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Investigation Of Some Physical Properties For Nitrogen Dioxide Sensor Applications Prepared By Two Methods

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***Abstract* — Structural and sensing properties of Zinc oxide films prepared by chemical spray pyrolysis ZnO_{Spray} and electrophoretic deposition ZnO_{EPD} methods were investigated. The responses to NO_2 gas with three different temperatures were studied. ZnO sensitivities to this gas increased with temperature. The mechanism of sensing NO_2 gas was discussed. X- ray diffraction (XRD) and Atomic force microscopy (AFM) was utilized to study structure and surface properties of sensors. ZnO_{EPD} has higher sensitivity than that of ZnO_{Spray} due to its larger roughness and grain size. The properties of deposition method have direct effect on sensor's response.**

Keywords— electrophoretic deposition; NO_2 Sensor; ZnO; sensitivity.

I. INTRODUCTION

In everyday sensors are utilized in unlimited applications of which many persons are never aware. Application of sensors spread in all modern human life cars, airplanes, medicine, aerospace and robotics are popular examples.

Despite the variety of nitrogen oxides (NO_X) the air pollution by nitrogen dioxide is most interest from view point of human health. This gas is soluble in water, strong oxidant and reddish brown color. Due to its absorption to visible radiation this gas has a direct role in changing of global climate if its concentrations were high. In troposphere; concentrations of Ozone (O_3) is determined by NO_2 due to its photolysis which represents the starter of ozone photochemical formation [1].

In big cities especially in regions of vehicle traffic; NO_2 amount emitted as pollution can be dangerous. Formation of a wide group of toxic products likes nitroarenes can easily occur by reaction NO_X with common organic chemicals. Some of this dangerous materials cause biological effects [2].

Current paper aims to study the response of ZnO films prepared by two methods to NO_2 gas.

II. EXPERIMENTAL PARTS

The details of ZnO_{EPD} films preparation by electrophoretic deposition on stainless steel (SS) substrate were written in [3]. A second homogeneous ZnO_{Spray} thin film is deposited on glass slide by spray pyrolysis using chemical solution prepared as following; dissolving 0.1 M ($Zn(CH_3COO)_2$) with 99.99% purity in hot distilled water (100ml) [4].

$$Zn(CH_3COO)_2 + 2H_2O \rightarrow ZnO + CO + CH_4 + steam \quad (1)$$

During deposition the substrate is put on hot plate maintained at 400^oC. The distance between glass nozzle and substrate is 28 cm. A carrier gas of chemical solution is air with 2ml/min spraying rate.

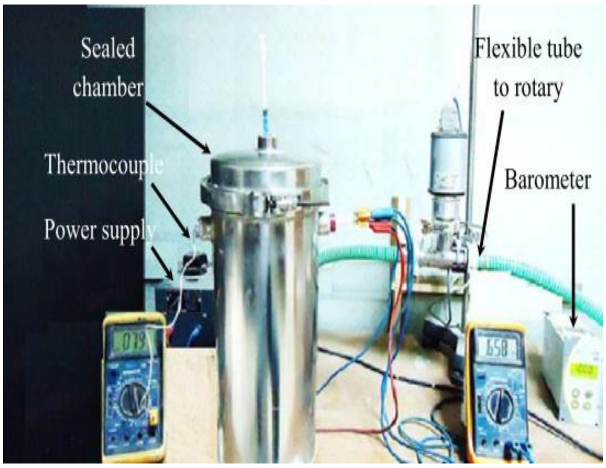


Fig. 1. Parts of gas sensor testing system.

The volume of chamber is six liter. Vacuum system was utilized to evacuate the chamber from gases after test. Depending on the amount of gas, there were two methods to enter gas inside the chamber. First one (for small amount) by evaporating appropriate chemical solution inside output unit and then transfer produced gas to the evacuated chamber. Second method (for large amount) by direct chemical solution injection inside the chamber where there is a hot plate to evaporate it to gas . To evaporate small chemical solution and produce appropriate gas amount, micropipette type (DRAGONMED-made in china) volume: 5-50µl was used. H_2SO_4 acid and KNO_3 was mixed to produce a chemical solution give HNO_3 vapor after evaporation according to the following equation:[5]

$H_2SO_4 + KNO_3 + (Heat) \rightarrow HNO_3 \uparrow + KHSO_4$
(2)

Ellis et al. showed the dissociation of HNO_3 acid to NO_2 according to the following equation

$$2HNO_3 \Leftrightarrow H_2O + 2NO_2 + \frac{1}{2}O_2 \qquad (3)$$

The decomposition of acid is strong at room temperature and it increases rapidly with temperature increasing [6]. After each test, the gas or vapor was withdrawn by the vacuum system outside the chamber.

