ZnO/TiO_2 p/p^+ heterojunctions for hydrogen gas sensors at room temperature

S. K. Hazra, S. Roy and S. Basu*

Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

Abstract

Room temperature hydrogen sensitivity was obtained with $Pd/ZnO/TiO_2$ heterostructure. The heterojunction was fabricated by depositing ZnO on TiO_2 thin films. Pd dots were deposited on ZnO surface for catalytic contact. The current-voltage characteristics were studied at different concentrations of hydrogen. Sharp response was obtained with hydrogen gas concentration down to 500 ppm at room temperature. From the current-voltage characteristics the junction ideality factor, leakage current and barrier height were calculated. Pd dots were then deposited on the TiO_2 surface in ZnO/TiO_2 heterojunctions to fabricate $Pd/TiO_2/ZnO$ sensor structures. The $Pd/TiO_2/ZnO$ heterostructure was also sensitive to hydrogen at room temperature but the change in barrier height due to hydrogen was less than the $Pd/ZnO/TiO_2$ sensor structure. There was a little difference in the response time for the two structures. An equilibrium energy band diagram was drawn to illustrate the hydrogen sensitivity phenomenon in the two sensor structures.

Key words: Zinc oxide, titanium dioxide, heterojunction, electrical conductivity, hydrogen Sensors

1. Introduction

Oxide gas sensors operating at room temperature are in increasing demand. ZnO and TiO_2 are suitable materials for gas sensors because they are easily available with moderately low cost of productions and high sensitivity to reducing and oxidizing gases. Recently a Co_2O_3/SnO_2 p-n structure has been reported for gas sensors[1].

* Corresponding author: Tel: +91-3222-283972; fax: +91-3222-255303
Email: sukumar_basu@yahoo.co.uk (S. Basu)

In this article we report on the hydrogen sensitivity of the Pd/ZnO/TiO_2 heterostructures. The heterostructures were fabricated by depositing ZnO on the TiO_2 thin films. The films were individually characterized by Hall effect experiment. Pd dots were deposited on the ZnO surface for catalytic contact. The static current-voltage characteristics and the dynamic transient response characteristics were studied. In a separate study the Pd dots were deposited on the TiO_2 surface in the heterostructures to fabricate the Pd/TiO_2/ZnO structure. The current-voltage characteristics for this reversed heterostructure were also studied for hydrogen sensitivity. A comparative analysis of the sensing mechanism was done using a simplified energy band diagram for the two structures.

2. Experimental

The oxide heterojunctions were fabricated using two separate growth techniques. A solid solution of high purity titanium and aluminium (2-wt%) was prepared in a "Tungsten Inert Gas" (TIG) electric arc furnace. Using this solid solution a thin film was deposited onto a cleaned alumina substrate by e-beam evaporation. This film yielded rutile TiO_2 upon oxidation at 950 ^oC for 1 hour in 1% O_2/Ar ambient[2]. Thin-film of ZnO was deposited at 220 ^oC onto a selected area (by masking) of this TiO_2 film by an indigenously modified chemical vapour deposition (CVD) method using zinc acetate solution (in methanol) as the precursor[3]. The samples were in situ annealed at 350 ^oC for 30 minutes after the deposition.

Hall effect study of the individual oxides was performed using van der Pauw configuration with Al ohmic contact for ZnO and Ti ohmic contact for TiO_2[2].

Pd dots were deposited by e-beam evaporation method on the ZnO surface in ZnO/TiO_2 heterostructure to fabricate Pd/ZnO/TiO_2 sensor structure. Similarly Pd dots were deposited on the TiO_2 surface in ZnO/TiO_2 samples to form the reversed Pd/TiO_2/ZnO sensor device.

The static current-voltage characteristics and the dynamic transient response characteristics for both the sensor structures were measured in hydrogen. The test gas was introduced into the chamber using Tylan and Digiflow mass flow controllers and mass flow meters respectively.

