



GAS DETECTION SENSITIVITY AND CLUSTER SIZE

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Abstract—*A theoretical investigation of the dependence of gas sensitivity of nanostructured semiconductor gas sensors on cluster size is presented. The clusters are represented as spheres and the adsorbed gas as a surface state density. The sensitivity is calculated as a change in conductivity over a change of surface state density. The results show that there is a critical cluster size, which is material dependent, at which the sensitivity is maximal. The cluster size for maximum sensitivity of several metal oxide gas sensors of practical interest, such as ZnO, SnO₂, TiO₂ and In₂O₃, is predicted and discussed. ©1999 Acta Metallurgica Inc.*

1. INTRODUCTION

Solid state gas sensors are widely used today in a variety of domestic and industrial applications because they combine high sensitivity with low cost and easy interface electronics. The main problem with this kind of sensors is their poor selectivity, which is due mainly to the nature of chemisorption phenomena. In order to improve the selectivity, the sensitivity for the detection of specific gases should be selectively improved. A number of techniques have been recently developed such as the dispersion of small amounts of noble metals in the sensor's surface which act as activators (1), the use of metal-insulator-semiconductor devices (2), of the thermoelectric effect (3) and of neural networks for gas recognition (4).

In recent years however, a novel impetus has been introduced into this field with the advent of nanostructured gas sensors, the sensitivity of which is expected to increase significantly with decreasing constituent cluster size (5,6). However it has been difficult to quantify experimentally the dependence of sensitivity on cluster size (6).

The purpose of the present study is to investigate theoretically whether and to what extent the gas detection sensitivity of nanostructured semiconductor sensors depends on the size of the clusters. Thus, a theoretical model is developed in which clusters are represented as semiconductor spheres and the current between the clusters is calculated, taking into account both the thermal emission and tunneling of carriers. A surface state density represents the chemically adsorbed gas. The depletion width is calculated based on the abrupt junction model (7) and considering a uniform distribution of surface states over the semiconductor energy gap. Finally, the sensitivity is

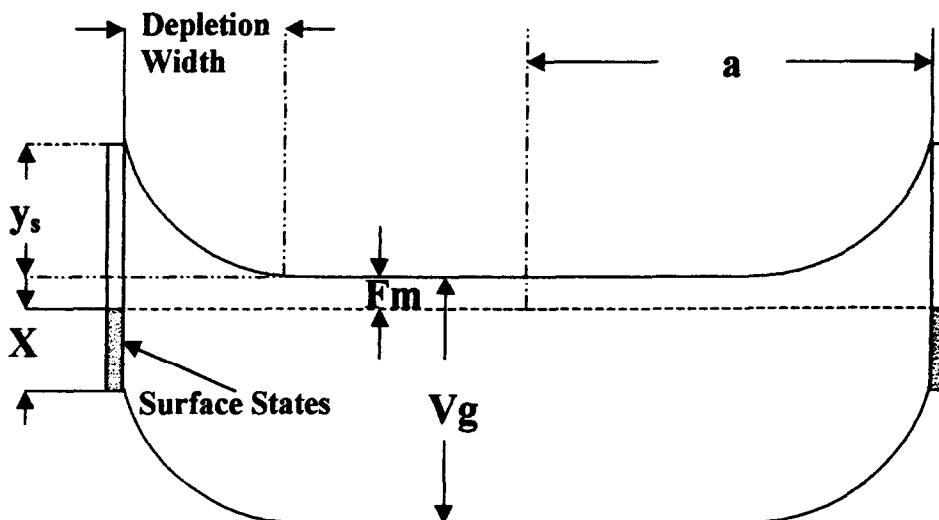


Figure 1. The energy band diagram of an n-type semiconductor spherical grain in depletion.

calculated taking the derivative of the logarithm of the conductivity over the surface state density (8).

