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Detecting of NH_3, CO_2 polluted gases by using ZnO- In_2O_3 thin films

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ABSTRACT

Polycrystalline ZnO-In_2O_3 thin films for gas sensor were prepared on to glass substrates by using spray pyrolysis method from solution of 0.1 M $ZnCl_2$ and 0.1M $InCl_3$ at 300^oC temperature and 100 course of spray. A number of techniques including X-ray diffraction (XRD), atomic force microscope (AFM) and scanning electron microscope (SEM) are used to study the morphology of ZnO-In_2O_3 thin films. Polycrystalline structured of as-obtained films was confirmed by using these techniques. Optical properties, and sensitivity of thin film to NH_3, CO_2 gases was also studied.

KEYWORDS: *Thin films, crystalline structure, ZnO-IN_2O_3 thin films, sensors.*

I. INTRODUCTION

Metal oxide thin films like indium oxide and zinc doped indium oxide have unique characteristics such as good conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to substrates and chemical stability and photochemical properties. These properties are resulted from their n-type semiconductor behavior and wide band gaps. Therefore, indium oxide and zinc doped indium oxide are used in a wide range of applications including solar energy conversion and photovoltaic devices, flat panel displays and biocatalytic redox transformation. New applications require IZO films with lower resistivity and higher optical transmissions over the visible wavelength region. In order to obtain optimal characteristic i.e. high transparency and low sheet resistance, the parameters such as thickness of the film, dopant type and its amount and the other deposition conditions have to be optimized. It is well known that the electrical and optical properties of semiconducting oxides like In_2O_3 depend strongly on defect density created by external doping or disturbed stoichiometry as well as their preparation and growth conditions [1-5].

However, high cost of In_2O_3 has motivated efforts to develop substitutes. Recently, zinc oxide (ZnO) is a promising material in the above applications. It has a great interest in wide band gap semiconductors, because of the ever increasing commercial desire for short wavelength light emitting devices. As a good candidate, ZnO nano structured films have wide band gap (3.37 eV) [6] at room temperature (RT). The efficiency and performance of any optical and electrical nano devices are directly determined by the properties of underlying nanostructures, which are in turn greatly dependent on the crystallographic orientation, size, shape, and morphology. A highly transparent ZnO films have been prepared by many different deposition techniques and their corresponding deposition parameters play an important role in controlling the morphology and physical properties of the nanostructures. Both physical deposition, including thermal evaporation, sputtering, spray pyrolysis, metal organic chemical vapor deposition (MOCVD), pulsed laser deposition, molecular beam epitaxy (MBE) [7-15], and chemical synthetic routes, including hydro thermal, sol-gel, electrochemical, chemical bath deposition [16-26] have been successfully employed to prepare a wide variety of ZnO nanostructures.

Spray pyrolysis technology is a convenient for the deposition of semiconductor thin films and has the several advantages in comparison with other deposition techniques such as low cost of the source materials, producing high quality films using comparatively simple deposition equipment, moderate substrate temperatures, deposition scaled for large area and uniform deposition with very thin layers with specific composition, morphology, good adhesion between the deposited film and controlling the shape and sizes. The morphology of the material depends on the thermal treatment [27].

Gas sensor play vital role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere at very low concentrations. Semiconductor gas sensors in the form of thin films are highly sensitive and reliable, having a performance/price ratio comparable to that of microelectronic components [28].

In the present investigation , pyrolysis methods has been used to prepared a polycrystalline ZnO-In_2O_3 thin films, the structural characterization from XRD,SEM and AFM were studied .Optical properties, and Sensing properties also was calculated for NH_3 , CO_2 gas.