3. Results and Discussion

3.1. Hall effect study:

For a set of ZnO films the I-V measurements at room temperature with van der Pauw configurations (and Al ohmic contact) gave excellent linearity both in forward and reverse biased regimes, indicating good ohmic contact between ZnO and aluminium. The Hall effect measurement for a set of five magnetic fields (5000 – 10,000 gauss) at room temperature gave positive Hall coefficient, which clearly indicates the p-type conductivity of the ZnO matrix. Basically the stoichiometry in the ZnO matrix with almost negligible number of oxygen vacancies is responsible for the weak p-type conductivity[4]. The Fermi level is pushed just below the intrinsic level in the forbidden energy gap. The obtained carrier density for ZnO is ~ 10^{12} cm^{-3} & resistivity ~ 6.4×10^3 ohm-cm. Similar experiments were done with the TiO_2 thin films with carrier density ~ 10^{12} cm^{-3} & resistivity ~ 1.84×10^3 ohm-cm. TiO_2 was doped with aluminium (group III) to make the matrix more p-type with respect to ZnO.

3.2. Pd/ZnO/TiO_2 & Pd/TiO_2/ZnO Sensor Study:

From the I-V curves of Pd/ZnO/TiO_2 structure in air, 500 ppm and 2000 ppm hydrogen [Fig. 1a] the junction parameters like barrier height, saturation current & ideality factor were calculated [Table I].

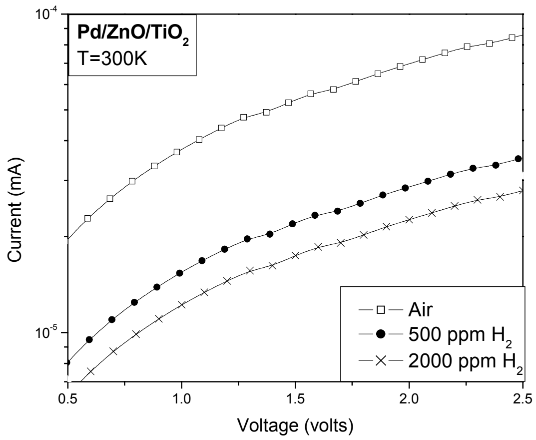

Fig. 1a

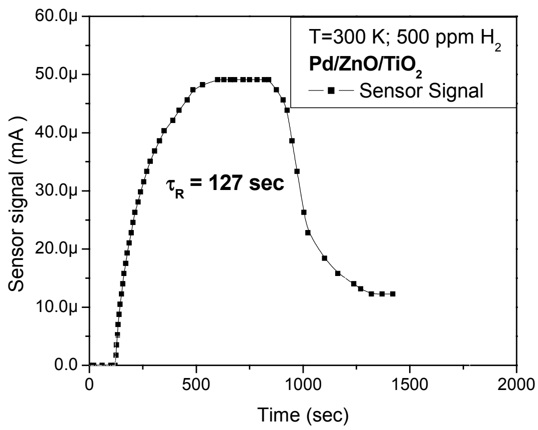

Fig. 1b

The barrier increases with the increase in hydrogen concentration owing to the p-type conductivity and the band alignment at the interface. The ideality factor improves due to the passivation of the dangling bonds at the interface. As a result the increase in barrier height decreases the saturation current. The transient response in 500 ppm hydrogen at room temperature reveals a response time of 127 sec [Fig. 1b]. The drift in the sensor signal as it appears from the baseline shift maybe due to the trapping of the hydrogen atoms at the Pd/ZnO interface. Same experiments for Pd/TiO_2/ZnO were conducted [Fig. 1a & 1b] and the results are shown in table I.

