Theoretical modeling of Pd-SnO\textsubscript{2} based ethanol gas sensor

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\textbf{Abstract:} In this paper, we fabricate two devices, undoped tin oxide (UTO) and 1 wt\% palladium-doped tin oxide (PdTO) thick films for ethanol (C\textsubscript{2}H\textsubscript{5}OH) gas sensors. UTO and PdTO samples were deposited on alumina substrate using screen-printing technology. The fabricated UTO and PdTO sample was used as ethanol gas sensor in range (0-5000 ppm) at operating temperature 473 K. The results showed the highest response (~71\%) for varying concentrations of ethanol (5000 ppm) at operating temperature 473 K. Also response/recovery time was observed and it was ~41 s / 125 s. our experimental data was well supported by the proposed theoretical model.

\textbf{Keywords:} Pd-doped SnO\textsubscript{2}; Gas sensing response; Ethanol gas sensor; Theoretically model

1. Introduction

In the gas sensor field, semiconductor technology has been a major subject of intensive research and continuous development occurred during the last few decades. The detection of chemical species and their concentration is a big concern of the researchers as well as many industries. Solid-state oxide film gas sensors function by measuring the change in electrical resistance of a sensing film as a function of varying concentrations of a given gas. Such devices of potential importance are relatively cheap, reproducible, and small of the size that can be dependent upon resistor [1-3]. SnO\textsubscript{2} is one of the synergic materials widely used for detecting alcoholic and toxic gases [4]. Yadava et al studied that the sensing mechanism and theoretical modeling of Pd/TiO\textsubscript{2}/Si devices with help of Langmuir adsorption and Frenkel-pool theory of emission parameter. They found that the fabricated devices are appropriated devices for acetone over ethanol and TCE [5]. Kumar et al studied a Co-doped SnO\textsubscript{2} sample was used for liquefied petroleum gas and compressed natural gas detection. They found that response to LPG increased from 3.4 to 35.3 for Co-doped SnO\textsubscript{2} at 1600 ppm [6]. Yadava et al investigated the sensing response of CdS-SnO\textsubscript{2} thick film gas sensor, which not only exhibits the highest response but is also more selective for methanol over LPG or acetone [7].

In this paper, we report UTO and PdTO sensing devices for the investigation of gas sensing response with the theoretical model of C\textsubscript{2}H\textsubscript{5}OH gas at 473 K. Pd-doped SnO\textsubscript{2} thick films were fabricated with help of screen-printing method on alumina substrate. We found that enhancement sensing behavior toward the ethanol gas and experimental data well supported the theoretical model.
2. Fabrication

We fabricate two-sample as UTO and PdTO using a prepared using screen printing machine on an alumina substrate. The detailed preparation process of sensing devices was earlier reported by Vishwakarma et al [8].

3. Gas sensing property and mechanism

The gas sensing response of fabricated UTO and PdTO device is evolved by Schottky-barrier theory [9]

\[ I = \left[ AT^2, \left(e^{\frac{-q\Phi}{kT}}\right)\left(e^{\frac{qV}{kT}}\right)^{-1}\right] \]  

Where, \( \Phi \) = height of the barrier, \( A \) = Constant (Richardson constant), and \( V \) = voltage. Change in \( R \) across \( V \) is defined as

\[ \Delta R = \left[ \frac{dI}{dV} \right] \]  

at \( V = 0 \) then \( \Delta R = \left[ \frac{k}{ATq}.e^{\frac{-q\Phi}{kT}} \right] \) we put \( A' = \left[ \frac{k}{ATq} \right] \) then it may be written as

\[ \Delta R = A'.\left[ e^{\frac{q\Phi}{kT}} \right] \]  

Jei et al [10] explained the relation between \( \Delta \Phi \) and \( \theta \) is given by,

\[ \Delta \Phi = \left[ \frac{eN_s^2\theta^2}{2\varepsilon_0\varepsilon N_D} \right] \]  

Where \( N_s \) = No. of free charge, \( N_D \) = No. of ionized charge. Equation (ii) and (iii) gives \( \Delta R = A'\exp\left[B\theta^2\right] \)

According to Freundlich adsorption isotherm (when \( K = aRTn_a \))

\[ \theta = KC^b \]  

Putting the value of \( \theta \) in equation (iv) we get

\[ \Delta R = A'\exp\left[B K^2 C^{2b}\right] \]

Putting \( B' = BK^2 \), \( b' = 2b \) in the above equation the results indicated as

\[ \Delta R = A'\exp\left[B' C^{b'}\right] \]  

Using limiting values \( C=0 \), \( A' = R_a \) then equation (vi) modified and it is \( \Delta R = R_a \exp\left[B' C^{b'}\right] \) or

\[ \frac{\Delta R}{R_a} = \exp\left[B' C^{b'}\right] \quad \text{or,} \quad \log\left[\frac{\Delta R}{R_a}\right] = B' C^{b'} \]  