II-EXPEREMENTAL

Chemical spray pyrolysis is one of the major techniques used to deposit a wide variety of materials including metal or alloy oxides. Generally, spray pyrolysis deposition system which is mainly consists of the following four sections: (a) the reactants and carrier gas assembly connected to the spray nozzle at the entrance of the reaction chamber, (b) the reaction chamber in which there is a resistive heater used to heat the substrate to the required temperature for thin film deposition, (c) the temperature controller that monitors the deposition temperature and controls the desired substrate temperature and (d) the exhausting gas module, as it shown in figure (1). The substrate temperature was measured using a K-type thermocouple to an accuracy of ± 1 K. The film were prepared on clean glass substrates, the slides first cleaned in distilled water in order to remove the impurities and residuals from their surfaces, followed by rinsing in chromatic acid (for two day), to introduce functional groups called nucleation and /or epitaxial centers, which formed the basis for layer films growth. Then the samples were washed repeatedly in deionized water, and finally put in ultrasonic agitation with distilled water for 15 min then dried. The solution used for the preparation the films investigated here had the following amounts: the mixture of 1.1425 gm of $ZnCl_2$ and 0.88212 gm of $InCl_3$ at (50:50) molar ratio, at molarities 0.1M for both solutions. The glass substrate temperature was 300^{o}C. The atomization of the solution into a spray of fine droplets was carried out by the spray nozzle with 1 mm inner diameter, with the help of compressed air as carrier gas. During the course of spray (100 course), the substrate temperature was monitored using a thermocouple with the help of digital millimeter. The slides then were placed on the surface of a substrate heater when sprayed. The nozzle-to-substrate distance was 25 cm.

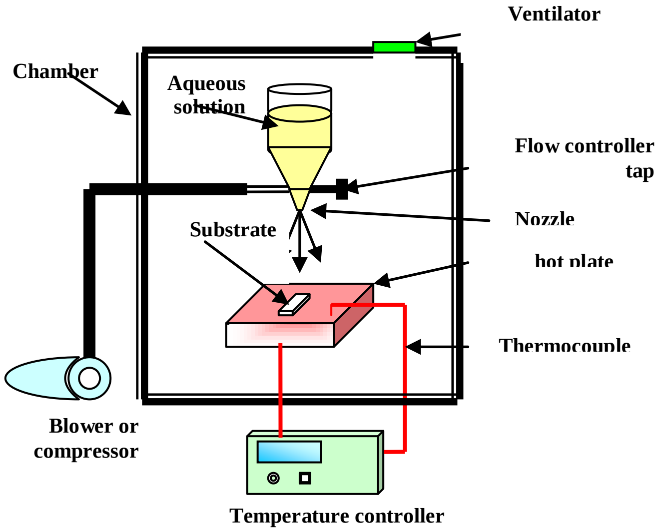


Figure (1): Spray Pyrolysis System

III- RESULTS AND DISCUSSION

3.1 The structure and morphology of films :

Typical XRD pattern for ZnO - In_2O_3 films prepared by pyrolysis method is presented as in figure (2) . As exhibited in figure (2) the films show a crystalline structure. Diffraction peaks at 2θ= 31.592^o and 34.357^o were assigned to hexagonal ZnO planes (100) and (002) respectively) based on comparison with JCPDS standard [28]. In the same pattern can be observed at 2θ= 35.981^o and, the reflection of (400) planes of In_2O_3 cubic structure [29], this results are the same with the other research [28,30]. Table (1) refers to the structural parameters to the prepared samples.

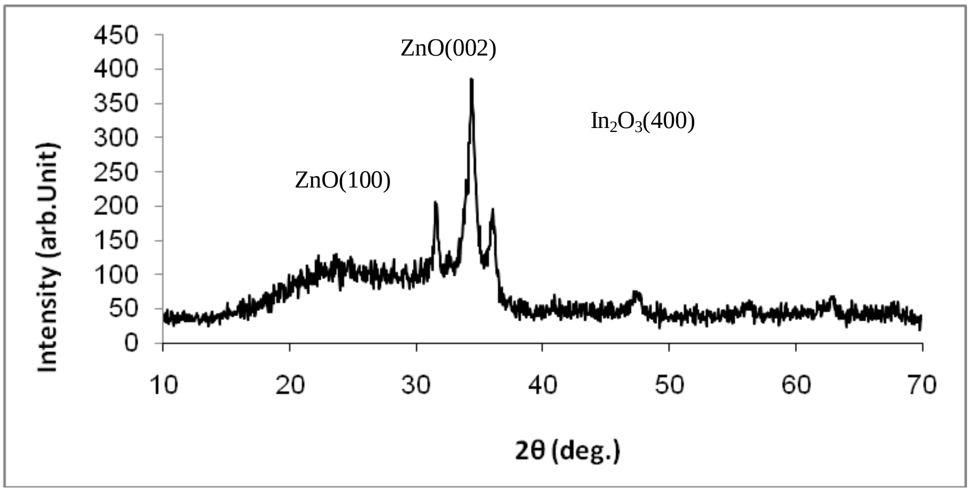


Figure (2) XRD pattern of ZnO-In_2O_3 sample prepared by pyrolysis method

Table (1): Values of some structure parameters of ZnO-In_2O_3 thin film

Sample	2Theta(deg)	d(A°)	hkl	FWHM
ZnO	**31.592**	**2.82977**	**100**	**0.6154**
ZnO	**34.357**	**2.60807**	**002**	**0.8504**
In_2O_3	**35.981**	**2.49499**	**400**	**0.7889**

