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Characterization of nanosized TiO_2 based H_2S gas sensor

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Abstract The present investigation deals with the fabrication of H_2S gas sensor based on semiconducting oxide,TiO_2. Among the various metal oxide additives tested, Al_2O_3 is outstanding in promoting the sensing properties of nanosized TiO_2 based H_2S gas sensor. XRD pattern of TiO_2 /Al_2O_3 shows complete phase formation with anatase structure and grain growth 45 nm. The TiO_2 sensor loaded with 5 wt% Al_2O_3 and 0.5 wt% Pd shows increase in sensitivity to H_2S. The cross sensitivity of 0.5 wt% Pd:5 wt% Al_2O_3 doped TiO_2 also checked for CO, LPG and H_2 gases. The highest sensitivity for low concentration of H_2S was observed using TiO_2 based mixed Al_2O_3 and Pd. The H_2S sensor shows high sensitivity and undesirable cross sensitivity effect using TiO_2/Al_2O_3/Pd as sensing materials.

Introduction

Metal-oxide semiconductors are extensively used as gas sensors due to their property, which changes their conductivity under gas exposures. TiO_2 seems to be one of the most interesting candidates for gas detection and has commercially been used as lambda sensor in exhaust pipes. Likewise, its sensing capability has been improved with the addition of foreign atoms such as Pt [1–3], Cu [4, 5], Cr [6] or Nb [7–9].

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Hydrogen Sulfide is a toxic gas often produced in coal or natural gas manufacturing. The threshold limit value for Hydrogen sulfide is 10 ppm. When the concentration of H_2S is higher than 250 ppm, it is dangerous to human body and may cause death. Reliable, low cost H_2S consumption is in high demand for environmental safety and industrial control purposes.

Numerous efforts have been directed to develop H_2S gas sensors by mainly employing solid electrolytes such as alkali metal sulfates [10] by adding hydrophonic silica [11], ZrO_2 [12], CeO_2 [13] to the sensor element. It was also found that addition of as noble metal, Ag makes the material very sensitive to H_2S [14].

Owing to extensive investigation, the properties of solid electrolyte H_2S sensors are reaching the levels for practical applications [15]. On the other hand, electronic interaction between H_2S and SnO_2 was first studied [16]. Thereafter, H_2S sensing properties of semiconductor metal oxides such as CeO_2 [17] and SnO_2 [18] have been studied. However little was known about H_2S sensing properties of other semiconductor metal oxide materials.

In doped semiconducting oxides two types of sensitization mechanisms have been proposed, viz chemical sensitization and electronic sensitization [19]. In chemical sensitization, the sensing gas molecule gets adsorbed at the sensor surface where it is dissociated or activated with the help of a dopant. This dissociated molecule at the sensor surface interacts with the semiconducting oxide. This will lead to a change in the conductivity at the sensor surface. On the other hand, electronic sensitization is followed by direct exchange of electrons between added dopant and the semiconductor surface. There is a change in the oxidation state of dopant on contact with sensing gas molecule due to electron exchange from dopant to oxygen which leads to a change in the conductivity of the sensor surface.

In this paper, structural and sensing characteristics of undoped and doped TiO_2 has been reported. In addition, attempts were made to improve the H_2S sensing properties of TiO_2 by addition of small amount of various metal oxides. The basic characteristics of H_2S gas sensor using TiO_2/Al_2O_3/Pd as sensing material such as sensitivity, working range and cross sensitivity were further studied.

The homogeneity of the compound was confirmed by X-ray diffraction using SIEMEN D.5000 with copper target, K_α radiation (λ = 1.5406 Å). The additives were added to the base material TiO_2 with different weight percentages. For the gas sensing measurements, the calcinated compound was mixed with 2% polyvinylalcohol (PVA) binder to make a paste and coated onto alumina tube substrates which are already provided with platinum wire electrodes for electrical contacts.