III. RESULTS AND DISCUSSION

Figure 2 shows the variation of ZnO_{EPD} resistance with time due to NO_2 injection. The effect of sample's temperature is clear. With increasing this temperature to a high values; the sensitivity of this sensor increases as figure 3 confirms. But with increasing injected NO_2 gas volume the sensitivity decrease and then saturates.

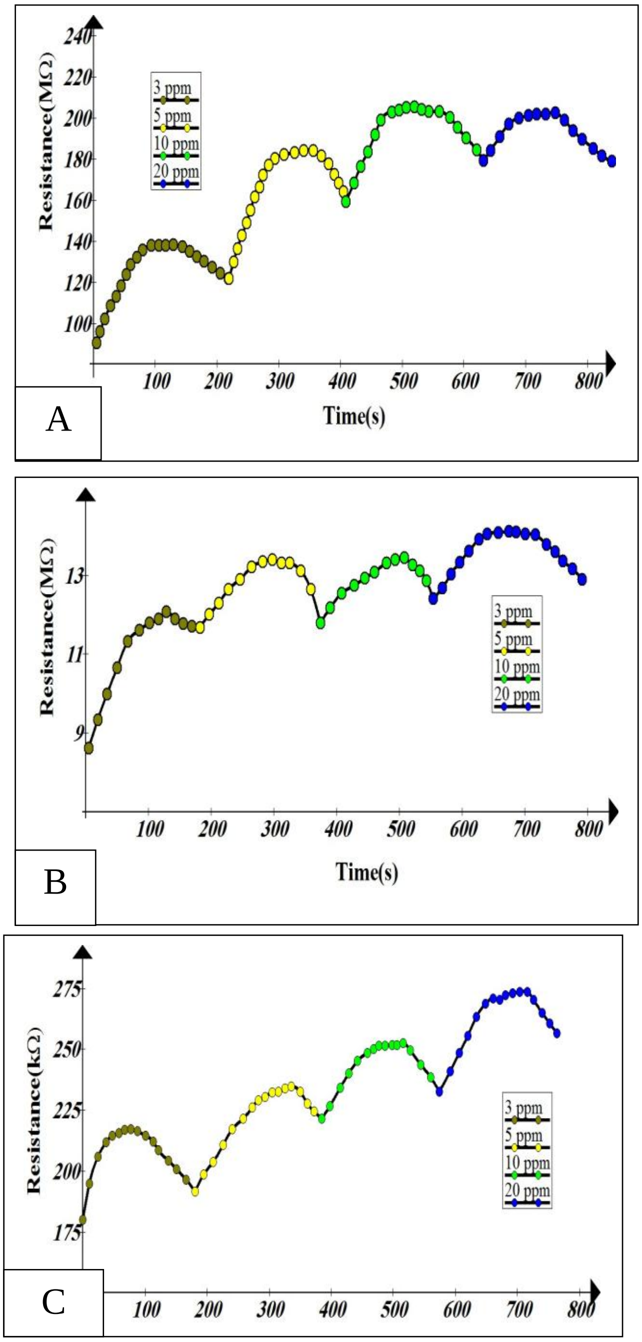


Fig . 2. Variation of ZnO_{EPD} resistance with time for different NO_2 concentrations. Sample's temperature: A-75 ^{0}C, B- 100 ^{0}C and C-150 ^{0}C.

Saturated sensitivity at high NO_2 concentrations agrees with that obtained by Chougule et al [7] . who attribute this result to increased surface reaction.

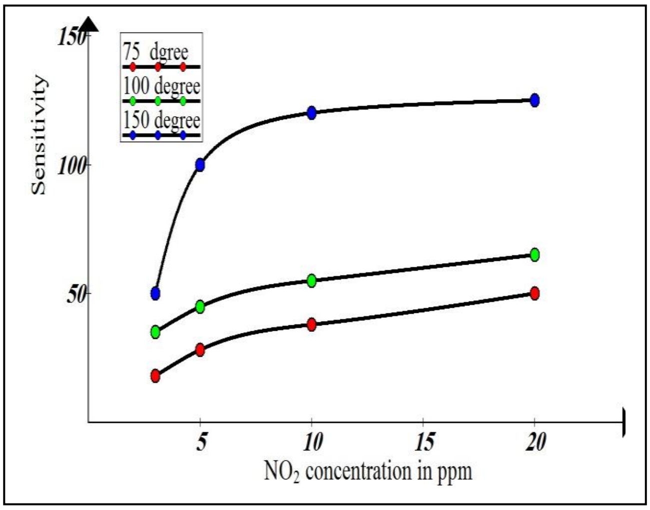


Fig. 3. *ZnO_{EPD} sensitivity to NO_2 gas.*

The following two equations shows trapping electrons from ZnO films inside oxygen or NO_2 gas atmosphere [8].