From the XRD patterns it is possible to evaluate the average grain size (D) of the ZnO-In_2O_3 thin films by using the Well –known Deby- Scherer's formula [31].

D=Kλ/βcosθ,………………………….(1)

Where, the constant K is a constant of the order unity, λ is the wavelength of X-rays (1.4506A°) for CuK_α), θ is the Bragg's angle and β is the full width at half maximum. The dislocation density (δ) has been evaluated from Williamson and Smallman's formula [31].

$\delta=1/D^2$ lines /m^2……………....………(2)

The micro strain (ε) is obtained using the relation [31].

ε=β cos θ/4……………….......………..(3)

All these parameters are calculated and presented in Table 2.

Table (2) structural parameters of ZnO-In_2O_3 thin films

Samples	Grain Size (D)X10 nm	Density (δ) $x10^{15}$ Lines/m^2	Micro strain (ε) $x10^{-3}$
ZnO (100)	14.010	5.094	2.589
ZnO (002)	10.209	9.594	3.554
In_2O_3 (400)	11,059	9.594	3.278

The surface morphology of the thin films was also investigated. SEM and AFM characteristic photographs are shown in figure (3) and (4).

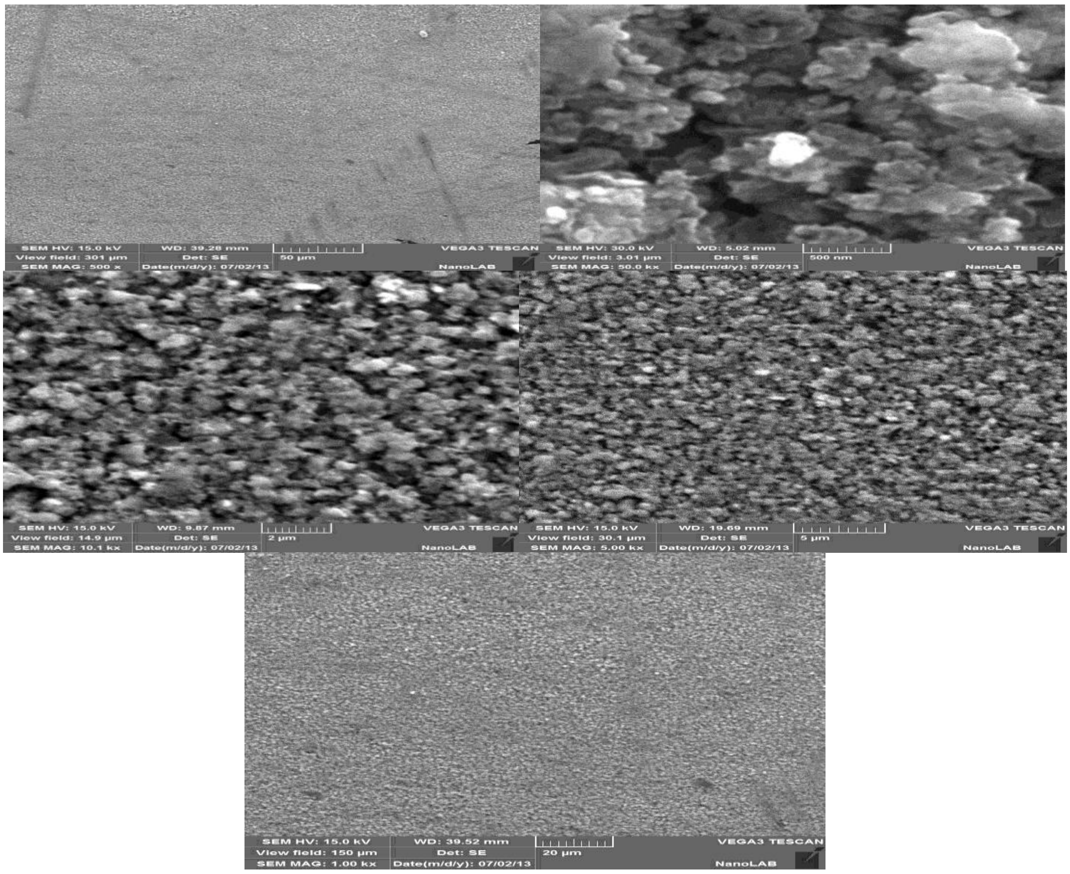
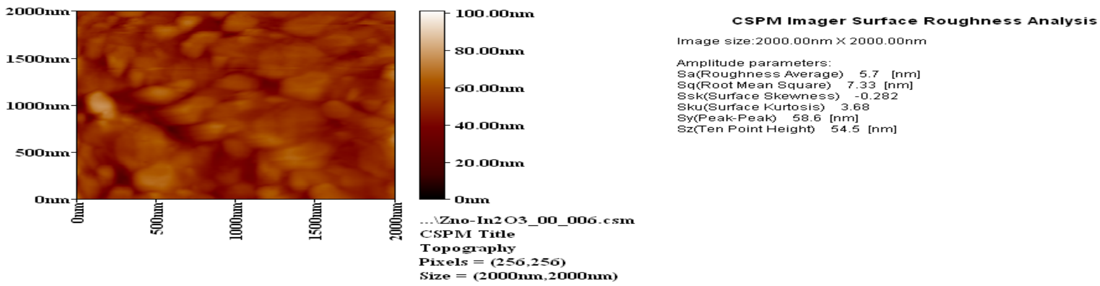