2. THEORETICAL CALCULATIONS

Chemical adsorption of ambient constituents can have a dominant effect on the electrical properties of a variety of substrates used in microelectronics. The most common model used to account qualitatively for this effect considers the fact that strong adsorption of particles involves charge transfer of conduction electrons to or from the solid corresponding to a donor or acceptor type of adsorption (9,10). Moreover, in the case of metal oxides, the presence of oxygen or reducing gases in the environment, cause a very pronounced change of electrical conductivity. This cannot be explained solely by the change of the concentration of conduction electrons, but one must consider the Schottky potential barriers at the cluster boundaries, caused by the acceptor or donor type of adsorbates, which control the flow of electrons between the clusters (10).

Figure 1 shows the band diagram of an n-type semiconductor metal oxide in depletion. The basic parameters are the bandgap V_g of the semiconductor, the distance of the Fermi level from the conduction band F_m , the bending of the surface y_s , the surface state density N_0 (N_0 states over unit area and energy) and the distance X of the Fermi level from the valence band. The following calculations will be performed in the case of a n-type semiconductor without loss of generality. The Poisson equation for the conduction band in spherical coordinates and in the depletion region (assuming spherical symmetry) gives:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dy}{dr} \right) = \frac{qn_o}{\epsilon_s} \quad [1]$$

where r is the distance from center, y is the conduction band bending, q is the electron charge, n_o is the concentration of electrons in flat band condition and ϵ_s is the dielectric constant of the semiconductor. Equation 1 can be written in dimensionless form:

$$\frac{1}{p^2} \frac{d}{dp} \left(p^2 \frac{dy}{dp} \right) = 1 \quad [2]$$

where $p = \lambda r$ and $\lambda^2 = qn_o/\epsilon_s$. Solutions of equation 2 are of the general form:

$$y = \frac{1}{6} p^2 + \frac{c}{p} + d \quad [3]$$

where c, d are constants. The following two cases are distinguished:

a. The depletion width is smaller than the cluster radius α . Then, the solution for y is:

$$y = \frac{1}{6} p^2 + \frac{1}{3} \frac{\lambda^3 W^3}{p} - \frac{1}{2} \lambda^2 W^2 \quad [4]$$

where $(\alpha - W)$ is the depletion width. The charge conservation law gives

$$4\pi a^2 q N_o q X = \frac{4}{3} \pi a^3 q n_o \left(1 - \frac{W^3}{a^3} \right) \quad [5]$$

where X is the distance of Fermi level from the valence band as it is shown in Figure 1 and is equal to $V_g - F_m - y_s$. The left-side term of equation 5 is the charge transferred in the surface states and the right-side term is the charge of the cluster. The bending of the conduction band at surface y_s is calculated by setting $p = \lambda \alpha$ in equation 4. Then, replacing in equation 5, we get

$$u^2 \left\{ \left(\frac{\lambda^2 a^2}{3} - \frac{n_o a}{3 N_o} \right) u - \frac{\lambda^2 a^2}{2} \right\} = (V_g - F_m) - \frac{\lambda^2 a^2}{6} - \frac{n_o a}{3 q N_o} \quad [6]$$

where u is a dimensionless parameter taking values from 0 to 1 and is equal to W/α . The sensitivity now can be expressed as the derivative of the logarithm of the conductivity over the surface state density. Assuming exponential dependence of conductivity on the surface barrier height y_s , we get