Experimental detail

Nanosized TiO_2 thick films were prepared from titanium butoxide ($Ti(OC_4H_9)_4$)) with 99% purity. The TiO_2 precursor solution was made by a mixture of $Ti(OC_4H_9)_4$), butanol and 37% HCl (as the catalyst) in a molar ratio of 1:42:0.2 and then with continuous stirring for 12 h at room temperature. The mixture was slowly evaporated and then dried in an oven at 120 °C overnight. The dried material was crushed and calcined at different temperatures in the range of 450–850 °C for 6 h in air. Similar procedure was applied for Cu, Pb, Mn and Al as additives. The solution of chloride salt was added to these solutions in the appropriate concentration.

In order to increase the sensitivity, different concentrations of noble metal were incorporated in TiO_2-based mixed metal oxide. Noble metal was incorporated by dissolving appropriate amounts of metal chlorides and TiO_2-based mixed metal oxide material in deionised water. The mixture was vigorously stirred for 1 h and dried on a water bath. The fine powder obtained was calcined at 200 °C for 2 h to eliminate the chloride ions. For 5 wt% Al_2O_3 doped TiO_2 with noble metals, the maximum sensitivity to H_2S gas was obtained with 0.5 wt% Pd.

Sensor fabrication

For the gas sensing measurements the sensor element was provided with a heater inserted in an alumina tube and was coated with 2–3 μm thickness of the sensor material. The electrical resistance of the element in dry air is measured by means of conventional bridge circuitry in which the element is connected to an external resistor at a circuit voltage of 10 V to calculate the electrical resistance of the element. The sensitivity S, is defined as the ratio of change of resistance in a test gas $S = \Delta R/R_a = IR_a - R_g\, I/R_a$, where R_a and R_g is the sensor resistance in the presence of the air and test gas [20].

In the region of saturation, i.e. where S reaches values near to unity, the sensitivity has been defined as,

$$S = \log(R_a/R_g)$$

Result and discussion

Figure 1 shows XRD pattern of undoped TiO_2 and 5 wt% Al_2O_3 doped TiO_2 calcined at 650 °C. XRD pattern of TiO_2:5 wt% Al_2O_3 is identical to that of undoped TiO_2 with anatase structure, indicating the formation of a solid solution of Al_2O_3 in TiO_2. The crystalline size D was calculated according to the Scherrer equation, $\Delta(2\theta) = K\alpha/D\cos\theta$ where $\Delta(2\theta)$ is the width at half maximum intensity (in radiant) and θ is the Bragg's angle of the (101) diffraction peak, K is constant depending on the line shape profile (current K = 1), α is the wavelength of the X-ray source (in case of Cu radiation, λ = 1.5406 Å. and D is the crystallite size [21]. The crystallite sizes of TiO_2 were observed in the range of 50–60 nm for different calcined compound ranging from 450 °C to 850 °C. It is well known that, as the calcination temperature increases, the crystallite size increases. No phase transitions were observed within our limit. As seen from XRD of Al_2O_3 doped TiO_2 no peak was observed for Al_2O_3, this may be due to Al^{3+} substituted Ti^{4+}. Whyoshup et al. [22] also observed similar observation for NiO doped WO_3. It was also observed from the figure that the intensity of peaks

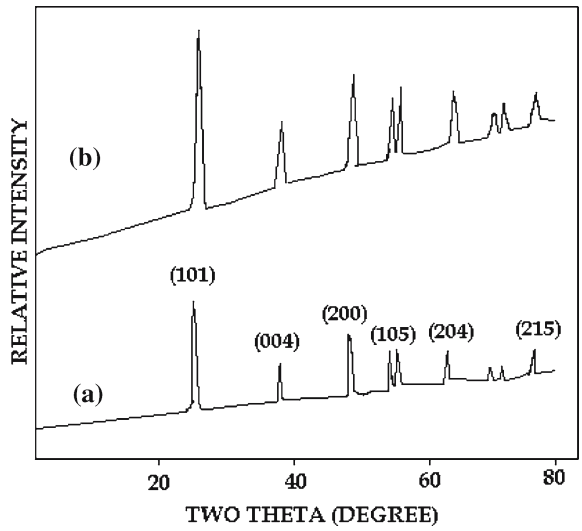

Fig. 1 X-ray diffraction of (**a**) Undoped TiO_2 calcined at 650 °C. (**b**) 5 wt% Al_2O_3 doped TiO_2 calcined at 650 °C

