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A simple and cost-effective zinc oxide thin film sensor for propane gas detection

Vinoth Kumar Jayaraman*, Arturo Maldonado Álvarez, María de la Luz Olvera Amador

Departamento de Ingeniería Eléctrica, Centro de Investigación y de Estudios Avanzados del IPN, Apartado Postal, 14740 México City, Mexico

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ABSTRACT

In this letter, we have reported a cost-effective thin film of zinc oxide (ZnO) sensor for propane gas detection. ZnO thin films were deposited on soda lime glass by ultrasonic spray pyrolysis using zinc acetylacetonate as a precursor in the starting solution. Thin film deposition was carried out at 450 °C, by varying the water content in the spraying (starting) solution. Structural, morphological, and gas sensing properties were studied in detail. Variations in the water content resulted change in crystallinity, geometries, and gas sensitivity. ZnO thin film exhibited maximum sensitivity ~7, when measured at 100 °C.

1. Introduction

Propane is a colorless, odorless, flammable and non-toxic gas, which is one of the major hydrocarbon in LPG (Liquefied Petroleum Gas) used in day to day life. According to National Fire Protection Association report, propane is an important source of energy. In addition, when propane is used as a fuel in vehicles, causes less pollution than other petroleum products [1]. Therefore, it is mandatory to design a sensor to detect propane leaks in houses, and industries to ensure safety for the environment. Such sensors should be cost effective, and easy to fabricate. Zinc oxide is one among the metal oxide semiconductors which is preferred for gas sensing applications due to their fast response, low cost, ease availability. Zinc oxide, a wide band gap (3.37 eV) II–VI group semiconductor material which has been investigated extensively in recent times [2]. ZnO finds a place in various technological applications such as gas sensors, light emitting diodes, solar cells, and catalysts [3–6]. ZnO thin films can be deposited by several deposition techniques, such as thermal evaporation [7], sputtering [8], spray pyrolysis [9], chemical vapor deposition [10], the sol gel technique [11], and laser ablation [12]. Among these, we have preferred the ultrasonic spray pyrolysis technique for its cost effectiveness, and simple experimental setup [13].

To our best knowledge, no efficient sensor has been designed for propane gas detection at low cost. Therefore, in this letter, we have reported the efficient and cost effective ZnO based propane gas sensor. The water content in the precursor plays an important role in the structural, morphological, and sensing properties of ZnO thin films which favor the detection of propane gas even at low concentration.

2. Experimental

Soda lime glass (2×2 cm^2) was used as substrates for the deposition of ZnO thin films. The experimental set up of ultrasonic spray pyrolysis is shown in Fig. S1 (in ESI). The film deposition was carried out for five different 0.2 M precursor solutions, with the variation in water content (Table 1). Zinc acetylacetonate ($C_{10}H_{14}O_4Zn \cdot xH_2O$, 98%, Sigma Aldrich) was dissolved in a mixture of deionized water, methanol (CH_3OH, J.T. Baker), and a constant acetic acid volume, 1.5 ml. The solution flow rate was 1 ml/min. Nitrogen (from Praxair) was used as a carrier gas. The deposition was carried out at a substrate temperature of 450 °C for 12 min. The samples were named based on their water content in the starting solution, namely S0, S2, S5, S7 and S10.

3. Results and discussion

Fig. 1. shows the XRD pattern of the deposited ZnO thin films. All the X-ray diffraction spectra fit well with the hexagonal wurtzite type ZnO structure according to the reported data in JCPDS file 01-089-0510. We can observe that all samples are polycrystalline with a (002) preferential orientation, and the other peaks presented in all spectra are (101), (102), and (103). The intensity of (002) plane increases, as the water content increases

* Corresponding author.
E-mail address: vkumarj@cinvestav.mx (V.K. Jayaraman).

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Table 1
Experimental conditions.

Sample ID	Water volume (ml)	Methanol volume (ml)	Acetic acid volume (ml)
S0	0	98.5	1.5
S2	2	96.5	1.5
S5	5	93.5	1.5
S7	7	91.5	1.5
S10	10	88.5	1.5

