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Gas Sensing Properties Of Titanium Dioxide Doped Zinc Oxide Thin Film By Spray Pyrolysis Technique

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Abstract*-Zinc oxide (ZnO) and titanium dioxide (TiO_2) materials are much important with their physical and chemical properties as well as due to the wide scope for the development of novel solutions in sensor technology. Both materials are widely useful for industrial, technological and sensor applications. TiO_2dopedZnOthin films are obtained by using an advanced spray pyrolysis technique with high transparency. The gas sensing properties of TiO_2dopedZnO thin films are studied.*

Keywords- *Gas sensor, Advanced spray pyrolysis, Zinc oxide and Titanium dioxide.*

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I. Introduction:

Sensor technology is one of the important trends in the field of flood, disaster management, earthquake, industry and engineering. Many of the researchers are working on the same with different aspects. Zinc oxide and titanium dioxides are important materials and more scope in sensor technology. In this research paper, the gas sensing properties of TiO_2 and ZnO mixed thin film are explained with an advanced spray pyrolysis technique.

Over the two decades, substantial efforts have been made to making ZnO films, bring down its operating temperature with a decrease the response time. For the said approaches, either decreasing the material size into nanoscale or introducing proper dopants are demonstrated effectively. The addition of certain dopants is one of the effective ways of improving the gas sensing properties of ZnO sensor. The transition element titanium dioxide (TiO_2) with an ionic radius to that of Zn2+ ion (0.07nm) and electronic shell structure, has many properties relevant to Zn [01, 17]. TiO_2 doped ZnO (ZnO:TiO_2) is one of the most promising electrical conductivity-controlled metal oxides [02, 18] and it has been demonstrated that ZnO films doped with TiO_2might be higher electrical resistance [03]. Such a high resistivity effect has been revealed to increase the sensitivity of the metal oxide gas sensors [04]. Earlier ZnO: TiO_2 films have been shown to sense carbon monoxide and ethanol [05-07]at high working temperatures. M. Zhao showed that response to low concentrations of H_2S gas can be greatly enhanced by TiO_2 doping [08]. Doping ZnO with TiO_2 may be a promising element for gas sensor sensitivity.

In this research, ZnO: TiO_2thin films has been made to synthesized at moderate substrate temperature by advanced spray pyrolysis technique. The gas sensing properties of ZnO: TiO_2 (TZO) thin films are studied and the H_2S gas sensing properties are justified. The results show that the incorporation of titanium dioxide into zinc oxide thin film plays an important role to increase the sensitivity of ZnO towards H_2S at moderate operating temperatures.

II. TitaniumDioxideZinc Oxide Thin Film Deposition Technique:

For the development of TZO, mixed metal oxide thin films advanced spray pyrolysis technique is used. The advanced spray pyrolysis method includes substrate cleaning, solution preparation, and deposition. The optimized preparative parameters were used to deposit the nano-crystalline and feasible TiO_2 films for gas sensing applications. Structural characteristics of TiO_2 thin films are characterized by X-ray diffraction. To carry out uniform films, cleaning of the substrate and proper surface treatment prior to the deposition is essential, as the contaminated surface provides nucleation sites facilitating growth resulting in non-uniform films with different orientations and impurities. The defect formation and density always depend on the cleanliness of the production environment so the effective surface cleaning method should be chosen as per substrate.

75×25×1.35mm dimension glass micro-slides have been used as the substrates. The procedure is adopted for substrate cleaning and washing with distilled water, boiled with chromic acid for 30 minutes and substrate washed by double distilled water. The substrate is cleaned ultrasonically and exposed with methanol vapors for 4-5 minutes, then substrates were used for deposition.