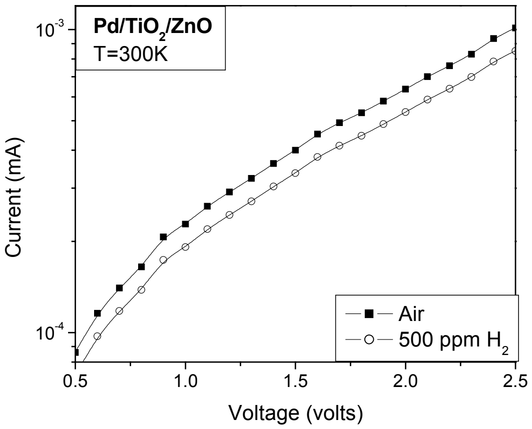

Fig. 2a

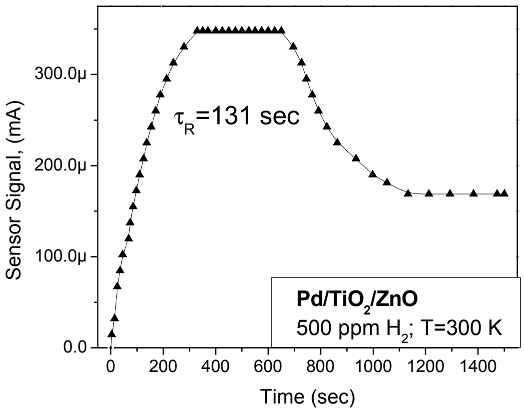

Fig. 2b

For 500 ppm hydrogen the change in barrier height, which is a measure of sensitivity, is less than Pd/ZnO/TiO_2 structure. The barrier height change and thus the difference in sensitivity are corroborated with an equilibrium energy band diagram for both the structures as discussed in section 3.3. The ideality factor for Pd/TiO_2/ZnO structure is somewhat better because of uniform grain size with low porosity and hence less defects at Pd/TiO_2 interface[2]. The extent of porosity plays a vital role in the adsorption of hydrogen and it affects the sensitivity of Pd/TiO_2/ZnO junctions. Also as expected, the improve in the ideality factor in presence of 500 ppm hydrogen may be due to the passivation of interfacial dangling bonds.

3.3. Equilibrium energy band diagram:

Figure 3a & 3b show the theoretically expected equilibrium energy band diagram of Pd/ZnO/TiO_2 and Pd/TiO_2/ZnO structures according to the standard theory of metal-semiconductor Schottky contact.

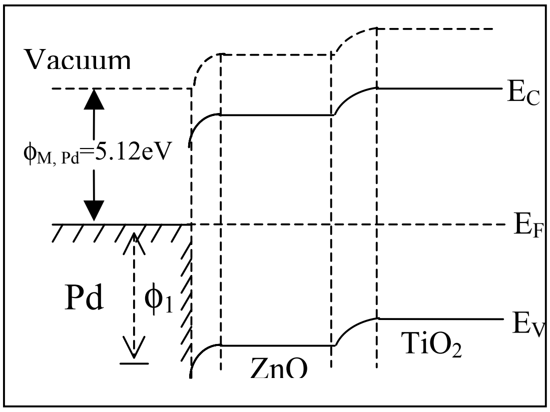

Fig. 3a

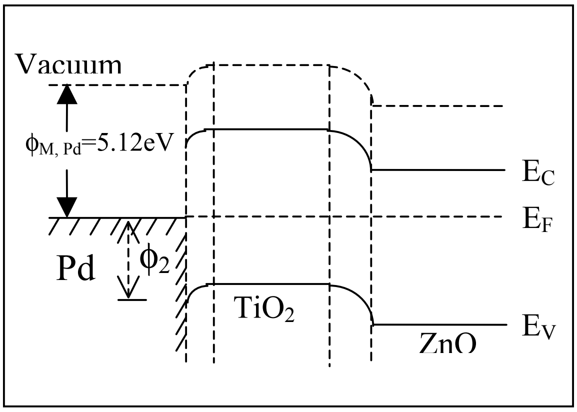

Fig. 3b

When the Pd/ZnO/TiO_2 sensor structure is exposed to hydrogen the workfunction of palladium decreases upon hydrogen adsorption[5]. This change shifts the fermi level upwards. Accordingly the contact potential of Pd/ZnO junction increases and also the oxide heterojunction band is stretched[6]. So the overall change in the barrier potential due to adsorption of hydrogen is the cumulative result of these two effects. For Pd/TiO_2/ZnO structure the change in barrier potential at Pd/TiO_2 interface is relatively small[2]. Hence the oxide heterojunction band is stretched till the contact potential between Pd/TiO_2 and TiO_2/ZnO equalizes. Once the potential is equalized the flow of charge carriers is prevented and no further change in barrier height takes place. Therefore the sensitivity of this junction is less than the Pd/ZnO/TiO_2 one although the response time is almost the same.

