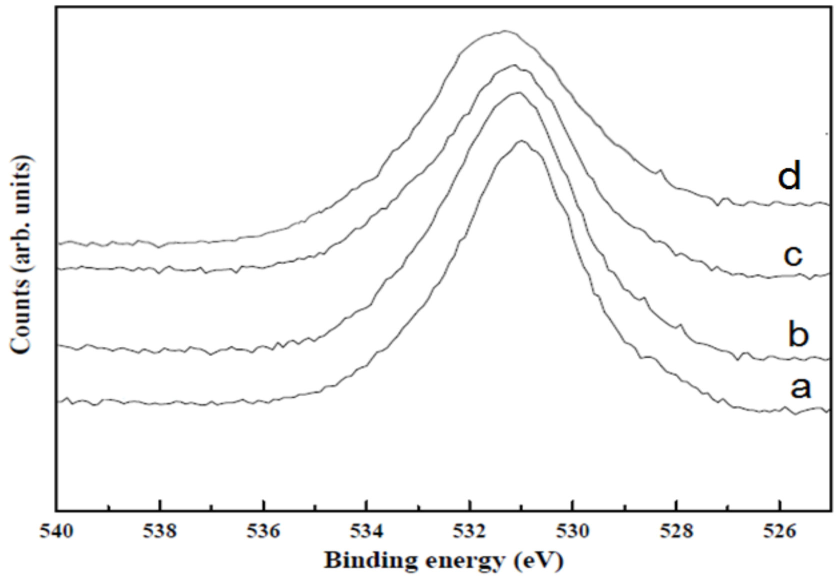

Fig. 5. XPS spectra of ZnO thin film with thickness (a) (213nm), (b) (315 nm), (c) (435 nm), (d) (560 nm) .

with increasing ZnO thickness (Eg = 3.18,3.1 2.97 and 2.93 eV) at thickness (213,315,435 and 560 nm) respectively. Table 1 shows the values of energy gap, reflectance and refractive index versus thickness of ZnO layer. The values in Table 1 are in good agreement with previously reported [29].

The optical energy gap of ZnO layers of all thickness are shown in the Fig. 10. It is clear that

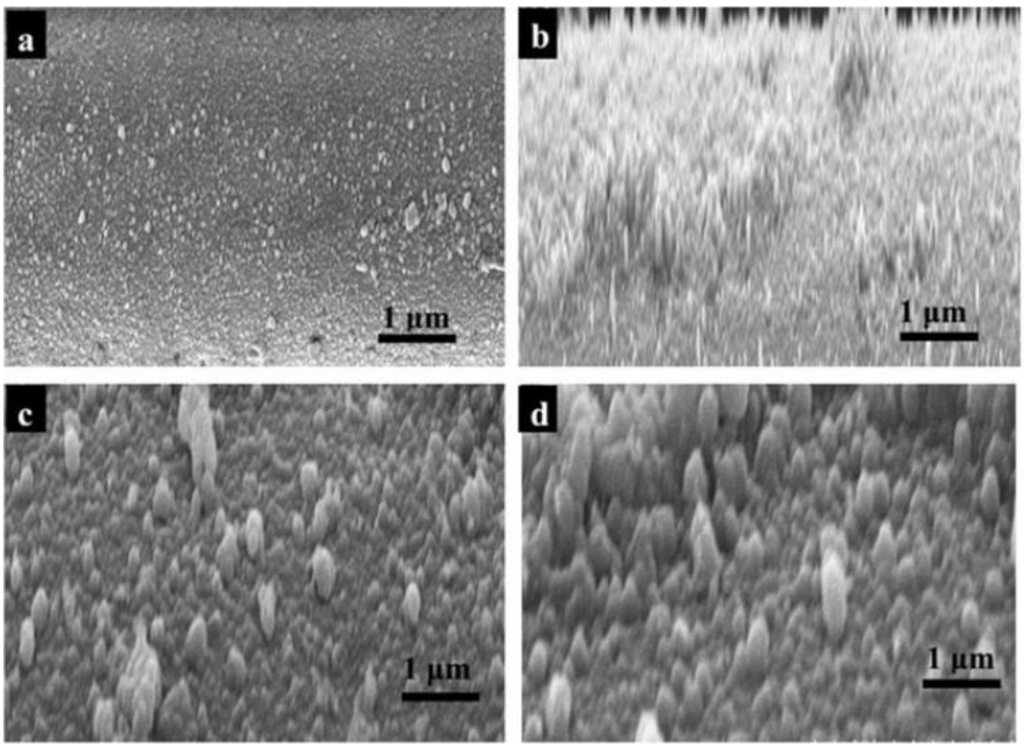

Fig. 6. SEM images of ZnO thin film with thickness (a) (213nm), (b) (315 nm), (c) (435 nm), (d) (560 nm) .