$$S = \beta \lambda^2 a^2 u (1 - u) \frac{du}{dN_o} \quad [7]$$

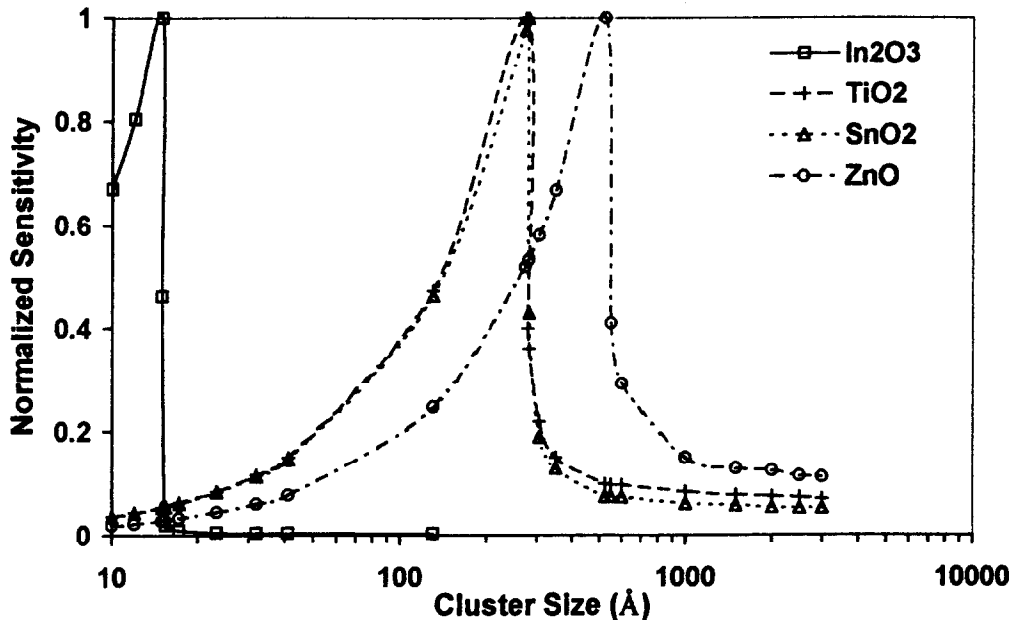


Figure 2. The theoretical calculated sensitivity-versus-grain size for as ZnO (circles), SnO₂ (triangles), TiO₂ (crosses) and In₂O₃ (squares) at 500°K.

where S is the sensitivity and $\beta=q/kT$. Calculating du/dN_o from equation 6 and replacing in equation 7, we find

$$S = \beta \lambda^2 a^2 \frac{n_o a}{3qN_o^2} \frac{u(1-u)(1-u^3)}{\lambda^2 a^2 u(1-u) + \frac{n_o a}{qN_o} u^2} \quad [8]$$

where u is arithmetically calculated from equation 6.

b. Consider now the case of deep depletion. Then, the constant c in equation 3 is zero. Following the same steps we find for the sensitivity

$$S = \frac{\beta}{q} \frac{n_o a}{3N_o^2} \quad [9]$$

The two expressions for sensitivity give the same result in the case that $u=0$, as it should. Although the sensitivity increases with increasing cluster size in the case of deep depletion, it decreases with increasing cluster size in the case where the depletion width is smaller than the cluster radius. This effect gives a maximum in the sensitivity, which corresponds to a critical cluster radius

$$a_{\max} = \sqrt{\frac{n_o^2}{q^2 \lambda^4 N_o^2} + 6 \frac{V_g - F_m}{\lambda^2} - \frac{n_o}{q \lambda^2 N_o}} \quad [10]$$

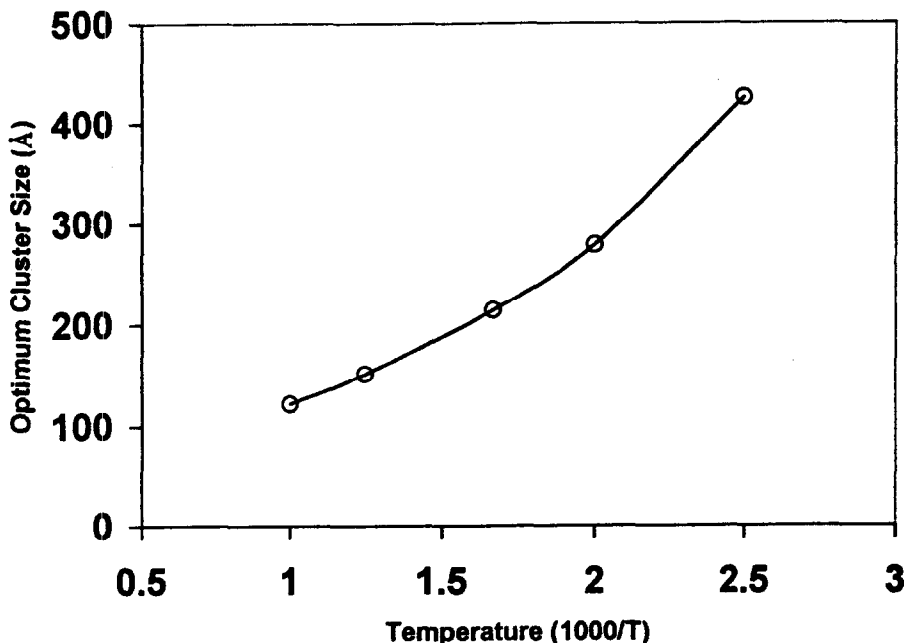


Figure 3. The cluster size at which the maximum of sensitivity occurs versus temperature, in the case of SnO_2 .

