International Journal of Advance and Innovative Research
Volume 6, Issue 1 (XIX): January - March, 2019 : Part - 1
ISSN 2394 - 7780

TEMPERATURE DEPENDENT GAS DETECTION OF SPRAY DEPOSITED ZNO THIN FILMS

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ABSTRACT
ZnO semiconductor thin films were prepared by cost effective chemical spray pyrolysis technique. The effect of temperature on different gases detection properties has been studied. The ZnO film showed more selectivity for LPG over Ethanol and Acetone at an operating temperature of 300 ^{0}C. The effective surface area for LPG to react increased and so the response increased, which offered more efficient surface area for interaction with LPG molecules on the surface as well as inside porous structure, compared to other films.

Keywords: Spray pyrolysis; ZnO films; sensing properties; dynamic response.

INTRODUCTION
There has been a great deal of interest in zinc oxide (ZnO) semiconductor materials lately, as seen from a surge of a relevant number of publications. The interest in ZnO is fueled and fanned by its prospects in optoelectronics applications owing to its direct wide band gap (Eg~3.3 eV at 300 K). Some optoelectronic applications of ZnO overlap with that of GaN, another wide-gap semiconductor (Eg ~3.4 eV at 300 K) that is widely used for production of green, blue-ultraviolet, and white light-emitting devices (LED). However, ZnO has some advantages over GaN among which are availability of fairly high quality ZnO bulk crystals and a large exciton binding energy (60 meV). ZnO also has much simpler crystal-growth technology, resulting in a potentially lower cost for ZnO-based devices [1-8]. As a direct wide-band-gap material, ZnO is attracting a lot of attention for a variety of electronic and optoelectronic applications. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower noise generation, and high temperature and high-power operation. Among the tetrahedrally bonded semiconductors, ZnO has the highest piezoelectric tensor or at least one comparable to that of GaN and AlN. This property makes it a technologically important material for many applications, which require a large electromechanical coupling [9-15].

EXPERIMENTAL DETAILS
Zinc oxide films were deposited by spray pyrolysis method using an aqueous zinc nitrate solution. The Zinc oxide thin films were deposited

a) By varying the concentration of sprayed solution from 0.10 to 0.75 M by changing the amount of zinc nitrate dissolved in an aqueous solution. The deposited thin films were termed as ZM1, ZM2, ZM3 and ZM4.

b) By varying the spray rate as 2 ml/min, 2.5 ml/min, 3 ml/min and 4 ml/min and the deposited films were denoted as ZS1, ZS2, ZS3 and ZS4.

c) By varying the substrate to nozzle distance as 30 cm, 28 cm and 2 cm and films were termed as ZD1, ZD2 and ZD3.

d) By varying the substrate temperature from 425 °C to 475 °C at an interval of 25 °C and deposited films were labeled as ZT1, ZT2 and ZT3

The solution was sprayed through a glass nozzle onto the ultrasonically cleaned glass substrates kept at various temperatures. The substrate temperature was optimized to 450 °C. The spray rate was maintained using air as a carrier gas and the spray rate of 3 ml/min was optimized. The temperature was controlled using electronic temperature controller. Hazardous fumes that evolved during the thermal decomposition of initial ingredient were expelled out. The nozzle to substrate distance was optimized as 28 cm. Here, after the deposition process completed, the films were kept on the heater at deposition temperature for 30 min in order to provide sufficient time and temperature for recrystallization.

RESULTS AND DISCUSSIONS
Temperature dependent gas detection
Fig. 1 and Fig. 2 shows the histogram of gas response to different gases with operating temperature for the optimized sample for (a) 0.5 M molar concentration (ZM3), (b) spray rate of 3 ml/min (ZS3), (c) substrate to nozzle distance of 28 cm (ZD2), (d) substrate temperature at 400 ^{0}C (ZT2). The histogram revealed that the sensor offered maximum response to Ethanol (16%) at 300 ^{0}C, Acetone (27%) at 300 ^{0}C and LPG (47%) at 300 ^{0}C. The sensor selects a particular gas at a particular temperature. Thus, by setting the temperature, one can use

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the sensor for particular gas detection. The same sensor could be used for the detection of different gases by operating it at particular temperature for a typical gas. Different gases have different energies for adsorption, desorption and reaction on the metal oxide surface, and therefore, the response of the sensor at different temperatures would depend on the gas being sensed. The ZnO film showed more selectivity for LPG over Ethanol and Acetone at an operating temperature of 300 ^{0}C.