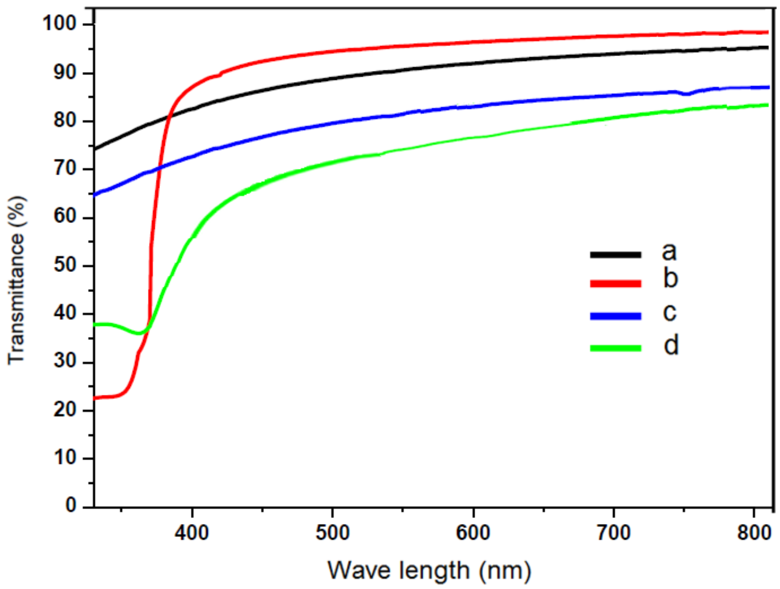

Fig. 7. Transmittance versus wavelength of different ZnO with thickness (a) (213nm), (b) (315 nm), (c) (435 nm), (d) (560 nm) .

the energy gap decreases with increasing Zinc oxide thickness (Eg = 3.18,3.1 2.97 and 2.93 eV) at thickness (213,315,435 and 560 nm) respectively. Table 1 shows the values of energy gap, reflectance and refractive index versus thickness of ZnO layer. The values in Table 1 are in good agreement with previously reported [30].

Raman Spectroscopy

Raman spectra show the main peaks are characteristic of the wurtzite phase . It is clear the peak positions shift toward the low frequency at high thickness . the strong relative intensity of the longitudinal optical (LO) band at 520 cm^{-1} ,this can be attributed to the reconfiguration of crystal structure of ZnO thin films and the formation of oxygen vacancies [31].

Photoluminescence (PL)

