Relationship of the electric potential inside the nano crystallite with the chemisorbed gas molecules at metal oxide semiconductor surface and its effect on gas sensor response

Anil Kumar\textsuperscript{a}, Ravi Kumar\textsuperscript{a}, Rakesh Singh\textsuperscript{a}, B.Prasad\textsuperscript{a}, Dinesh Kumar\textsuperscript{a,b}, Mukesh Kumar\textsuperscript{a}

\textsuperscript{a}Electronic Science Department, Kurukshetra University, Kurukshetra, 136119, India
\textsuperscript{b}J. C. Bose University of Science and Technology, YMCA, Faridabad, India

Corresponding Author: anilgurjar84@gmail.com

Abstract. The metal oxide semiconductors surface exhibit great gas sensing response when the size of the grains becomes much smaller i.e. in the range of debye length. In the presented study, the effect of crystal size and surface states has been studied on gas sensing properties for cylindrical shaped nanostructures of metal oxide semiconductors. To calculate the grain potential Poisson’s equation coupled with electroneutrality condition in cylindrical shaped nanostructures has been solved. The shape of the potential profile inside the nanograins has been calculated as a function of available surface states, surface temperature and occupied surface states. Eventually, the sensitivity of the gas sensor has been simulated and compared for different sizes of nanocrystals.

1. Introduction

Metal oxide semiconductors (MOX) based chemo resistive gas sensors were among the first materials which were studied vastly and have been used commercially for gas sensing applications. [1-3]. These materials are quite popular and highly used because of the easy fabrication processes and very well explained gas sensing mechanisms [3, 4]. Also, the possibility to change the conductivity by doping, capabilities to sense a large group of gases and chemical compounds and of course the cheaper implementation cost are the add-ons in the popularity of MOX materials [3].

Wolkenstein’s approach to studying the adsorption of gas adsorbents on the gas sensor surface considers the physical as well as chemical adsorption. Physical adsorption is considered as weak adsorption bound with generally weak Van Der Walls forces of attraction whereas the chemical adsorption has large binding energy and is bound with the strong forces due to charge sharing with the sensor surface [5-7]. The primary mechanism for the gas sensing by the Metal oxide gas sensor surface is the interaction between the adsorbed oxygen molecules and the target gas molecules. Chemical adsorption of environmental oxygen as a function of the partial pressure of gas and energy ban bending has been studied in detail [8-9]. Also, crystallite size is one of the most critical parameters which is responsible for affecting the gas sensitivity in MOX based gas sensors [10]. Net effective carrier concentration inside the grain is a function of the potential (ϕ) and the width of the depletion region (X0) formed at sensor surface due to removal of electrons from the conduction band of the semiconductor by adsorbed oxygen [11]. It has been reported in the literature that gas sensitivity increases significantly when the crystallite size becomes smaller than the X0 [12]. A theoretical model has been suggested to demonstrate the effect of grain size on gas sensitivity [13]. Although, this model is more quantitative still it clears the doubts about the significant rise in gas sensitivity after a critical reduction in size. This model describes three possible cases of grain size relative to the width of depletion region X0 as shown in fig. 1.a. When the size (Diameter; D) of the crystallite is quite larger than X0 i.e. D >>2 X0, in this case there exist a thin surface charge layer at the sensor surface due to removal of free electrons.
from the conduction band of the material. Now, if the grain size is decreased further till the grain size becomes comparable to depletion region width i.e. \( D \geq 2X_0 \) (fig. 1.b). In this situation, the depletion region width increases towards the centre of the crystallite. These two events are considered the case of partial depletion as shown in fig. 2. Beyond the depletion region till the centre of the spherical grain, the bulk is still neutral and its radius is represented by \( R_0 \). The total potential in the grain exists at the surface only. This potential is denoted by the surface potential \( V_s \). So, a barrier develops between the sensor surface and the oxygen gas adsorbates.

Fig.1. Conduction mechanism in SnO\(_2\) sensing film; (a) when \( D \gg 2X_0 \), the conduction will be controlled by the boundaries of neighbouring grains (b) When \( D \geq 2X_0 \), the electrical conduction will be through the necks of the grains and (c) When \( D < 2X_0 \), the conduction will be through the grain volume; as there will be no barrier between grain boundaries [12].

In the third case, for a further decrease in the grain size so that \( D < 2X_0 \), depletion region will expand rigorously towards the centre of the grain as a large number of electrons are captured by the oxygen gas atoms at the surface. Eventually, the whole volume of the grain is depleted of the free electrons and the grain is fully depleted. It has been shown by fig. 1 (c). In spite of the lesser conductivity in full depletion case, the sensitivity is remarkably high [12]. A comprehensive numerical study has been carried out in the presented work for a better understanding of the role of grain size in cylindrical shaped metal-oxide based gas sensors.

