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A Study of Detection Mechanism of Metal Oxide Gas Sensor Under UV Radiation

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Abstract

The presented paper deals with the effect of UV radiation and change in rate of recombination on the operation of metal oxide gas sensors. The performance of a simple metal oxide sensor is simulated first and the relation between absorbed gas concentration and resistance is monitored in absence of UV radiation. Later, the same performance is monitored in the presence of UV radiation on the sensor with the occurrence of surface recombination phenomenon. The performances are simulated on MATLAB. The Grain boundary resistance (R_{gb}), neck resistance (R_n) and total resistance (R) were obtained by simulating standard equation on MATLAB software. The effect of the surface recombination on absorption of gas concentration and change in resistance is also taken into account. It has been observed that the resistance of the sensors depends on the grain size (L), flux density, absorbed gas concentration (N_r), depletion width (W).

Key words: Semiconductor Gas Sensor, Matlab, Environmental monitoring, Thin Film Sensor, Generation and Recombination.

Introduction

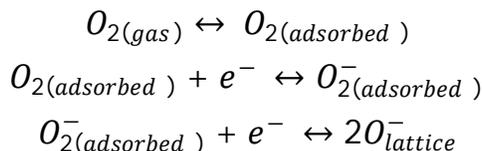
Semiconductor metal oxide gas sensor is one of the most investigated groups of gas sensors. They have attracted much attention in the field of gas sensing under the atmospheric conditions because of the simplicity of their use, their capability to detect large number of gases and potentially wide range of applications. The detection of the gas can be performed by measuring the change of capacitance, work function, mass, optical characteristics energy released by the gas-solid interaction¹.

Semiconductor gas sensors are widely used for the application of gas sensing. The metal oxide gas sensors are wide-band gap semiconductors, therefore, their conduction mechanism is dependent on the temperature. As they require high temperature for operation, this results to high power consumption. Thus, to reduce the temperature of operation, catalysis or doping is done. It was observed that UV radiation brings down the temperature of operation to room temperature. A number of experimental works has been done for analyzing the effects of UV radiation but, very few studies have been done on analyzing the effect of surface recombination².

Many scientists and engineers have studied metal oxide thin films as electronic materials due to their semiconducting behavior, structural simplicity and low cost. In the field of gas /chemical sensing, it has been known that the electrical conductivity of semiconductors varies with the composition of the gas / chemical atmosphere surrounding them. Gas sensors have a great influence in many areas such as environmental monitoring, domestic safety, public security, automotive applications, air conditioning in airplanes, space crafts and houses, sensors networks. Semiconductor oxide-based gas sensors are classified according to the direction of the conductance change due to the exposure to reducing gases as “*n*”-type (conductance increases, e.g., In₂O₃, ZnO, and SnO₂) or “*p*”-type (conductance decreases, e.g., Cr₂O₃ and CuO). This classification is related to the (surface) conductivity type of the oxides, which is determined by the nature of the dominant charge carriers at the surface, that is, electrons or holes³.

2. Working Principle of MOS based Gas Sensors :

The sensing element of resistive type sensors normally comprises of a semiconducting material with high surface-to-volume ratio on a glass substrate with ohmic contacts to measure the change in resistance/conductance. At elevated temperatures, reactive oxygen species such as, O²⁻ and O⁻ are adsorbed on the surface of metal oxide semiconductor. The sequence of processes involved in the adsorption of oxygen on the metal oxide surface can be described by the following formula:



During the adsorption of oxygen species on the surface of sensing element, capturing of electrons from conduction band and the associated decrease in the charge carrier concentration (e⁻) leads to an increase in the resistance of the n-type sensing element until it attains equilibrium. Thus, the surface resistance increases and attains equilibrium during the chemisorptions process. Any process that disturbs the equilibrium leads to a change in the resistance of metal oxide semiconductor.

According to the conductivity behavior of semiconductor metal oxide, the response varies. In n-type semiconductor, the majority charge carriers are electrons. When it interacts with a reducing gas, an increase in conductivity/resistivity occurs. On the other hand, an oxidizing gas depletes the charge carriers, leading to a decrease in conductivity/resistivity.

Similarly, in the case of p-type semiconductors, where positive holes are the majority charge carriers, an increase in the conductivity/resistivity is observed in the presence of an oxidizing gas (the target gas increases the number of positive charge carriers or holes). On the other hand, an increase in resistance is observed in the presence of reducing gas, where negative charge introduced into the material reduces the positive (hole) charge carrier concentration.