Photoluminescence spectra illustrated that one

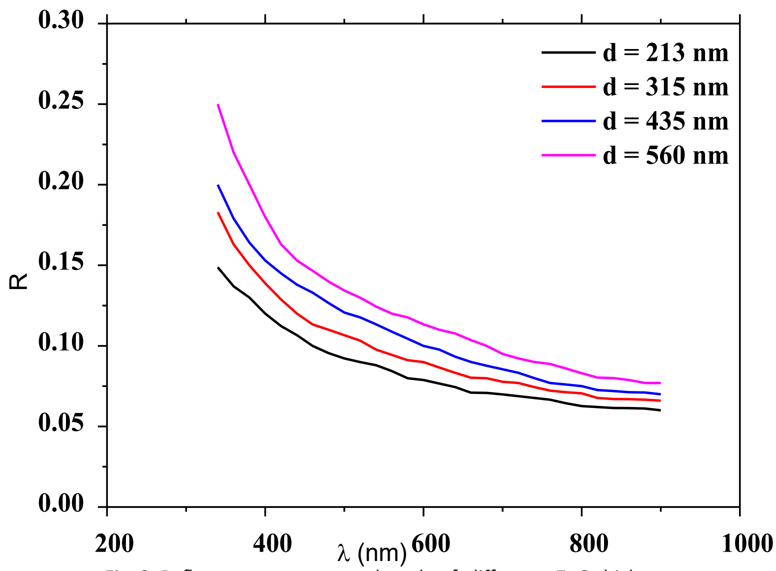

Fig. 8. Reflectance versus wavelength of different ZnO thickness

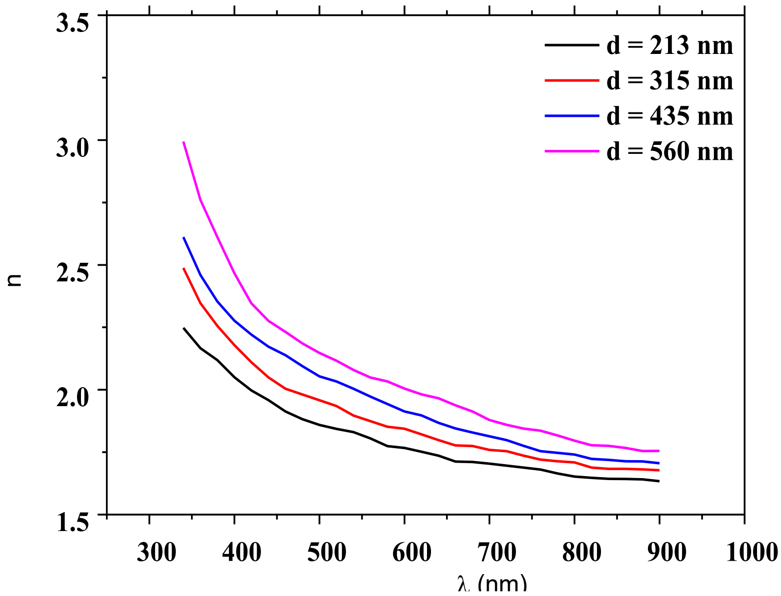

Fig. 9. Refractive index versus wavelength of different ZnO thickness.

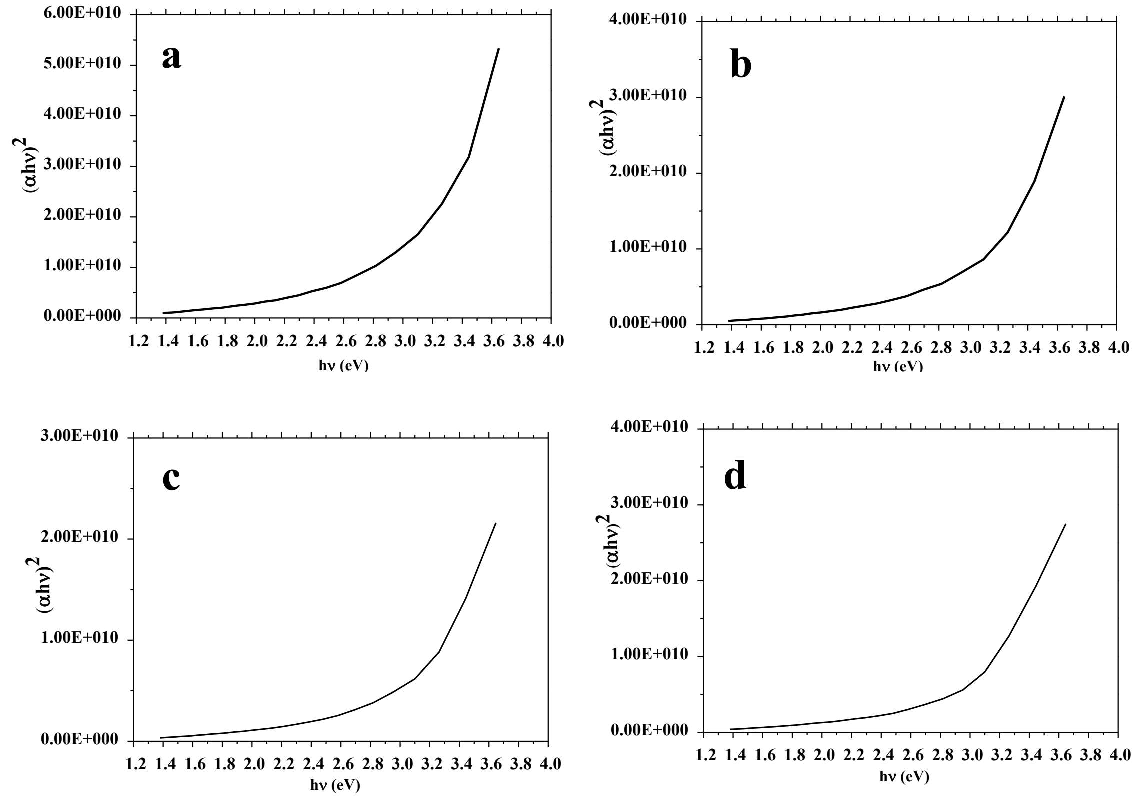

Fig. 10. Relationship between $(\alpha h\upsilon)^2$ and $(h\upsilon)$ of ZnO different thickness (a) 213nm,(b) 315nm,(c) 435nm,(d) 560nm

broad peak at visible region of the ZnO films was exhibited and shifted towards UV region near band edge at high thickness, attributed to the structural defects for insistence zinc and oxygen vacancies as Fig. 12. The increasing the thicknesses of zinc film can improve the structural quality, which can contribute its usage as a wave guide sensor applications [32].