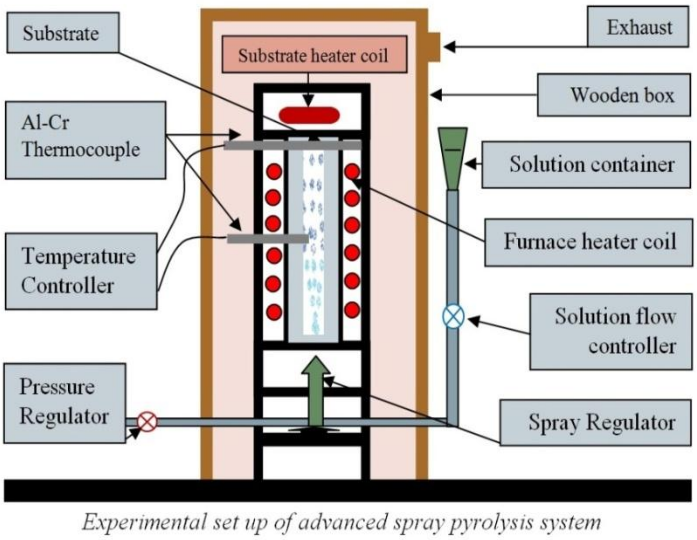

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Figure 1: Advanced spray pyrolysis system

The advanced spray pyrolysis system is shown in figure 1, consists of reaction chamber, substrate heater, temperature controllers, and nozzle assembly. For the synthesis of TZO thin films, initially, the spraying solution was prepared by mixing the proper amount of equimolar (0.1M) non-aqueous solution made by dissolving pure zinc acetate [$Zn(CH_3COO)_2{\bullet}2H_2O$] (Thomas Baker) and titanium isopropoxide [$Ti\{OCH(CH_3)_2\}_4$] (sd Fine-Chem) in ethanol.Four different concentrations (1,2,3 and 4 wt %) were selectedto dope TiO_2 in ZnO thin films. The resulting solution was sprayed at an optimized substrate temperature of 673 K. While deposition, the optimized deposition parameters such as core temperature (798 K) spray rate (8 ml min-1), nozzle to substrate distance (40 cm) and carrier gas pressure (10 LPM) were kept constant. The substrate and core temperature were controlled using electronic temperature controllers throughout the experimentation. Hazardous gases were expelled out during the thermal decomposition. ZnO thin films deposited with 1,2,3 and 4 wt %, TiO_2 doping denoted as 1TZO, 2TZO, 3TZO and 4TZO respectively. The TZO films were characterized using various techniques in order to get information on their structural, morphological and optical properties. TiO_2 doping concentration effect on the performance of the gas sensors characteristics are studied.

III. Characterization:

The spray deposited ZnO: TiO_2films were characterized by structural, morphological, and optical. The gas sensing properties of ZnO: TiO_2 are studied.

IV. Results and Discussion

4.1 Doping Concentration

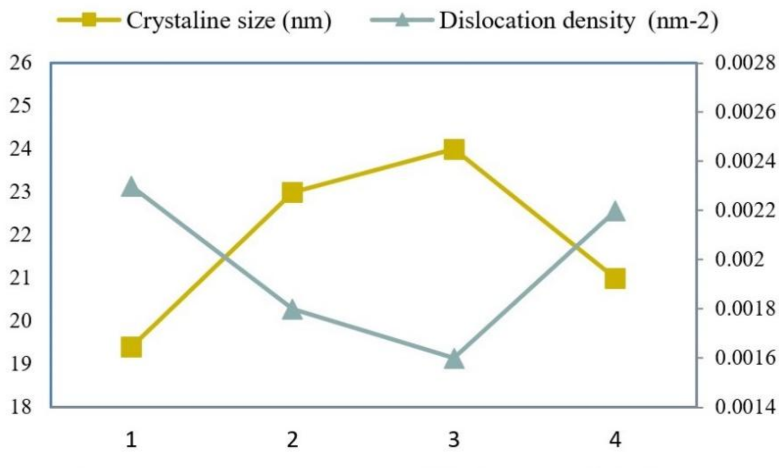

Figure 2: Size and density as a function of TiO_2 doping concentration.