Figure (3) SEM micrographs characteristic of ZnO-In_2O_3 thin film

From figure (3), the SEM micrograph of as-deposited film shows uniform deposition over the substrate well. SEM characteristic micrograph, given the extremely small crystallite size, few tens or even few hundred nm and reveals that the ZnO film consists of round shape particles. In figure (4), a typical 2×2 □m^2 sized AFM image of ZnO-In_2O_3 film surface is shown. The film crystallites are well shape and uniform in size. It was observed, from 3D image that, the films exhibit a surface columnar morphology, which can be a consequence of crystalline preferential orientation. The film roughness was 5.7 nm. AFM images indicate that the used preparation conditions of the films are more favorable to obtain sample with excellent surface morphology. All used investigation techniques reveal the polycrystalline structure of the obtained films.



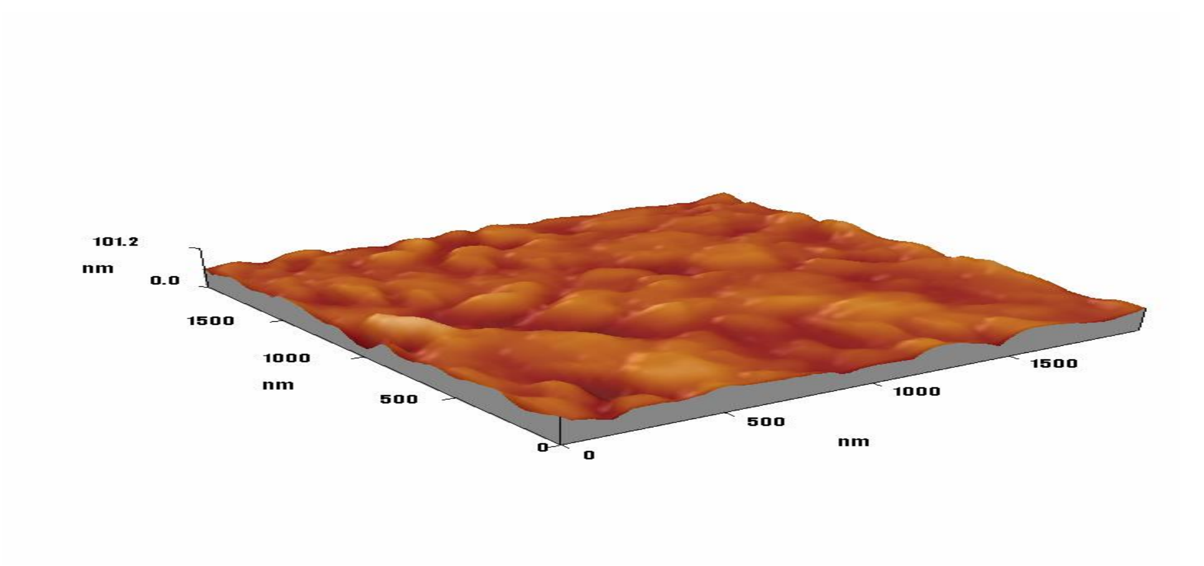


Figure (4) AFM micrographs characteristic of ZnO-In_2O_3 thin film

3.2 Optical properties

The optical properties of a material provide information about the electronic band structures, localized states and the nature (types) of optical transitions, the optical properties are very important for the understanding of the materials. Figure (5) shows the combination of optical absorbance spectra for ZnO- In_2O_3 thin film . The spectra of the deposited thin film was measured using UV-VIS spectrum (Optima Sp – 300 Plus) in the wavelength region of 305-900 nm**.**

Figure (6), show the variation between absorption coefficients (α) with wavelength. The $(\alpha \nu h)^2$ versus $h\nu$ for optical band gap of the ZnO- In_2O_3 thin film was studied. The optical band gap values have been determined by the extrapolation of the linear portion on the energy axis. The value of the optical band was 3.11 eV as it shown in figure (7).