increases with Al_2O_3 loading. The high intensity of peaks indicates a good crystallization with grain growth of 45 nm. In order to maintain the crystallite size and better sensitivity, TiO_2 calcined at 650 °C is chosen as a base material for all the experiments.

Gas sensing properties

Figure 2 shows the sensitivity of undoped TiO_2 thick films for H_2S, LPG, H_2 and CO as a function of operating temperature. It is clear from the figure that, as operating temperature increase in the range of 250–350 °C, there is an increase in sensitivity from 0.27 to 0.5 for H_2S gas. Above 325 °C, the sensitivity remains constant to 0.5 as the operating temperature increase to 350 °C.

The gas sensing characteristics of semiconductor gas sensors depend on the catalytic or surface chemical properties, as well as on physical properties such as grain size or porosity [23]. In order to improve the gas sensing properties, a great variety of atoms or additives are introduced in the base-sensing semiconductor.

Among the examined metal oxides, Al_2O_3 was singularly outstanding in promoting the sensitivity shown in Fig. 3. For further improvement in the sensitivity, Al_2O_3 with concentrations ranging from 0 to 15 wt% was added in the base material. Figure 4 shows sensitivity as a function of different amount of Al_2O_3 doped TiO_2 for H_2S at an operating temperature 325 °C. It has been observed that 5 wt% Al_2O_3 shows maximum sensitivity. 5 wt% Al_2O_3 was the optimal dopant for TiO_2-based H_2S sensor for further study.

In case of Aluminum doped titania, microstructure and electrical changes are observed. Aluminum introduces electronic states at the surface or into the bulk that modifies

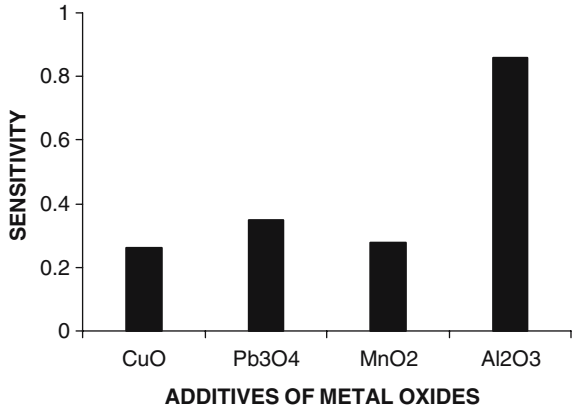

Fig. 3 Sensitivity as a function of different metal oxide doped TiO_2 for H_2S at an operating temperature 325 °C

the base material. When an oxygen molecule gets adsorbed at the sensor surface, it extracts electrons from the conduction band of the host material. This reduces the concentration of electrons in the conduction band of the host material, leading to a decrease in the conductivity of the host material. As oxygen concentration increases, the number of conduction band decreases further and conduction starts taking place through holes [24].

The sensor cross sensitivity effect played by LPG, CO and H_2 interfering gases at various operating temperatures are shown in Fig. 5. It is clear from the graph that the sensitivity for H_2S gas is more than other reducing gases. As expected the sensitivity increased with an increase in the operating temperatures. For H_2S the sensitivity increased and reached saturation values around 250 °C.