3. SnO₂ Gas Sensor :

Semiconductor gas sensors are widely used for several applications in gas sensing. J. Saura⁷ studied

the gas sensing properties of SnO₂ films subjected to UV radiation and found that thermally-treated SnO₂ films are capable of fast detection of gaseous compounds even at room temperature. It has been seen that thermally-treated pyrolytic SnO₂ films develop strong conductivity changes under irradiation with band gap light⁸. Many authors have shown that SnO₂ films are sensitive to oxygen and other reducing gases like CO under UV light illumination at room temperature^{9,10}. It has been shown that exposure of UV radiation results in significant decrease in the response and recovery time of tin oxide gas sensor at low temperature with no poisoning effect when NO₂ come in contact¹¹. Several experimental studies are available on the effect of UV radiation on the metal oxide sensing properties but no works has been done on the theoretical modeling of the sensing mechanism in the presence of the UV radiation. It has been assumed that the metal oxide films are polycrystalline in nature and that the metal oxide grains are connected to each other either by grain boundaries or necks. When UV radiation falls on the metal oxide films, electron-hole pairs are generated and it increases the intra-grain conductivity by modifying the surface potential. When UV radiation falls on the metal oxide polycrystalline film, electron-hole pairs generated in the grin depletion region. Photo excitation decreases the inter-grain barrier, thereby increasing the density of free carriers throughout the material. Under the approximation, the Poisson's equation is given by:

$$\frac{\partial^2 V(x)}{\partial x^2} = -\frac{q}{\epsilon} (N_d - n) \quad (1)$$

Where $V(x)$ is the potential across the depletion region, N_d is the donor density, and n is the number of photo-generated carriers per unit volume given by:

$$n = \alpha \varphi \tau_n \exp(-\alpha x) \quad (2)$$

where α is absorption coefficient, τ_n is the minority carrier lifetime, and φ is the photon flux density. Solution of Eq. (1) using Eq. (2) gives the grain boundary barrier height as:

$$V_B = \frac{q}{\epsilon} \left[\frac{1}{2} N_d w^2 - \varphi \tau_n \left(w + \frac{1}{\alpha} \exp(-\alpha w) \right) \right] \quad (3)$$

Here, q is the charge and w is the depletion width. Assuming that the conduction is mainly due to thermionic emission, the current density across the grain boundary is given by:

$$\begin{aligned} J &= q N_d \left(\frac{k_B T}{2\pi m_n} \right)^{1/2} \exp\left(-\frac{q V_B}{k_B T}\right) \left[\exp\left(-\frac{q V_A}{k_B T}\right) - 1 \right] \\ &= q^2 N_d \left(\frac{k_B T}{2\pi m_n} \right)^{1/2} \exp\left(-\frac{q V_B}{k_B T}\right) V_A \end{aligned} \quad (4)$$

Here, m_n is the effective mass of an electron which is equal to 0.275 times its rest mass (m_0), N_d is the free electron density and V_A is the voltage across the grain boundary. Putting the value of V_B in Equation (4):

$$J = q^2 N_d \left(\frac{k_B T}{2\pi m_n} \right)^{1/2} \exp\left[\frac{-q^2 N_d w^2}{2\epsilon k_B T}\right] \exp\left[\frac{-q^2 \varphi \tau \left(w + \frac{1}{\alpha} \exp(-\alpha w) \right)}{\epsilon k_B T}\right] V_A \quad (5)$$

Using equation (5), the grain boundary resistance R_{gb} can be expressed as:

$$R_{gb} = \left[\frac{(2\pi m_n k_B T)^{1/2}}{A_{gb} q^2 N_d} \right] \exp\left[\frac{1}{\epsilon} \left(\frac{-q^2}{k_B T} \right) \left[\frac{1}{2} N_d W^2 - \varphi \tau \left(w + \frac{1}{\alpha} \exp(-\alpha w) \right) \right] \right] \quad (6)$$

Here A_{gb} is the cross section of grain boundary. If the carrier density in the depletion region is N_d , the neck resistance is given by:

$$R_n = \frac{V_n}{I_n} = \frac{LE_n}{I_n} = \frac{L}{2\pi} \left[N_d \exp \left[\frac{1}{\varepsilon} \left(\frac{q^2}{k_B T} \left(\frac{N_d w^2}{2} - \varphi \tau \left(w + \frac{1}{\alpha} \exp(-\alpha w) \right) \right) \right) \right] \right] \frac{1}{\mu_p (r_n - w)^2 + N_d \mu_d \left(\frac{r_n \varphi}{\alpha} \right)^2 - (r_n - w)^2} \quad (7)$$