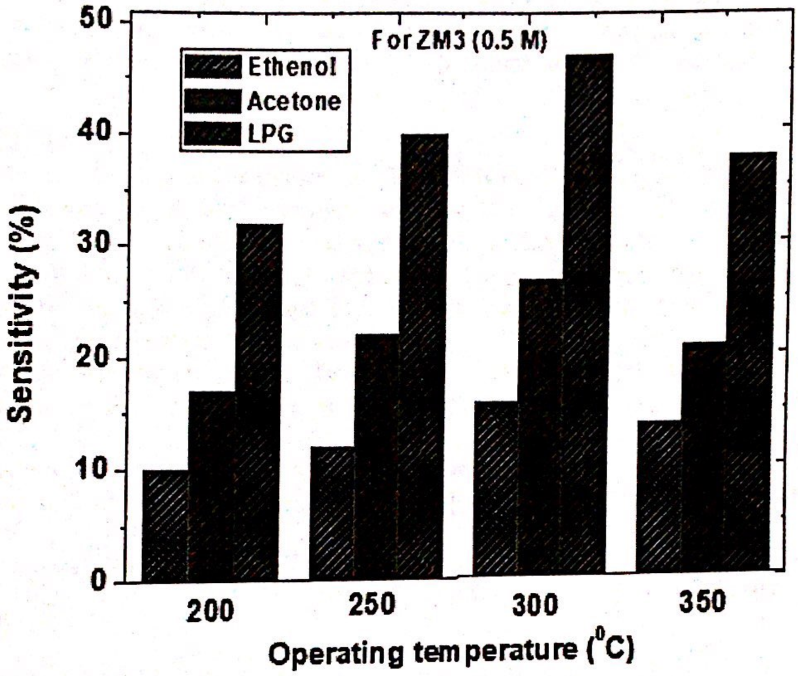

Figure-1: Gas response of ZnO film (0.5M) with operating temperature for different gases at a fixed gas concentration 1000 ppm.

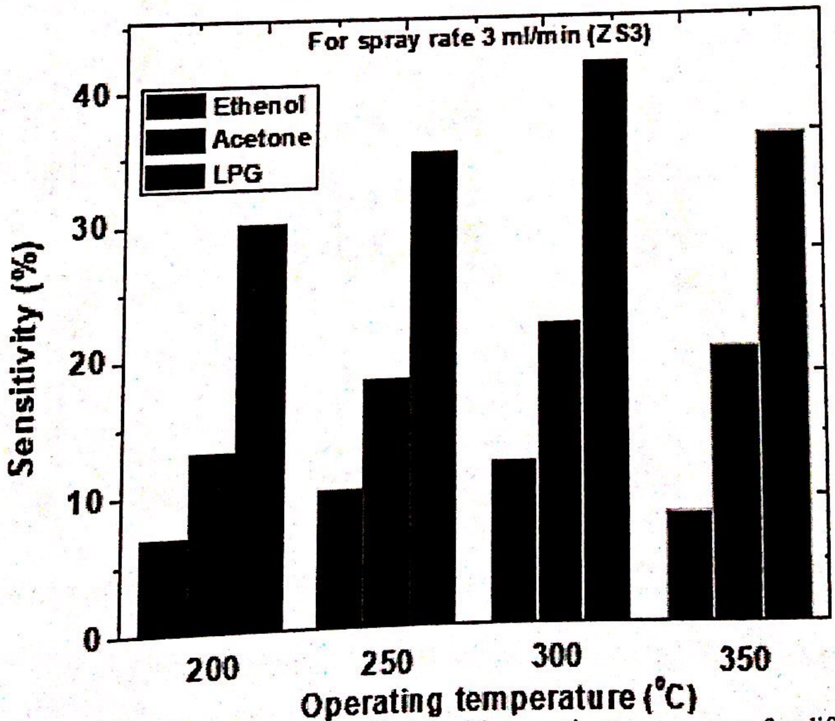

Figure-2: Gas response of ZnO film (spray rate 3ml/min) with operating temperature for different gases at a fixed gas concentration 1000 ppm.

It revealed that LPG is the more selective against other two. The response of all the films does not exhibit any significant difference at lower temperatures. At a low operation temperature, the low response can be expected because the gas molecules do not have enough thermal energy to react with the surface adsorbed oxygen species. As the electrons are drawn from the conduction band of the ZnO by the adsorbed oxygen, and a potential barrier to charge transport is developed. At higher temperatures the thermal energy obtained was high enough to overcome the potential barrier, and a significant increase in electron concentration resulted from the sensing reaction. The response of a semiconductor oxide gas sensor to the presence of a given gas depends on the speed of the chemical reaction on the surface of the grains and the speed of diffusion of the gas molecules to that surface which are activation processes, and the activation energy of the chemical reaction is higher. In this case, at low temperatures the sensor response is restricted by the speed of the chemical reaction, and at higher temperatures it is restricted by the speed of diffusion of gas molecules. At some intermediate temperature, the speed values of the two processes become equal, and at that point the sensor response reaches its maximum [16].