The above equation (vii) may be written as, \( \Delta R = R_a \exp\left[B' C^{b'}\right] \) the gas sensing response of the device UTO and PdTO is defined as if we put \( \Delta R = R_a - R_g \). The change in electrical resistance in the sample on exposure to a chosen gas of a known concentration is defined as a response as follows,

\[ S = \frac{(R_a) - (R_g)}{(R_a)} \times 100 \]  

(iiiiiii)
where \( R_a \) = resistance is absent of target gas and \( R_g \) = resistance in the presence of target gas [11-13]. The resistance of the fabricated sensors in the air and gas environment is measured with the help of a Dual DC power supply (LD-3202) and Digital Multimeter (Aplab 107N).

**Figure 1.** The sensing response of \( \text{C}_2\text{H}_5\text{OH} \) gas for UTO and PdTO devices.

We observed that response of sensors enhanced with Pd-doping for varying concentrations of \( \text{C}_2\text{H}_5\text{OH} \) in the air. The maximum response of the device UTO and PdTO obtained for \( \text{C}_2\text{H}_5\text{OH} \) is given in Table 1. The values for \( \text{C}_2\text{H}_5\text{OH} \) are 71\% for UTO and 21\% for PdTO devices, respectively. As portrayed in Figure 1 the PdTO response is 3.38 times the UTO value. It is seen that Pd-doping results in a remarkably improved response for \( \text{C}_2\text{H}_5\text{OH} \) of the PdTO device.

**Table 1.** Gas sensing response and transient time of \( \text{C}_2\text{H}_5\text{OH} \) for UTO and PdTO device

| Device | Gas sensing response (% | Response time (s) | Recovery time (s) |
|--------|-------------------------|-------------------|-------------------|
| UTO    | 21                      | 68                | 205               |
| PdTO   | 71                      | 41                | 128               |

At time 10 min, 5000 ppm \( \text{C}_2\text{H}_5\text{OH} \) was injected in the test chamber to get maximum response, and then the chamber was opened for recovering the initial state of the sensor. Figure 2 shows that in device PdTO the response time and recovery time reduce from 68 s to 41 s and 205 s to 125 s, respectively, for \( \text{C}_2\text{H}_5\text{OH} \) (5000 ppm) at 473 K.
Using equation (vii), we plot $\log \frac{\log (R - R_a)}{R_a}$ vs. $\log (C)$ for the varying concentration of the ethanol (0-5000 ppm) which is shown in figure 3. It is clear from figure 3, sensor exhibits a linearly logarithmic response ($R^2 = 0.9619$ with $Y = 0.5318 \times - 0.0232$) with $C_2H_5OH$ concentration. The curve between $\log C$ vs. $\log \frac{\log (R - R_a)}{R_A}$ is gives a straight line and it is in good agreement with earlier reported work [13]. The response behavior of the device UTO and PdTO to exposed $C_2H_5OH$ can be explained based on a refined microstructure of $SnO_2$ on a Pd-doping, which promptly adsorbs oxygen species. It is found that PdTO has pretty enhanced exposing the surface area of refined crystallites. It contains structural defects, vacancies, and dangling bonds, which play an important role in conducting mobile charge carriers. The result found that $C_2H_5OH$ put up maximum oxidation with chemisorbed ionic $O_2$ lineage and, thereby, supplies more free electrons to the conduction band. A possible model is
shown in figure 4. The fast response of device PdTO for C\textsubscript{2}H\textsubscript{5}OH is due to free e\textsuperscript{--} being released with exposing C\textsubscript{2}H\textsubscript{5}OH gas.

![Figure 4. The proposed reaction model of PdTO for C\textsubscript{2}H\textsubscript{5}OH.](image)

4. Conclusions

We report the sensing behavior with the theoretical model of the device PdTO for C\textsubscript{2}H\textsubscript{5}OH. The gas sensing property of sensing device UTO and PdTO exhibits a more sensitive fast response towards C\textsubscript{2}H\textsubscript{5}OH at 473 K. The response of sensing device PdTO for the fixed concentration of C\textsubscript{2}H\textsubscript{5}OH is \sim71\% with transient time 41 s and 125 s. The possible sensing mechanism of fabricating sensing devices PdTO is observed. Also, we found that our proposed theoretical model fitted approximately with experimental results.

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Notes:

- C\textsubscript{2}H\textsubscript{5}OH = ethanol
- PdTO = 1 wt % Pd-doped tin oxide
- Pd = Palladium
- SnO\textsubscript{2} = tin oxide
- UTO = Undoped tin oxide

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