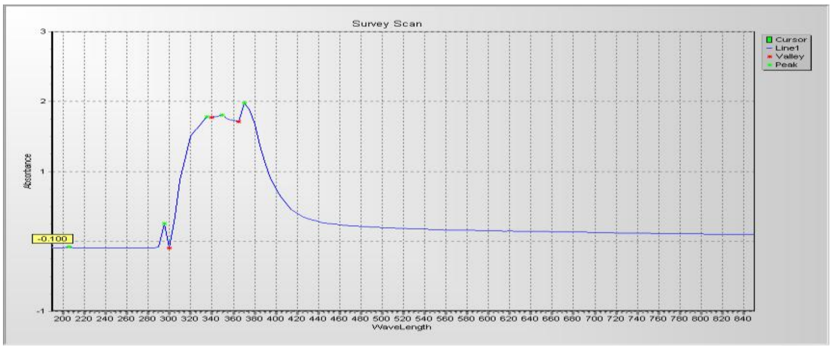


Figure (5) Typical optical absorption spectra for ZnO- In_2O_3 thin film

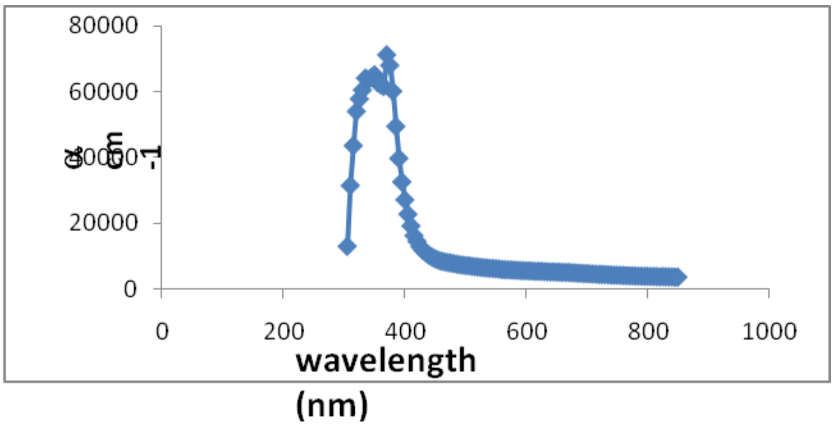


Figure (6) Plot of α versus wavelength curve of ZnO- In_2O_3 thin film

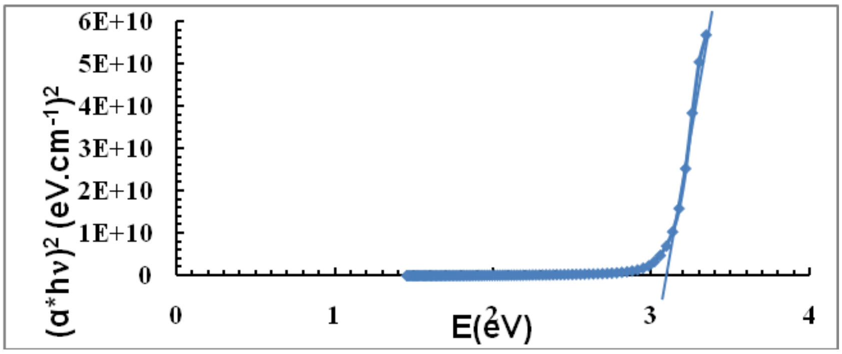


Figure (7) Plot of $(\alpha h\nu)^2$ versus $(h\nu)$ curve of ZnO -In_2O_3 thin film

3.3 Response to gases vapor

The experimental arrangement for sensitivity measurement for NH_3, CO_2 gases vapor is shown in figure (8). Nitrogen gas was purged for 20 min to clean the sample environment, examined gases (NH_3, CO_2) was injected by micro-syringe into test chamber and sensing characteristics of the sensor was then observed. The change in electrical resistance of a sensor was measured by electrometer. The time taken by the sensor for all of resistance was considered as response time of a sensor. The ratio of measured resistance before and after exposing the sample surface to gas vapor gives the value of sensitivity [26], as it calculated from the equation (4). Figure (9) shows the sensitivity of the sensor to gases.

$$S = \left| R_{(air)} - R_{(gas)} \right| / R_{(air)} \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