The microstructural parameters such as crystallite size (D) and dislocation density (d) for TZO films were estimated using the relevant formulas [09-10] and represented in figure 2. It is observed that the crystallite size increases from ~19 to ~24 nm, with an increase in TiO_2 doping concentrations from 1 to 3 wt %. But for further increase in TiO_2 concentrations i. e. at 4 wt %, the crystallite size decreases. The results imply that the crystallinity and degree of orientation of the TZO films were closely associated with the TiO_2 doping concentration. However, the structural parameters like dislocation density (d) show a decreasing trend with the TiO_2 doping concentration up to 3wt %, which tends to a reduction in the concentration due to lattice imperfections. The larger crystallite size (D) and smaller values of dislocation density (d) at 4 wt % TiO_2 doping, indicate better crystallization of the 4TZO film.

4.2 Response of H_2S Gas at Different Temperatures

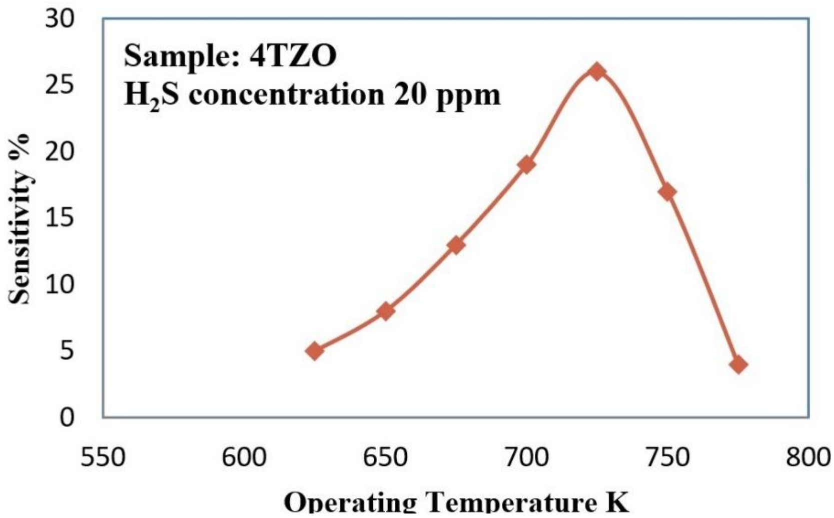

Figure 3: Sensitivity and operating temperature for 4TZO film

In figure 3, the sensitivity curves to 20 ppm H_2S of 4TZO sample is shown as a function of operating temperature. It shows that operating temperature plays a vital role to determine the sensitivity of the film. The sensitivity to H_2S is increased with increasing the operating temperature, which attains the maximum at 724K, and then decreases for a further rise in the operating temperature. However, in the range of 624-784K, the maximum sensitivity (28 %) appears at 724K and accordingly, 724K is believed to be theoptimized temperature and it is applicable in all occurances.

4.3 Response of H_2S Gas

The transient response of ZnO films with different TiO_2 doping concentrations at 724 K to 20 ppm of H_2S gas is shown in figure 4. It shows that the H_2S sensing properties are strongly influenced by TiO_2 doping concentration in ZnO films. It is also observed that the sensitivity tends to increase from ~14 to ~28 % as the TiO_2 doping concentration increases from 1 to 4 wt %, respectively. An increasing response towards H_2S gas may be attributed to the modification of the surface morphology from irregular crystalline morphology to the columnar structured morphology as the TiO_2 doping concentration increases. It seems that the columnar 4TZO film growth exhibits well-distributed space charge layers in comparison to the polycrystalline 1TZO, which helps to enhances the chemical interaction of H_2S gas with film and the charge transfer inside the film. This makes stronger the output signal and film sensitivity [11]. Again, it is observed that the small crystallite size helps to increase the exposed area to the hydrogen sulfide gas and this causes enhancement in the resistance of the sample [12-13, 16].