Table 1. The values of ZnO thicknesses , energy gap, reflectance and refractive index at wavelength (520 nm).

Thickness of ZnO (nm)	Energy gap (eV)	Reflectance (R) (at λ= 520 nm)	Refractive index (*n*) (at λ= 520 nm)
213	3.18	0.08	1.84
315	3.1	0.1	1.93
435	2.97	0.11	2.03
560	2.93	0.13	2.1

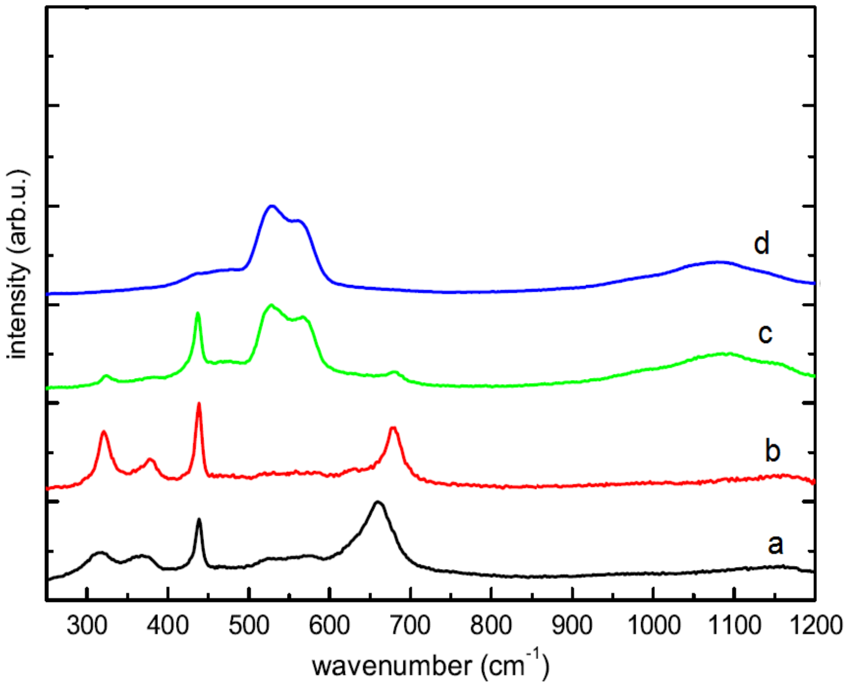

Fig. 11. Raman spectra versus wavelength of different ZnO with thickness (a) (213nm), (b) (315 nm), (c) (435 nm), (d) (560 nm) .

Sensitivity Measurement of Waveguide Sensor

To investigate the response of the waveguide sensor coated with different thickness of ZnO layer experimentally, the waveguide sensor was exposed to a different glucose concentrations of 0,1, 0,2 , 0,3, 0,4 and 0,5. In this case, the ZnO layer coated waveguide sensor contacted directly with the glucose solution. Therefore, the intensity of incident light decreased and this leads to increase the power losses [33]. Fig. 13 shows the relationship between the power losses (dB) and glucose concentration that having Zinc oxide thicknesses of 213 nm, 315 nm, 435nm, and 560 nm. It is clear that the power losses increase when the glucose concentration is increased for all ZnO thickness. Also, it can be seen that the ZnO thickness has a very influence on the sensitivity of the waveguide sensor. Additionally, the power losses have almost a linear behavior with respect to the glucose concentration. Fig. 13 also shows that the waveguide sensor with the thickness of 560 nm ZnO layer offers the maximum sensitivity that equal to 1.1 dB compared to that of 213 nm, 315 nm and 435 nm, which have sensitivities equal to 0.79 dB, 0.87 dB and 0.96 dB, respectively. It can be concluded that the zinc oxide nano particulates coated glass substrate as a waveguide sensor capable to detect different glucose concentrations.