2. Case I: Partial depletion (Cylindrical Shape)

In this model following assumption are considered for n-type SnO\(_2\) material:

1. The energy level (\( E_{SS} \)) created below the fermi level is solely because of the chemisorption mechanism at surface of n-type SnO\(_2\) material. The effect of dangling bonds, defects and other surface irregularities/impurities have been neglected.
2. The semiconductor is homogeneously doped.
3. Environmental oxygen is chemisorbed in dissociated form at the sensor surface at the available trap centres.

The parameters considered for the numerical solutions are as follows:

- Band gap \( (E_g) \approx 3.6 \) eV, Induced energy level w.r.t to fermi level = -1.21 eV, doping concentration \( (N_D) = 10^{24} \text{ m}^{-2} \), Dielectric constant of SnO\(_2\) = 12, Debye length = 21.8 nm.
If deposited sensing film consists of nano structured grain of cylindrical shape (i.e. nano rods, nanowires) and grain size is such that the whole volume of the grain is not depleted i.e. the case of partial depletion. This condition can be understood analytically as $qN_T[O^-] < qRN_D$, where $N_T[O^+]$ is the density of surface states occupied by negatively charged oxygen atoms. The potential developed inside the grain can be given by the Poisson’s equation in cylindrical co-ordinates in the following form [15]:

$$\nabla^2 \phi(r) = \frac{d^2 \phi(r)}{dr^2} + \frac{1}{r} \frac{d \phi(r)}{dr} = -\frac{\rho(r)}{\epsilon}$$

(1)

Where $\phi$ is the potential inside the grain, $r$ is the distance from the centre of grain at any given point, $\rho$ is total charge density and $\epsilon$ is the permittivity of the semiconductor.

Total charge inside the depletion region can be expressed as:

$$\rho = \frac{2qN_D}{\epsilon}$$

(2)

$q$ is the electronic charge and $N_D$ is the doping concentration. Equation (1) can be presented in form of barrier height $|qV_S|$ as:

$$\frac{d^2 V_S(r)}{dr^2} + \frac{1}{r} \frac{d V_S(r)}{dr} = \frac{2qN_D}{\epsilon}$$

(3)

Solution of barrier voltage $V_S$ is obtained after integrating equation (3). In case of partial depletion approximation one of the boundary condition for this solution is that potential vanishes; i.e. $V_S = 0$ at $r \leq R_0$ as shown in fig. 2.

Another boundary condition is that $\frac{dV_S}{dr} = 0$ at $r \leq R_0$. Applying these boundary conditions, we get the following solution:

$$V_S(r) = \frac{qN_D}{\epsilon} \left[ \frac{1}{2} \left( r^2 - R_0^2 \right) - R_0^2 \log \left( \frac{r}{R_0} \right) \right]$$

(4)

The barrier height between grains is directly dependent upon the amount of oxygen adsorbed ($N_T[O^+]$) with the available surface state density $N_T$ at the surface. So, to establish a relationship between barrier height and occupied surface states; equation (4) must be written as a function of $N_T [O^+]$. From the electro neutrality condition of space charge region, we know that electrons removed from conduction band must be equal to the electrons trapped by adsorbed oxygen atoms. Thus:

$$2qN_D A_1 = qN_T A_2$$

(5)

Where $A_1$ is the volume of cylindrical grain and $A_2$ is the surface area of the cylinder. Equation (5) becomes as:

Fig. 2. Partial depletion in sensor grain; $R$ is the radius of grain, $R_0$ is the radius of neutral region and $X_0$ is the width of depletion region in a spherical grain. $E_c^s$ and $E_c^b$ are the energy level of conduction band edge at the surface and in the bulk respectively.
\[ 2qN_D \pi \left( R^2 - R_0^2 \right) h = qN_T \left[ O - \frac{hN_T}{N_D} \right] 2\pi R \left( \frac{R}{2} + h \right) \]

(6)

Where \( N_D \) = doping concentration
\( R \) = Radius of the cylindrical nano grain
\( R - R_0 \) = radius of depletion or space charge region as shown in fig. 2.
\( h \) = Height of nanostructured cylindrical grain

\( R_0 \) can be obtained from equation (6) as a function of \( N_T [O] \):

\[ R_0 = \left[ R^2 \left( 1 - \frac{N_T [O]}{2N_D} \right) + R \left( \frac{hN_T [O]}{N_D} \right) \right]^{\frac{1}{2}} \]

(7)

Using value of \( R_0 \) from equation (7) in equation (4), we obtain potential barrier voltage \( V_s \) as a function of \( N_T [O] \):

\[ V_s (r) = \frac{qN_T}{e} \left[ R^2 \left( 1 - \frac{N_T [O]}{2N_D} \right) + R \left( \frac{hN_T [O]}{N_D} \right) \right] \left[ R^2 \left( 1 - \frac{N_T [O]}{2N_D} \right) + R \left( \frac{hN_T [O]}{N_D} \right) \right] \log \left( \frac{r}{R^2 \left( 1 - \frac{N_T [O]}{2N_D} \right) + R \left( \frac{hN_T [O]}{N_D} \right) \right] \left[ R^2 \left( 1 - \frac{N_T [O]}{2N_D} \right) + R \left( \frac{hN_T [O]}{N_D} \right) \right] \right) \]

(8)

In \( \text{SnO}_2 \) based gas sensor bigger grains will require more energy for the transfer of mobile electrons between the neighbouring grains. After the exposure of a reducing gas like CO at the sensor surface, interaction of CO and \( \text{O}_2 \) will result into a free electron shown in following equation:

\[ \text{CO}_{(\text{gas})} + \text{O}^\cdot_{(s)} \xrightarrow{k_{CO}} \text{CO}_2(\text{gas}) + e^- \]

Fig. 3. Relationship of Normalized surface potential and grain size in case of partial depletion of cylindrical nano grains.