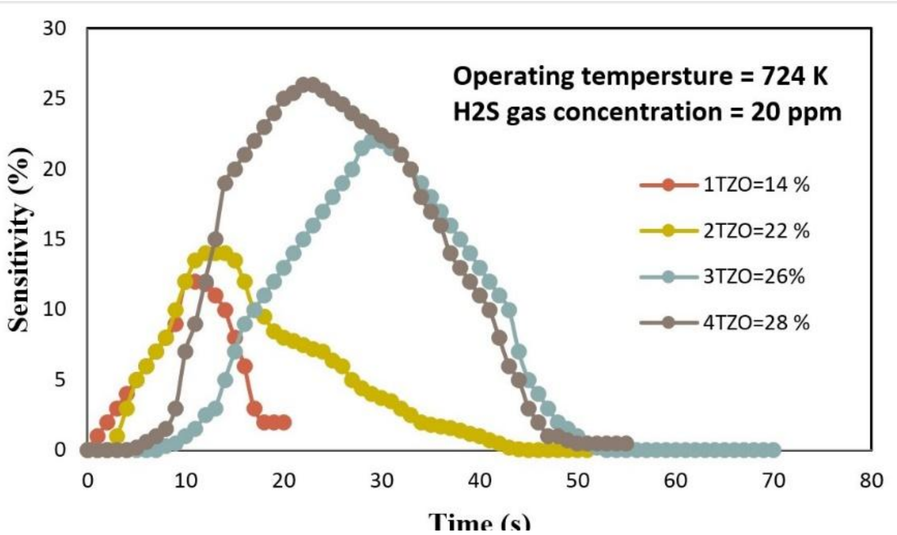

Figure 4: The transient response of TiO_2 doped ZnO films at 724 K.

The variation of response time and recovery time with TiO_2 doping concentration is shown in figure 5. From the figure, it seems that the response time is minimum for a sample with 1 wt % of doping and decreases with increasing TiO_2. At 2 wt %, the slowest response is observed and for higher doping concentrations it improves slightly. The recovery time also exhibits a similar trend in variation. The 3TZO film exhibited the response and recovery times 2 and 5 s, respectively.

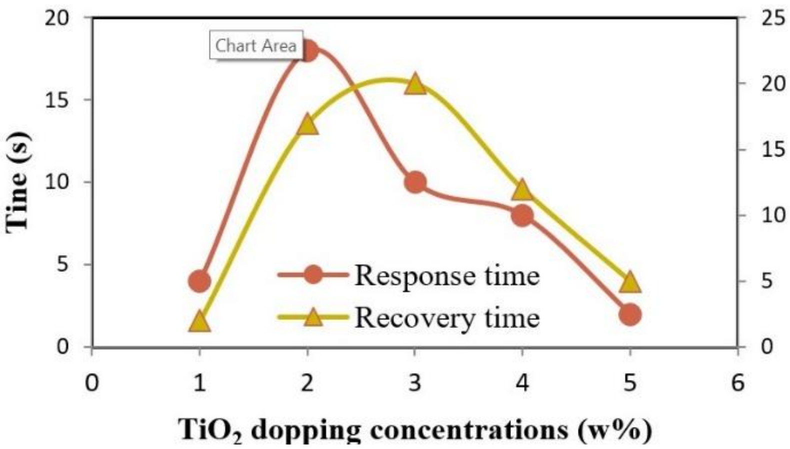

Figure 5: The response and recovery time with TiO_2 doping concentrations at 724K.

4.4 4TZO Film Sensitivity

In figure 6, it is observed that the sensitivity variation of typical sample 4TZO is a function of time with variation in H_2S gas concentration at 724 K operating temperature. It is also shown that at all concentrations of hydrogen sulfide response time is fast. Morever, at lower concentrations, the response time is slightly slow and with increases in concentration, the response time increases. The higher response at higher H_2S concentrations may be due to an increase in surface coverage with a high density of H_2S molecules. The recovery time of the film for all concentrations is almost remains the same.