CONCLUSION

The ZnO layer coated on the glass substrate by Sol-gel method as a wave guide sensor was

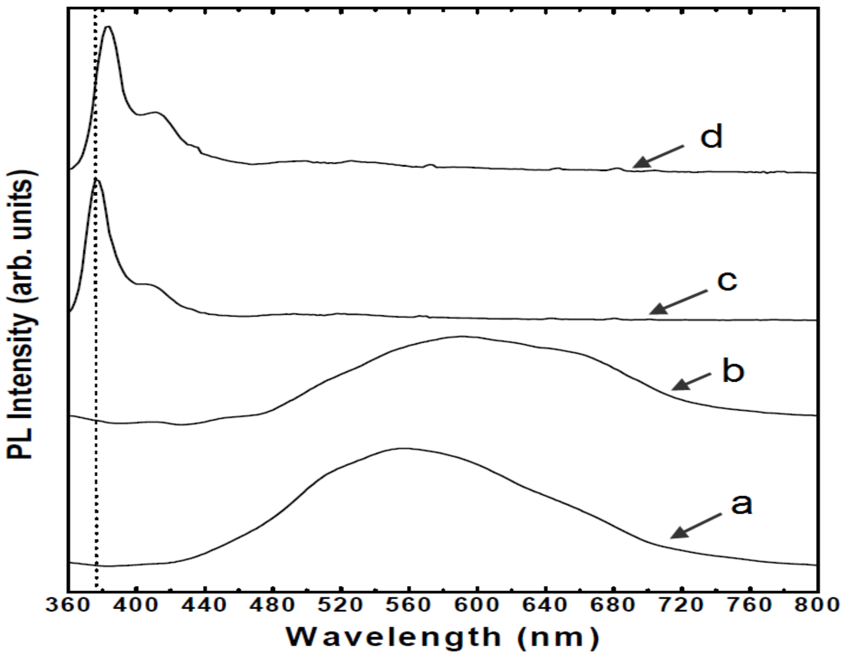

Fig. 12. PL spectra versus wavelength of different ZnO with thickness (a) (213nm), (b) (315 nm), (c) (435 nm), (d) (560 nm) .

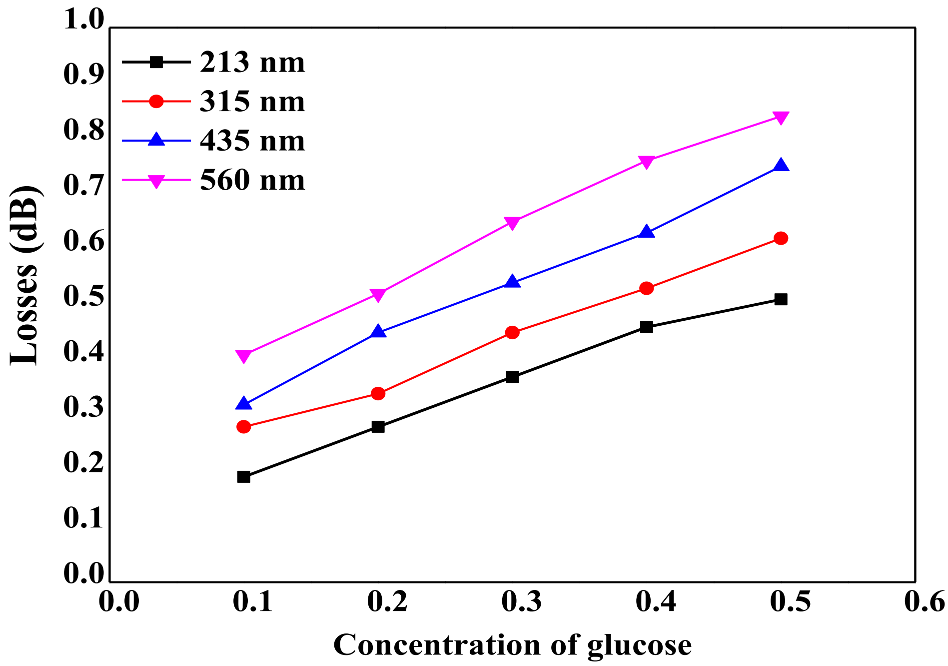

Fig. 13. The relationship between the power losses (dB) and glucose concentration of the waveguide sensors of ZnO thin films .

fabricated in this study. The proposed waveguide sensor exhibited a good response to glucose solution at room temperature. The deposited ZnO layer was confirmed by optical spectroscopies, XRD and SEM. The results showed that the highest sensitivity was equal to 1.1 dB at ZnO thickness of 560 nm, while the lowest sensitivities were found to be 0.79 dB, 0.87 dB and 0.96 dB at ZnO thicknesses of 213 nm, 315 nm and 435 nm, respectively.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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