As shown in fig. 3, the normalized surface potential increases with the increase in grain size. Greater is the value of potential barrier on the sensor surface, lesser will be the concentration of electron trapping at sensor surface and eventually the sensor response will decrease with increase in grain size. It has been shown in fig. 4 that the sensor response will be higher for shorter grains.
3. Case II: full depletion (Cylindrical Shape)

The condition of full depletion can be achieved if all the mobile electrons in the grain volume has been trapped at sensor surface. This case can be expressed analytically as:

\[ qN_{r}[O^+] = qRN_o \]  

Equation (8) can be modified for full depletion as:

\[
V_s(r) = \frac{qN_o}{\varepsilon} \left[ \frac{1}{2} \left( r^2 - \left( R^2 \left( 1 - \frac{R}{2} \right) + R^2 h \right) \right) - \left( R^2 \left( 1 - \frac{R}{2} \right) + R^2 h \right) \log \left( \frac{r}{R^2 \left( 1 - \frac{R}{2} \right) + R^2 h} \right) \right] 
\]  

Normalized potential inside grain can be derived as a function of \( V_s \) as:

\[
\phi(r) = -\frac{qV_s(r)}{kT} 
\]

Where; \( k \) = Boltzmann constant, \( T \) = Temperature of the sensor surface.

In case of full depletion of grain volume, the electrical conduction will take place through the grain volume and will be a function of total carrier concentration inside the grain.

\[ n_{\text{total}}(r), \text{ total Carrier concentration in a crystallite grain can be written as a function of Normalized potential } \phi(R) \text{ at surface i.e. for } r = R \text{ is given as:} \]

\[
n_{\text{total}}(R) = \frac{1}{\pi R^2 h} \int_0^{R^2 h} N_o \exp(-\phi(R)) dR
\]

To calculate the total carrier concentration as a function of doping density and the potential inside the grain volume, Electroneutrality condition has been solved to get \( \phi_0 \). Left Hand Side (LHS)

Fig. 4. Normalized sensor response of partial depleted nano grains.
term in this condition gives the total charge appeared after removal of the free electrons from the grain. Right Hand Side (RHS) presents the charge at the surface due to acceptance of electrons by chemisorbed oxygen. \(N_T\) is the available surface density for oxygen adsorption. After the interaction of oxygen gas with sensor surface, some of these surface states will be occupied. The surface state density which has been occupied by negatively charged oxygen atom is denoted by \(N_T[O^-]\). \(N_T[O^-]\) is a function of \(N_T\) and \(E_{SS}\). Where, \(E_{SS}\) is the corresponding energy level created by the chemisorption of oxygen gas at surface.

Fig. 5. Solution of Electroneutrality condition given by equation (4). The intersection of two shown curves represents the optimum solution for the grain potential \(\phi\), where \(\phi\) is related to surface barrier potential \(V_s\) as \(\phi = V_s / K T\).

Fig. 6. Relationship of total carrier concentration with the available surface state density as a function of grain size.

The relationship between the total carrier concentration inside the grain volume with the available surface state density as a function of grain sizes has been depicted in figure 6. It is clear that at a critical value of surface state density the carrier concentration decreases and then becomes saturate. The significance of this phenomenon lies in the fact that a specific value of surface states available for oxygen gas adsorption affects the sensing mechanism. It is also clear from fig. 6 that the value of critical surface density increases as the grain size increases. The simulated sensor response for full depletion case for cylindrical nano grains has been shown in fig. 7. The behaviour of sensor response in in good accordance with the experimental data [13, 16].
Fig. 7. Sensor response of cylindrical shaped nano grains as a function of grain size.

4. Conclusion

The effect of grain potential and surface states on the gas sensing response of SnO$_2$ metal semiconductor has been studied. The cylindrical shapes of the grains have been considered to simulate the sensor response. The effect of shapes (cylindrical) on barrier potential height $|qV_S|$, normalized potential $\phi$ inside the grain has been studied. Full depletion approximation was considered to present an extensive numerical study. Role of the density of surface states and surface preparation are very crucial while selecting the gas sensing material. Mathematical model for approximate analytical and numerical solution of Poisson’s equation along with the charge neutrality condition has been presented. It has shown that smaller nanostructured grains comparable with the twice of depletion width, could results into better gas sensing alternate. Presented model is general in nature which can be extended for both oxidizing and reducing gases and for p-type semiconductor model with necessary modifications.

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