It is also observed that the sensitivity increases rapidly in the lower concentration region (20 ppm) of H_2S, while it increases gradually above 20 ppm of H_2S. At a low concentration, there is a small number of H_2S molecules that interact with the sensor and hence the surface reaction gets down. With an increase in H_2S concentration, the surface reaction increases due to a larger surface coverage of H_2S molecules, resulting in higher sensitivity. For a increasing concentration, the surface reaction gets saturated, which leads to a slow increase insensitivity.

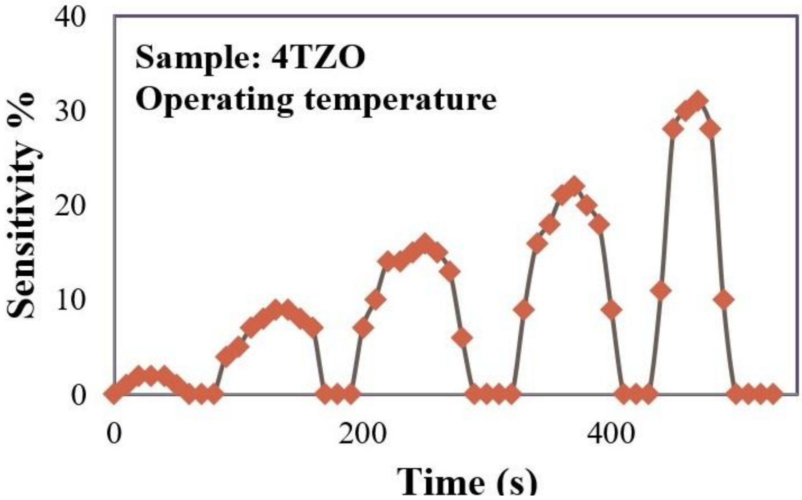

Figure 6: Sensitivity and time at various H_2S concentration for 4TZO thin film.

4.5 Selectivity

The selectivity of 4TZO film was investigated against different reducing gases and alcoholic vapors. Ethanol (C_2H_5OH), methanol (CH_3OH), and acetone (CH_3COCH_3) (for 20 ppm) were selected as target test gases (Figure 7 shows the results). The selectivity coefficient (QH_2S) of H_2S gas to another gas was defined asQH_2S = SH_2S +SX, where $SH_2S$and SX are the sensitivities of sensors in H_2S and 'X' gas, respectively [14]. The selectivity coefficients are also shown in Figure 7. The larger value of QH_2S means the sensor has a better ability to discriminate the target gas (H_2S here) amongst the mixture gases. It is clear from these results that H_2S can be detected selectively using a 4TZO film-based sensor with high sensitivity and a selectivity coefficient(~22 % towards 20 ppm H_2S).