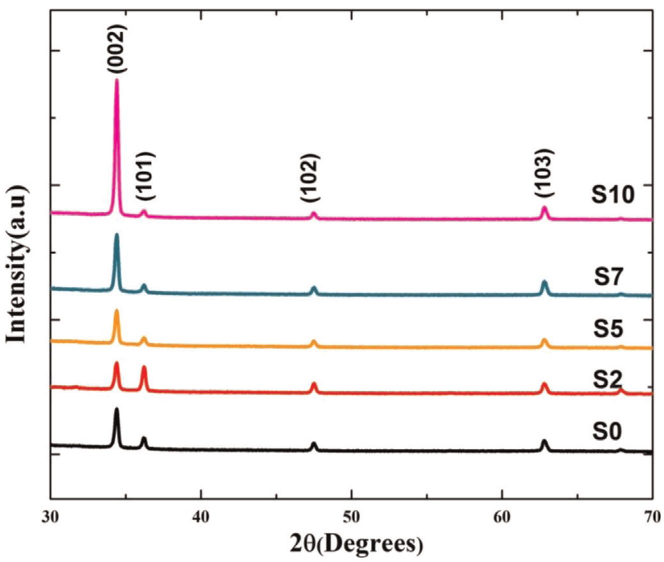

Fig. 1. XRD of ultrasonically sprayed ZnO thin films.

from 2 ml to 10 ml, which in turn enhances the crystallinity of the films. In addition, oxygen content in the water promotes the growth of (002) plane. From this result, it is believed that, the increase in water content changes the growth kinetics. The crystallite size was calculated by using the Scherrer's formula [14],

$$d = 0.94\lambda/\beta \cos \theta$$

where, d is the crystallite size, λ is the wavelength (1.5406 Å), and β is the full width at half maximum, FWHM, in radians of the (002). The crystallite size of the samples S0, S2, S5, S7, and S10 were found to be 23.25, 24.31, 29.08, 28.14, and 28.14 nm respectively.

SEM images are shown in Fig. 2(a–d). Fig. 2(a) shows the morphology of S0 sample (without water), where we can observe geometries like pyramidal, and tripods. Fig. 2(b) shows the surface morphology of ZnO thin films deposited with a water content of 2 ml. This SEM image shows a compact surface morphology conformed of rectangular grains of size around 200 nm, along with a few hexagonal slices. As the water content is increased to 5 ml, there is a dramatic change in the morphology of the films, features with hexagonal slices of size around 250 nm as in Fig. 2(c). The hexagonal grain size varies from 100 to 300 nm. Further increase in the water content (10 ml) gives rise to a surface covered by overlapped hexagonal thin slices of size around 300 nm (Fig. 2(d)). Thus, water content in the spraying solution influences the morphological characteristics of ZnO thin films.

The gas sensing mechanism of ZnO thin films can be explained as follows. In general, the oxygen moieties are adsorbed on the ZnO thin film surface, in turn changes the resistance of the thin film. When ZnO thin film is non-uniform, oxygen moieties (O^{2-}, O^-, O_{2-}, O_2^-) occupy in edges, surfaces, and the tip of the nanostructures, thereby more number of oxygen moieties are adsorbed on the thin film resulting in the formation of electron depletion layer. The adsorbed oxygen moieties in the depletion layer experience a chemical