The sensing mechanism of TiO_2 thick film gas sensors is usually based on the surface properties of the material. At elevated temperatures, adsorption of atmospheric oxygen takes place. The adsorbed oxygen extracts the conduction

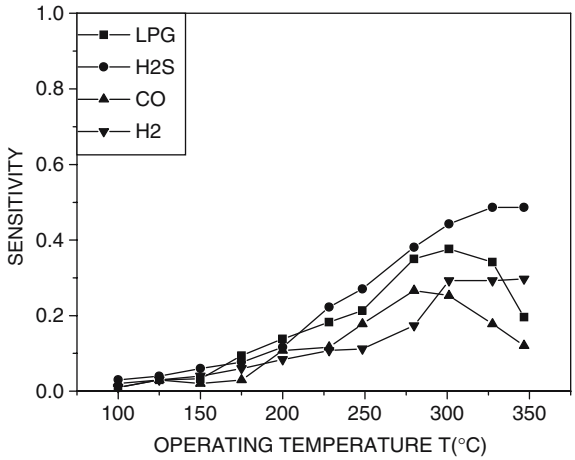

Fig. 2 Sensitivity of undoped TiO_2 thick films for H_2S, LPG, CO and H_2 calcined at 650 °C as a function of operating temperatures

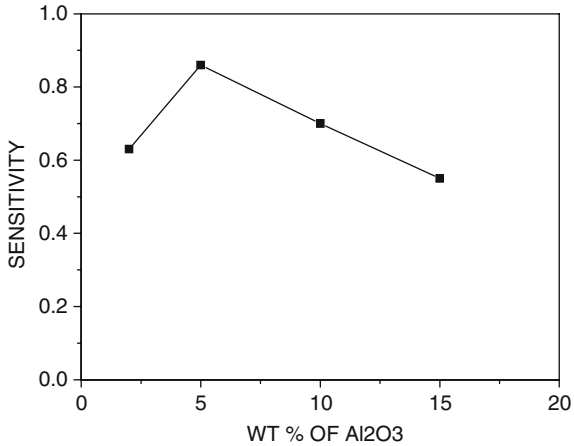

Fig. 4 Sensitivity as a function of different concentrations of Al_2O_3 doped TiO_2 for H_2S at an operating temperature 325 °C

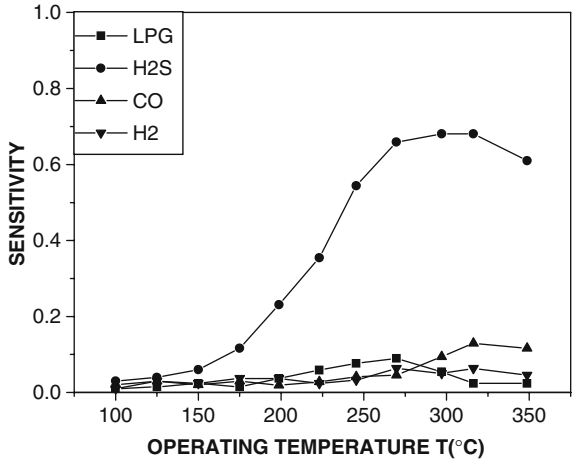

Fig. 5 Sensitivity as a function of operating temperatures for 5 wt% Al_2O_3-doped TiO_2 for H_2S, LPG, CO and H_2

electrons from the surface region of TiO_2 grains, leaving positively charged donor ions behind. An electric field develops between the positively charged donor ions and the negatively charged oxygen ions such as O^{2-} or O^- on the surface. The more the oxygen ions on the surface, the higher the potential barrier and therefore the higher the resistance. As the concentration of gas present in the ambient atmosphere increases, the amount of O^{2-} or O^- decreases due to the reaction with gas molecules, resulting in a decrease in resistance.

Figure 6 shows sensitivity for TiO_2-5 wt% Al_2O_3-0.5 wt% Pd for H_2S gas at an operating temperature 250 °C. It was found to be extraordinarily large indicating that the H_2S detection was sensitized quite effectively by small amount of Pd. The sensitivities to other gases remain almost unchanged with or without Pd addition. Such a feature seems to be favorable from the viewpoint of selective detection of H_2S. The increase in sensitivity when 0.5 wt% of Pd doped 5 wt% Al_2O_3:TiO_2 suggests the importance of the dispersion of Pd on the semiconductor surface.