Here μ_p and μ_d are the electron mobility in the neutral grain body and the depletion region respectively and E_n is the electric field. Using $r_n = 0.4L$, $N_b = N_d \exp(qV_B/k_B T)$. Total sensor resistance is given by:

$$R = R_n + R_{gb} \quad (8)$$

After the generation of electron-hole pairs, electrons move towards the surface where they recombine via deep traps either at surface or close to it. The surface recombination rate R' is given by:

$$R' = \frac{N_T k_n k_p (n_s p_s - n_t p_t)}{k_n (n_s + n_t) + k_p (p_s + p_t)} \quad (9)$$

Here, N_T is the trap density, k_n is the capture factor for electrons, k_p is the capture factor for holes, n_s and p_s are the surface carrier concentration for electron and holes respectively, which take on the values n_t and p_t .

Methodology :

From equation 6, 7 and 8 it is apparent that both grain boundary resistance and neck resistance and hence total resistance depends on the temperature (T), grain size (L) and free electron density (N_d). These equations were solved and simulated using MATLAB.

Adding $R' \frac{w^2}{a}$ in equation 6 and 7, to take into account the effect of the surface recombination on absorption of gas concentration and change in resistance, it is obtained that:

$$R'_{gb} = \left[\frac{(2\pi m_n k_B T)^{1/2}}{A_{gb} q^2 N_d} \right] \exp \left[\frac{1}{\varepsilon} \left(\frac{-q^2}{k_B T} \right) \left[\frac{1}{2} N_d W^2 - \varphi \tau \left(w + \frac{1}{\alpha} \exp(-\alpha w) \right) \right] \right] + R' \frac{w^2}{a} \quad (10)$$

$$R'_n = \frac{V_n}{I_n} = \frac{LE_n}{I_n} = \frac{L}{2\pi} \left[N_d \exp \left[\frac{1}{\varepsilon} \left(\frac{q^2}{k_B T} \left(\frac{N_d w^2}{2} - \varphi \tau \left(w + \frac{1}{\alpha} \exp(-\alpha w) \right) \right) \right) \right] \right] \frac{1}{\mu_p (r_n - w)^2 + N_d \mu_d \left(\frac{r_n \varphi}{\alpha} \right)^2 - (r_n - w)^2} + R' \frac{w^2}{a} \quad (11)$$

Taking into account the effect of surface recombination, grain boundary resistance (R'_{gb}), neck resistance (R'_n) and total resistance (R_T) obtained by adding equation 10 and 11, are simulated by MATLAB software. The effects of UV radiation and change in the rate of recombination on the operation of metal oxide gas sensors were analyzed in both the cases. In the first case the performance of a simple metal oxide sensor is simulated and the relations between absorbed gas concentration and resistance are monitored without applying UV radiation. As another case study, the same performance is monitored when UV radiation is incident on the sensor and surface recombination occurs.

Result

Figure 1 shows the variation of resistance of SnO₂ gas sensor with the concentration of adsorbed gas (N_r) in the absence any radiation flux density and without the occurrence of surface recombination phenomenon. Figure 2 shows the response of same sensor under UV radiation of flux density (8x10¹⁸m⁻²). The variation of neck resistance, grain boundary resistance and total resistance is plotted for comparison without surface recombination. Figure 3 shows, a comparative study between fig1 and 2, The more is the N_r the less is the resistance, but the value of resistance is significantly reduced when the UV radiation falls on the metal oxide film because of the occurrence of surface recombination phenomenon.

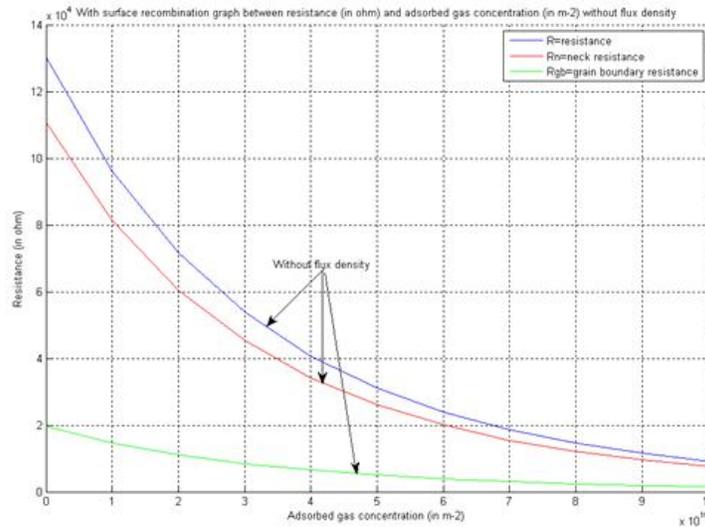


Figure 1: Variation of resistance (in ohm) and adsorbed gas concentration (in m⁻²) in the absence of UV radiation