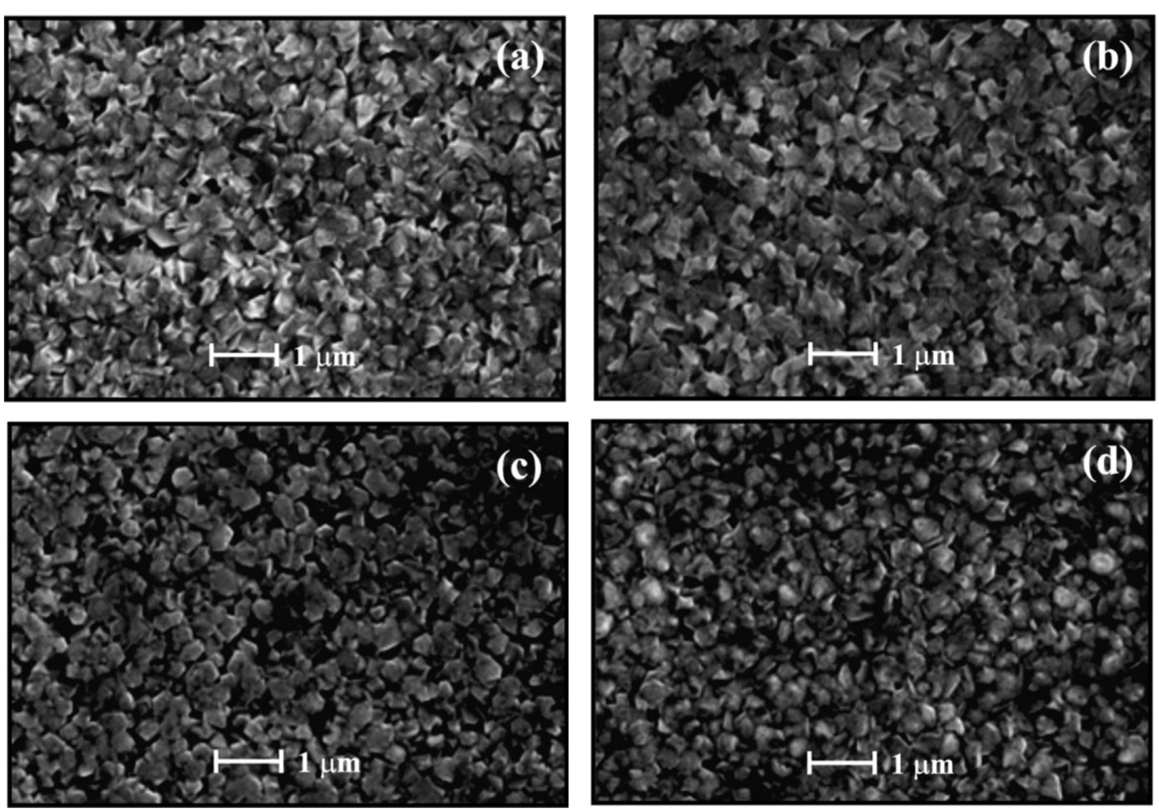

Fig. 2. SEM images of ultrasonically sprayed ZnO thin films with different water contents (a) 0 ml, (b) 2 ml, (c) 5 ml, and (d) 10 ml.

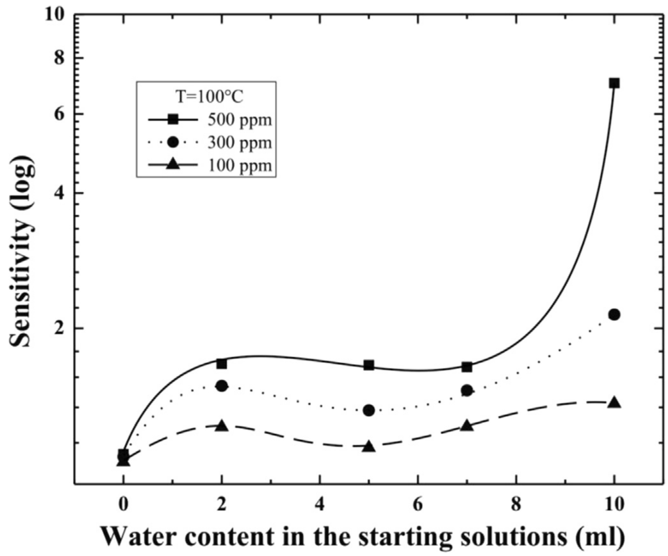

Fig. 3. Sensitivity of propane gas with respect to water content in the spraying solution measured at 100 °C for 100, 300 and 500 ppm.

reaction with the target gas and give away an electron to the ZnO surface giving rise to change in resistance [15,16]. The ratio of the resistance measured in vacuum to the resistance measured in testing gas atmosphere is called as sensitivity.

The reaction of oxygen species with propane gas can be described as below.

$$C_3H_8 + 10O_2^- \rightarrow 3CO_2 + 4H_2O + e^- \quad (1)$$

Fig. 3. shows the sensitivity of ZnO thin films as a function of the propane gas concentration with our homemade sensing measurement system (Fig. S2 (in ESI)). The sensitivity was measured at 100 °C for various propane gas concentrations, namely 100, 300, and 500 ppm. As discussed earlier, the morphology of the thin films was changed when the water content in the starting solution increased. The lowest sensitivity, ~1.05, was observed in S0 thin films (without water) due to high compactness, as compared with the rest of samples. The maximum sensitivity, ~7, was registered in the sample processed from the starting solution containing the maximum water content, S10 (water content, 10 ml) due to more oxygen moieties occupied on overlapped hexagonal slices. Samples deposited from solutions with intermediate water contents presented low and similar sensitivity values, ~1.5, since morphologies are also similar. The magnitudes of sensitivity increase as the propane concentration increases, as a result of more number of reactions between the film surface and gas species. Hence, ZnO thin films deposited from ultrasonic spray present good sensing properties for propane gas, and they are dependent on the preparation conditions of the starting solutions.

4. Conclusion

Zinc oxide thin films were deposited on glass substrates at 450 °C by ultrasonic spray pyrolysis technique. The influence of water content in the spraying solution on the structural, morphological, and gas sensing properties were investigated. Change in crystallinity, and morphology were observed from XRD, and SEM. Films deposited with high water content starting solution, exhibited highest sensitivity, ~7, at 500 ppm. Thin film sensors fabricated by ultrasonic spray pyrolysis are efficient, cost-effective, and reliable.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.matlet.2015.05.065

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