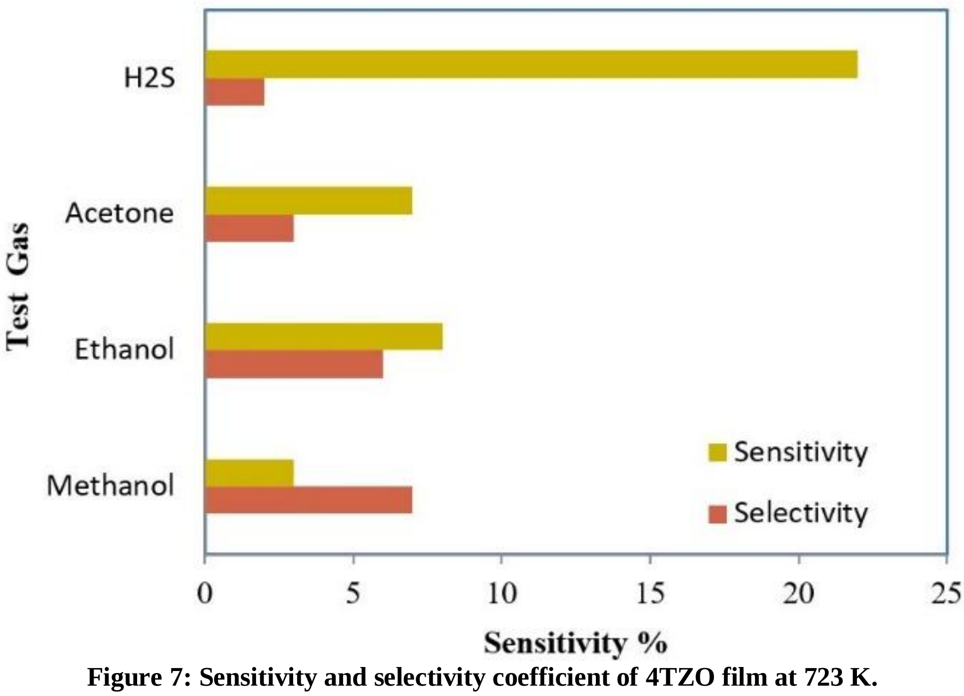

Figure 7: Sensitivity and selectivity coefficient of 4TZO film at 723 K.

4.6 Effect of Palladium (Pd) Sensitization

It is well known that adding up small amounts of noble metals such as Pt and Pd to the sensor film can promote not only gas sensitivity but also the rate of response. Therefore, in order to enhance the H_2S sensing performance of TZO films, a Pd catalyst was loaded on the 4TZO film, and gas sensitivity towards H_2S has been observed that very littleimprovement was observed in the response time, but the sensitization effect was found to enhance the rate of recovery slightly faster. Here, in the electronic type of palladium sensitization, the Pd in its oxidized state (PdO) acts as a strong acceptor for electrons of the 4TZO film. By reacting with reducing analyte such as H_2S, the palladium additive is reduced releasing the electrons back to the TZO film [15].

Figure 8, shows the response evaluation of Pd-sensitized 3TZO film several days after the first sensitivity measurement. The sensitivity measurements were performed at various operating temperatures. From the figure, it is evidently seen that the H_2S sensing performance of the film has remained almost the same after the initial decrease till 80 days. From the plot, it is observed that almost 50 % of the initial response was maintained after 120 days. Therefore, it can be concluded that Pd-sensitized 4TZO film can stand as a good sensor element for H_2S gas sensor applications.

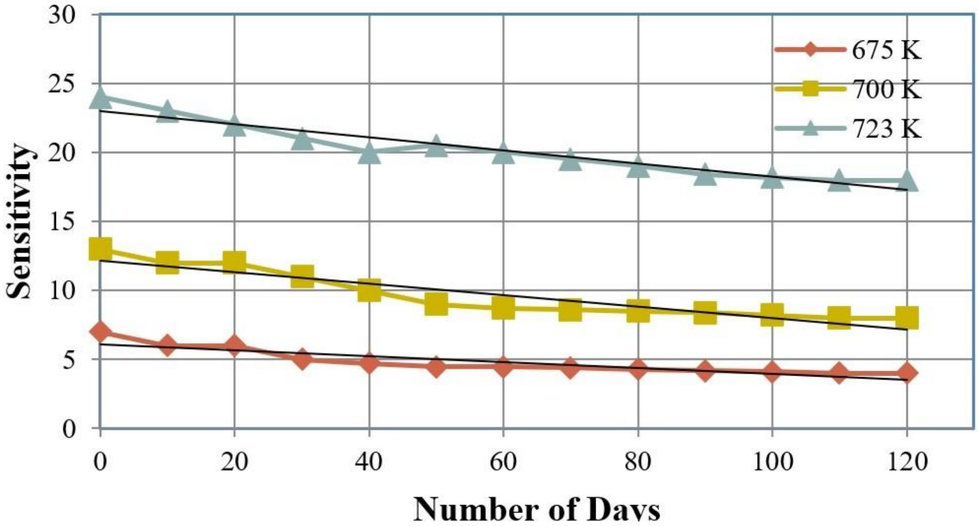

Figure 8: 120 days sensitivity of sensor for Pd-sensitized 4TZOfilm.

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