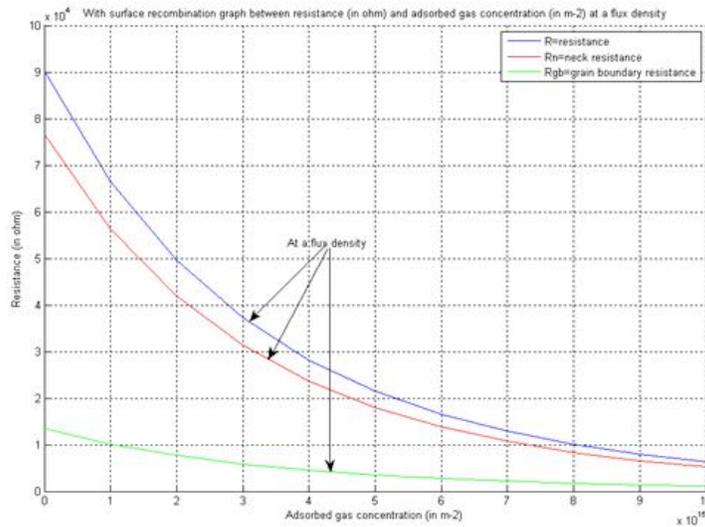


Figure 2: Variation of resistance (in ohm) and adsorbed gas concentration (in m⁻²) under UV exposure of flux density (8x10¹⁸m⁻²) with the occurrence of surface recombination.

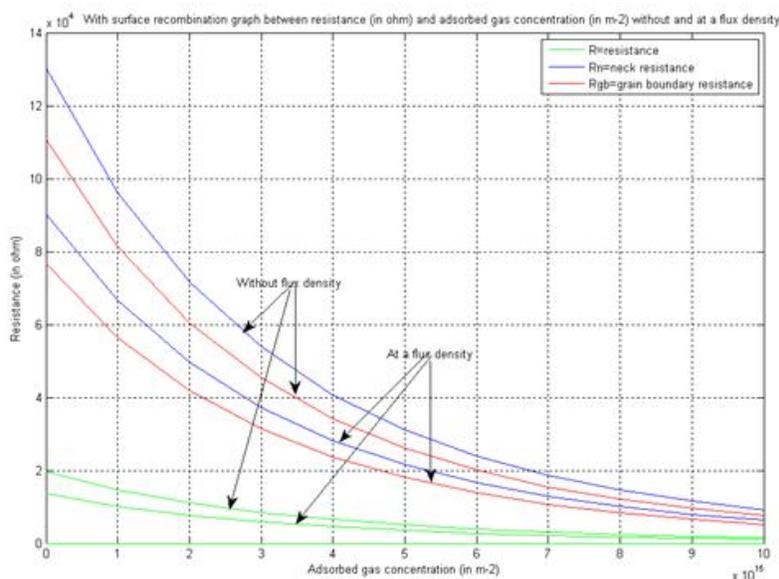


Figure 3: Variation of resistance (in ohm) and adsorbed gas concentration (in m^{-2}) without UV radiation and under UV radiation at a flux density ($8 \times 10^{18} \text{m}^{-2}$) with surface Recombination phenomenon.

Conclusion

In this paper the effect of UV radiation on the sensing mechanism of metal oxide gas sensor has been studied on the basis of theoretical assumptions. It is observed that when the gas is adsorbed on metal oxide surface in the absence of UV radiation then there is no change in the adsorbed gas concentration but the resistance is decreased due to surface recombination. Therefore, it can be concluded that UV radiation can significantly enhance the conductivity and sensitivity of a metal oxide gas sensor even at room temperature. The sensitivity is also found to be increased with increasing UV radiation flux density and decreased with increasing in grain size. Based on above studies it can be concluded that metal oxide based gas sensor (SnO_2) can be used in those areas where the high temperature limits the use of sensors and this widens its range of application.

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