O_2 (gas) + e^- → O_2^- (adsorption) (3)

NO_2 + e^- → NO + O^- (adsorption) (4)

At gas – solid interface this trapping process reduces the density of majority charge carriers. As a result depletion layer and potential barrier are formed at junctions between ZnO grains. Equation (4) describes the reason behind increasing ZnO_{EPD} film resistance after covering it with an NO_2 atmosphere as figure 2 shows.

The increasing of ZnO_{EPD} sensitivity to NO_2 gas with temperature in figure 3 agrees with the results of other workers [9]. Sensor temperature is important factor due to the dependence of adsorption and desorption on it [10]. All sensing mechanism that depends on adsorption and desorption will improve with increasing temperature. Because the reaction of NO_2 with ZnO_{EPD} depends on charge carriers density (which is affected by adsorbed oxygen) the sensitivity is temperature dependent as figure 3 confirms.

Another factor that must take into account is the transformation of HNO_3 vapor to NO_2 gas (as mentioned in experimental part) and its dependence on temperature. As the temperature increases NO_2 gas production increases and then ZnO sensitivity on it will increase.

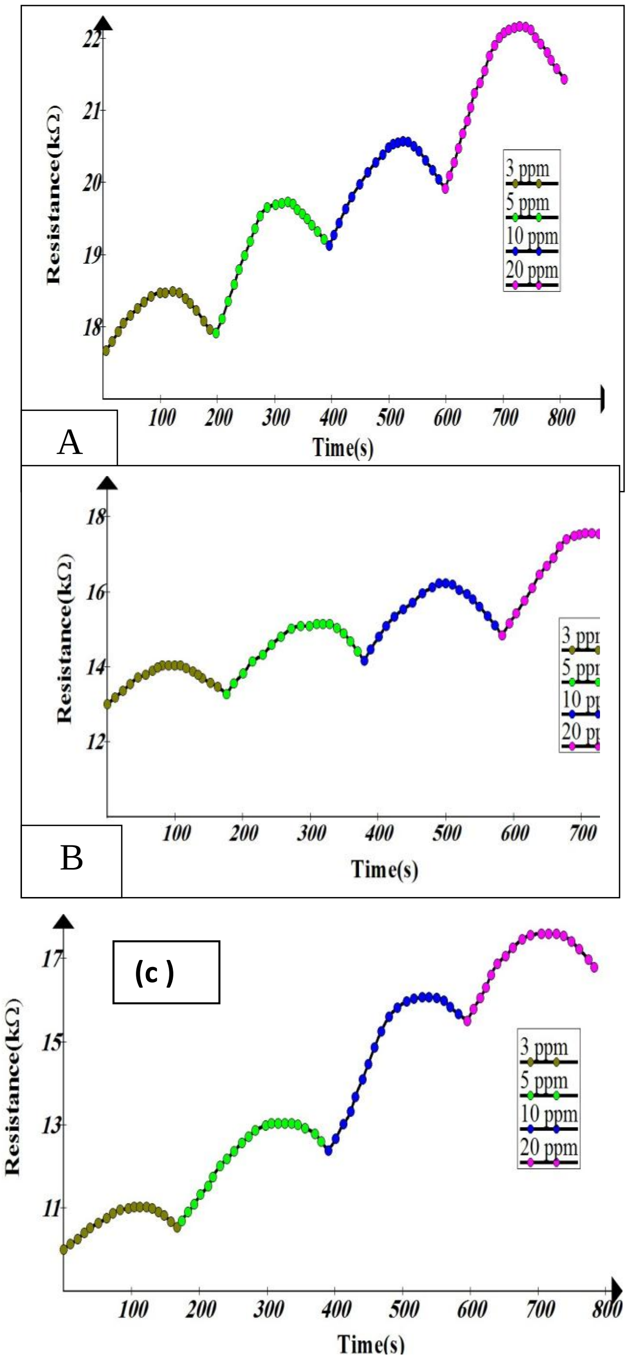


Fig. 4. Resistance versus time for ZnO_{Spray} . Sample's temperature: A-75 ^{0}C, B- 100 ^{0}C and C-150 ^{0}C

The sensitivity of ZnO_{Spray} to NO_2 gas is drawn in figure 5.