4. Conclusion

The multilayered Pd/ZnO/TiO_2 sensor structure is more sensitive to hydrogen down to 500 ppm at room temperature. The overall sensitivity is due to the change in barrier height at the two junctions i.e. Pd/ZnO and ZnO/TiO_2. The sensitivity drops down when the junctions are reversed i.e. Pd/TiO_2 and TiO_2/ZnO. Pd/TiO_2/ZnO junction is more ideal compared to Pd/ZnO/TiO_2 because of the compact structure of TiO_2 films and hence less number of dangling bonds. On the other hand Pd/ZnO/TiO_2 is less ideal due to presence of large number of dangling bonds due to porous nature of ZnO, which is responsible for higher sensitivity to hydrogen.

5. Acknowledgement

S. K. Hazra gratefully acknowledges "Council for Scientific & Industrial Research" (CSIR), New Delhi, India for the individual CSIR fellowship

6. Reference

1. Wang, Yu-De, Wu, Xing-Hui, Zhou, Zhen-hai, Novel high sensitivity and selectivity semiconductor gas sensor based on the p+n combined structure, *Solid-State Electronics* 2000, 44, 1603-1607
2. Hazra, S. K., Roy, S. & Basu, S., Growth of titanium dioxide thin films via a metallurgical route and characterizations for chemical gas sensors, *Mat. Sc. & Eng. B*, 2004, *In press*
3. Datta, A., Choudhury, T. K. and Basu, S., Deposition and characterization of Zinc oxide thin films for hydrogen sensor devices, *Mat. Sc. Eng. B*, 1992, 14, 31-35
4. Xiong, Gang., Wilkinson, John., Mischuck, Brian., Tuzemen, S., Ucer, K. B. and Williams, R. T., Control of p- and n-type conductivity in sputter deposition of undoped ZnO, *Appl. Phys. Lett.* 2002, 80(7), 1195-1197
5. Kobayashi, H., Kishimoto, K. and Nakato, Y., Reactions of hydrogen at the interface of palladium-titanium dioxide Schottky diodes as hydrogen sensors, studied by workfunction and electrical characteristic measurements, *Surface Science*, 1994, 306(3), 393-405
6. Kunimoto, A., Abe, N., Uchida, H., Katsube, T., Highly sensitive semiconductor No_x gas sensor operating at room temperature, *Sensors and Actuators B*, 2000, 65, 122-124

7. Figure captions

Fig 1. a: I-V characteristics of Pd/ZnO/TiO_2 in air & hydrogen

b: Transient response characteristics of Pd/ZnO/TiO_2 in 500 ppm hydrogen

Fig 2. a: I-V characteristics of Pd/TiO_2/ZnO in air & hydrogen

b: Transient response characteristics of Pd/TiO_2/ZnO in 500 ppm hydrogen

Fig 3. a: Energy band diagram of Pd/ZnO/TiO_2

b: Energy band diagram of Pd/TiO_2/ZnO

Table. I

Sensor structure	Ambient	Barrier height, (Volts)	Saturation current (mA)	Ideality factor
Pd/ZnO/TiO_2 T=300 K	Air	$0.795 = \phi_1$	3.81×10^{-6}	11.58
	500 ppm H_2	0.818	1.56×10^{-6}	11.15
	2000 ppm H_2	0.826	1.16×10^{-6}	9.39
Pd/TiO_2/ZnO T=300 K	Air	$0.794 = \phi_2$	6.99×10^{-6}	5.23
	500 ppm H_2	0.801	5.43×10^{-6}	5.22