as it can be found from equation 8 and 9. Taking into account that the product $q(V_g - F_m) \cdot N_o$ can be approximated by the Weitz limit (11) and evaluating the Taylor expansion of equation 10, we find

$$a_{\max} \approx \frac{10^{15}}{n_o} \quad [11]$$

as an estimation for the critical size.

3. RESULTS AND DISCUSSION

Figure 2 shows the results obtained for ZnO (12), TiO_2 (13), SnO_2 (10) and In_2O_3 (14). The calculations have been performed at 500°K and the sensitivity is normalized to the maximum. The point at which the maximum occurs depends mainly on carrier concentration and also on the energy gap of the semiconductor. In the case of ZnO and SnO_2 , which have almost the same carrier concentration, the small differences are caused by the differences in the energy gap. For very small cluster size, the sensitivity increases linearly with increasing cluster size up to the maximum. In this case, there is full depletion of carriers, which have moved to surface states. The charge conservation produces an offset to the conduction band, while the slope of the conduction band remains unchanged. Changes in surface state density are followed now by changes in this offset.

A change ΔX in this offset, which is followed by the same change in conduction band-surface bending, produces a change ΔN_o in occupied surface states. Because the total number of occupied surface states remains the same (and is equal to the total free electrons), the equation $\Delta X \cdot N_o = X \cdot \Delta N_o$ must hold (Figure 1). Thus, for the same change ΔN_o in surface state density, the conduction band bending is proportional to X (Figure 1), that is in the case of larger clusters. Therefore, the sensitivity is increased with increasing cluster size.

For cluster sizes larger than the critical size, the depletion width is smaller than the cluster radius. Moreover, since the number of surface states is proportional to the second power of the cluster radius, while the number of carriers is proportional to the third power of the radius, the percentage of trapped carriers is decreased with increasing cluster size. This of course leads to a decreasing sensitivity with increasing cluster size.

Figure 3 shows the size at which the maximum is located for tin oxide versus temperature. This size is decreased with increasing temperature because the carrier concentration is increased. Thus, the operation temperature of a gas sensor is critical for the optimum cluster size. Since the operation temperature depends mainly on the specific application of the sensor (for example in the case of tin oxide sensors, if the gas of interest is CO one has to heat the sensor to 300°C, but if methane is of interest, one has to move to 400°C due to different chemical activities of the two gases (15)), the optimum cluster size is closely related to the gas of interest.

Finally, consider the case that small amounts of noble metals, such as Pd and Pt, are dispersed as activators on semiconductor gas sensors. Beyond the spillover of adsorbates, there is an electronic interaction between these additives and the sensor (8). In this case, the active cluster size is smaller than the geometric one, leading to an increase in sensitivity for large clusters which is proportional to the metal work function, as it has been demonstrated in ref. 8. On the other hand, the well known drift in sensitivity observed often in the case of metal oxide gas sensors and has been assigned mainly to the change in the degree of oxidation (9), can be explained by considering the change of carrier concentration by the change of oxygen vacancies which are the main electron donors. Thermal annealing of such sensors stabilizes their response by saturating the oxidation process and thus fixing the carrier concentration.

4. CONCLUSIONS

Theoretical calculations for the dependence of sensitivity of semiconductor gas sensors on cluster size have shown that there is an optimum cluster size at which the sensitivity is maximal. This cluster size depends mainly on free carrier concentration, and thus on temperature too. Moreover, in the case of metal oxide gas sensors, this optimum size depends also on the degree of oxidation, the existence of additives and poisoning of the surface parameters, which are well known to control the carrier concentration. The identified turning-point dependence of sensitivity on cluster size renders the present theoretical predictions easily amenable to experimental verification.

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