The sensing properties were studied at low concentrations (9 ppm) of gases vapor. The optioned results in pyrolysis methods are promising for the preparation of sensitive and low cost gas sensor operating in room temperatures. It can be fabricating sensor to detect variety of gases.

Figure (8) Experimental arrangement system for gas detecting

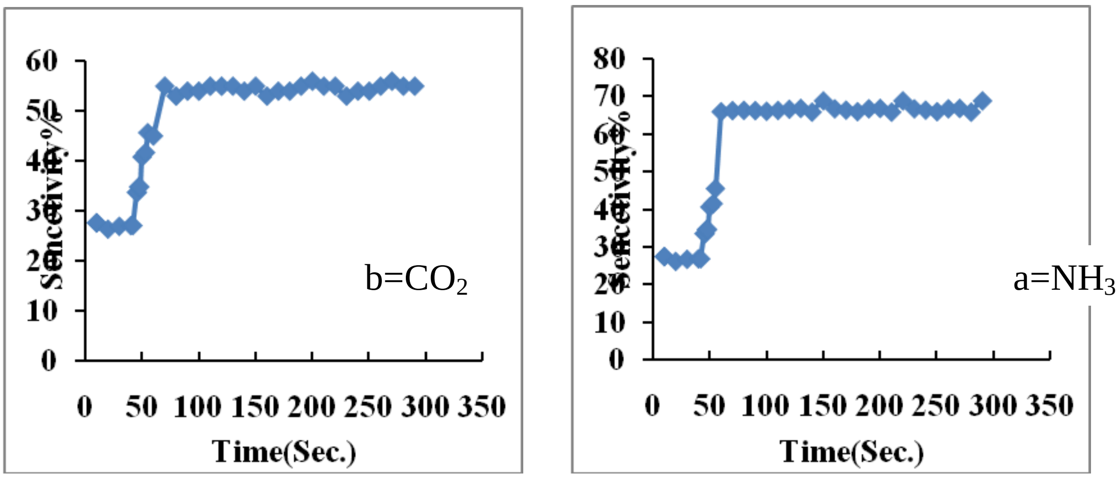


Figure (9:a,b) Sensitivity vs. time of ZnO-In_2O_3 thin film to NH_3, CO_2 gases

IV- CONCLUSION

Polycrystalline ZnO-In_2O_3 thin film sensor for NH_3, CO_2 gases has been prepared in pyrolysis method successfully. The films have been characterized by x-ray diffraction, SEM microscopic and AFM microscopic. From the optical properties of thin films we observe the optical gap which is about 3.11eV. The sensitivity of the sensor to NH_3, CO_2 has been obtained at room temperature. The ratio of sensitivity of NH_3 is better than CO_2 vapor. This result obtained in pyrolysis methods are promising for the preparation of sensitive and low cost NH_3, CO_2 sensor operating in room temperatures.

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