DYNAMIC GAS RESPONSE

Fig. 3 shows the dynamic gas response transients of ZnO films of different molar concentrations, spray rate, nozzle to substrate distances and substrate temperatures for LPG at 300 ^{0}C. The maximum response was obtained with film 0.5 M (ZM3), spray rate 3 ml/min (ZS3), substrate to nozzle distance 28 cm (ZD2) and substrate temperature at 400 ^{0}C (ZT2). In the gas sensitivity, the grain size and porosity of the film played an important role [17]. For film ZS3, ZM3, ZT2 and ZD2 have the porous and non-spherical grains were observed. As exposure area of these films increased, the sensitivity was gradually increased. One can observe from SEM image the spherical grains with more porosity. Such kind of morphology helped for providing larger surface area to expose and react on the outer surface as well as inside porous surface more efficiently. Thus, the effective surface area for LPG to react increased and so the response increased, which offered more efficient surface area for interaction with LPG molecules on the surface as well as inside porous structure, compared to other films. When LPG was introduced in the gas chamber, the gas response initially increased with time and then remained stable.

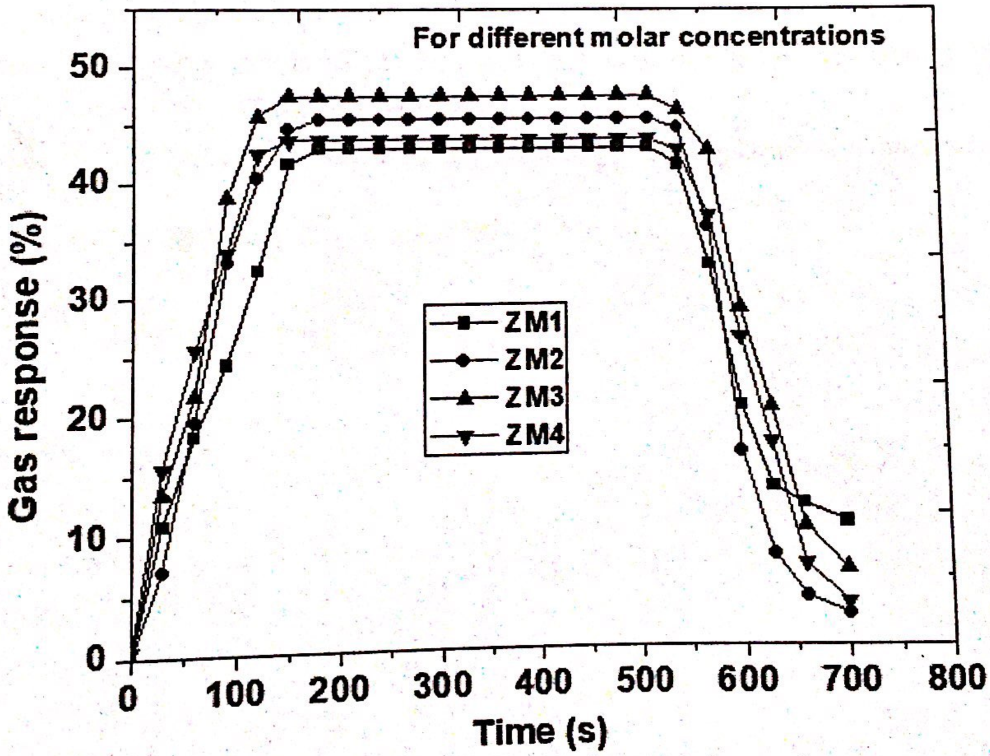

Figure-3: The dynamic response transients of ZnO films of various molar concentrations

CONCLUSION

- Zinc oxide films were deposited by spray pyrolysis method using an aqueous zinc nitrate solution.
- The sensor offered maximum response to Ethanol (16%) at 300 ^{0}C, Acetone (27%) at 300 ^{0}C and LPG (47%) at 300 ^{0}C.
- The ZnO film showed more selectivity for LPG
- The maximum dynamic response was obtained with film 0.5 M (ZM3), spray rate 3 ml/min (ZS3), substrate to nozzle distance 28 cm (ZD2) and substrate temperature at 400 ^{0}C (ZT2).
- The effective surface area for LPG to react increased and so the response increased.

ISSN 2394 - 7780

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