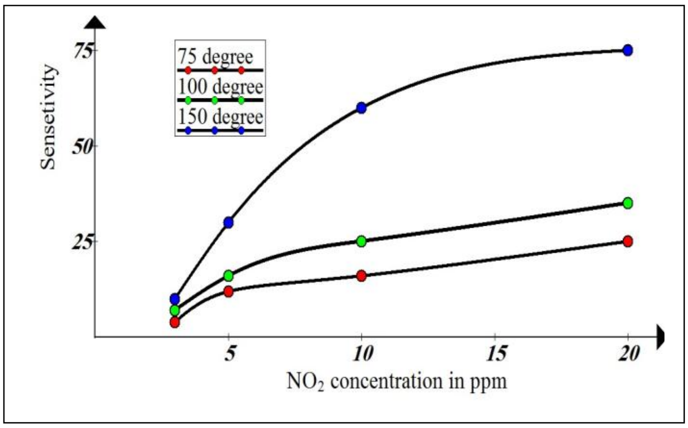
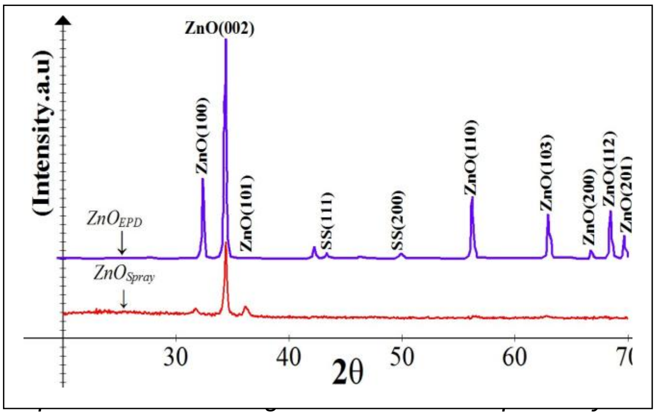


Fig. 5. *The sensitivity of ZnO_{Spray} to NO_2 gas.*

The behavior of figure 5 approximately looks like that of figure 3. In general sensitivity of ZnO_{EPD} is better than that of ZnO_{Spray} . This may a direct result to the differences between these two films.

The differences between ZnO_{EPD} and ZnO_{Spray} as NO_2 sensors are natural results to the following dissimilar characteristics of them:

1- The XRD patterns of ZnO_{EPD} is unlike to that of ZnO_{Spray} as figure 6 confirm.



2- The method of deposition gives each film specific surface topography and then different response. The roughness of ZnO_{Spray} and ZnO_{EPD} are 0.78 and 22 nm respectively. The grain sizes of them are 80 and 100 nm respectively. These numbers are extracted from figure 7 images.

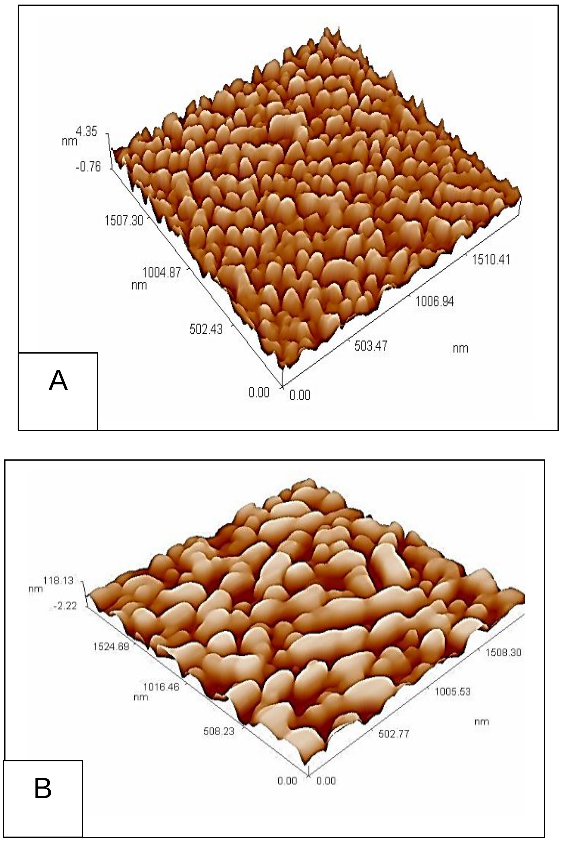


Fig. 7. *AFM images for A- ZnO_{Spray} and B- ZnO_{EPD} surface.*

IV. CONCLUSIONS

- The sensitivity of ZnO films depends on its deposition method.
- ZnO_{EPD} film has higher sensitivity due its higher roughness and grain size.

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