Palladium incorporation decreased the operating temperature from 250 °C to 225 °C. The reduction in temperature is considered to be very beneficial from the sensor point of view, since earlier work on sensors for H_2S report an operating temperature in the range of 200–300 °C [25]. An interesting observation is that the sensitivity to CO, LPG and H_2 remained low even for Pd doped elements.

Figure 7 shows sensitivity of 0.5 wt% Pd doped 5 wt% Al_2O_3:TiO_2 as a function of H_2S concentrations in air (ppm) at 225 °C. As seen from it, the sensitivity initially increases slowly with increasing concentration of gas and then linearly as the gas concentration increases from 600 to 1000 ppm. It is seen that the element TiO_2-5 wt% Al_2O_3-0.5 wt% Pd reaches the saturation value of sensitivity for concentration of 1000 ppm. The sensor is able to detect up to 200 ppm of H_2 with reasonable sensitivity at 225 °C.

Conclusion

TiO_2 and Al_2O_3-doped TiO_2 nanopowders have been synthesized with crystalline growth in nanosize calcined at different temperatures. The materials have been structurally characterized by means of X-ray diffraction. XRD shows anatase structure of TiO_2. The crystallite sizes of TiO_2 were observed in the range of 50–60 nm for different calcined compound ranging from 450 °C to 850 °C. The gas-sensing properties of nanosized TiO_2 thick films were depend on the addition of Al_2O_3 and noble metal, Pd. The sensor element of 0.5 wt% of Pd:5 wt% Al_2O_3 doped TiO_2 shows higher sensitivity and selectivity towards H_2S at

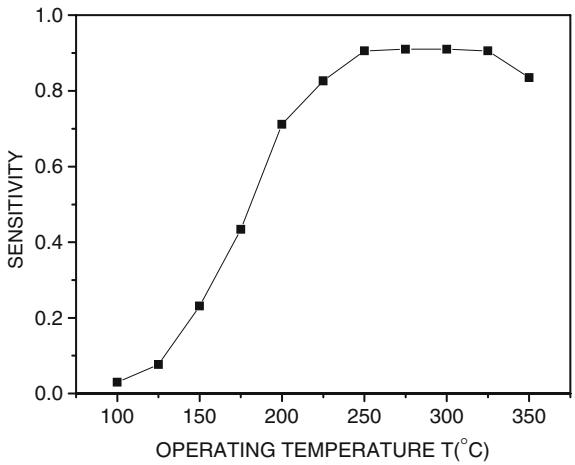

Fig. 6 Sensitivity of TiO_2-5 wt% Al_2O_3-0.5 wt% Pd as a function of operating temperature for H_2S gas

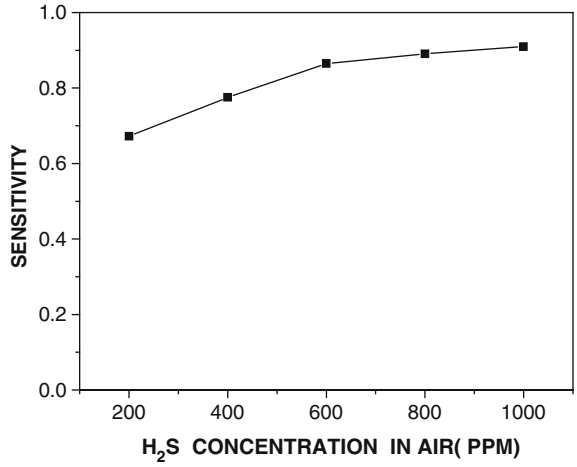

Fig. 7 Sensitivity of TiO_2-5 wt% Al_2O_3-0.5 wt% Pd as a function of different H_2S concentration in air (ppm) at 225 °C

225 °C. The sensor shows fairly good sensing performance to H_2S gas in air in the range of 200–1000 ppm at 225 °C.

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