Sensors and Actuators B 176 (2013) 217–224

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Conduction model of coupled domination by bias and neck for porous films as gas sensor

Li Yang [a], Shunping Zhang [a], Huayao Li [a], Guozhu Zhang [a], Chengyong Zhan [a], Changsheng Xie [a,b,*]

[a] State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, China
[b] Nanomaterials and Smart Sensors Research Laboratory, Department of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 12 March 2012
Received in revised form 17 July 2012
Accepted 3 September 2012
Available online 8 September 2012

Keywords:
Conduction model
Coupled domination
Valve effect
Porous film
Gas sensor

ABSTRACT

A conduction model valid for porous films was proposed in the condition that the transport behavior of the carriers was controlled by the coupled dominant mechanism with the existence of the bias and necks in the grain boundary. The characteristics of the necks can be described accurately by two important morphological parameters: the average neck width $\bar{W}_n$ and the average density of neck in the unit area $\bar{P}_n$. Both parameters were controlled by different sintering temperatures, and further optimized by statistical calculations based on the observations of the stereology derived from the FE-SEM images. The basic physical parameters: the barrier potential V_B and the depletion width W_n, were acquired by multi-parameter fitting based on *I–V* curves measured in dry air and methanol atmosphere. In this article, to elucidate the rationality of the conduction model, zinc oxide served as the sensitive porous layer, and *I–t* characteristics were evaluated. By using the physical parameters in conduction model, the *valve effect* was proposed to illustrate the diversity of response to methanol for ZnO porous films fabricated at different sintering temperatures. The valve control coefficient *Y* reveals the fact that only a suitable neck width has dominating contribution to the gas response.

1. Introduction

Metal oxide semiconductors (MOS) are widely applied in gas sensors, presumably because their advantages can be summarized as: good universal respond to volatile organic compounds, simple signal processing, low cost and small size [1–6]. In recent decades, a solid foundation has been laid about the sensitivity and selectivity due to the fact that a lot of work and efforts were invested on the basis of phenomenological level, while the controversy about gas sensitive mechanism of MOS still exists at present [7–9]. In general, the "pre-adsorptive oxygen ionization" model about the gas sensing mechanism is widely accepted, which generally includes two main stages: oxidizing gases in ambient atmosphere are adsorbed on the surfaces of the MOS as ions, and then reducing gases are sensed based on their reaction with the pre-adsorbed oxygen ions. The process of gas sensing is accompanied with electronic transfer of delocalized conduction-band electrons to localized surface states and vice versa [9–16]. In general, the information about the phenomenological level in the gas sensor field is described by electrical signals via the definition of relative resistance (*R*) or conductance (*G*) change when MOS is exposed to different atmospheres. However, the change of the *R* or the *G* value is directly determined by the carrier transport mechanism in sensitive materials. Therefore, a practical conduction model seems like a bridge to connect the gap between phenomenological appearance performances and sensitive mechanism.

To date, various attempts were made to yield insight into the conduction model for gas sensing materials. Taken as a whole, the curve fitting method was widely adopted to describe the conductive behavior, and to further extract the key physical parameters (e.g., grain boundary barrier V_B and depletion region width W_D) [17–20]. To our knowledge, some interesting conduction models were reported with their own emphases and styles. Moos and his research team dealing with the morphology, such as the grain sizes and neck radii, dependence of metal oxide materials with space charge regions by used the finite element method for the numerical calculation [17]. Barsan and his coworkers presented a comprehensive frame model to describe conductive behaviors of carriers for MOS [12]. In the process of conduction in grain boundary, some key contributing factors are distinguished in this model, such as the density (compact or porous films), the thickness (thick or thin films) and the relative grain diameter in comparison to its depletion layer width [12]. In other words, the conduction mechanism in polycrystalline MOS strongly depends on the

* Corresponding author at: State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, China. Tel.: +86 27 87556544; fax: +86 27 87543776.
E-mail address: csxie@mail.hust.edu.cn (C. Xie).

0925-4005/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2012.09.008

morphology of the layer and the grain size of the metal oxides. Similar to aforementioned work, some other researchers also emphasized the limitation effect, which results from the geometrical microstructural parameters of the neck between adjacent grains in the process of carrier transport [20–23]. However, the relationship between the material performance and sintering neck has yet to be qualitatively described.

In addition, Varpula group extended grain boundary barrier limited conduction model when the bias voltage applied in grain boundary. The crucial basic physical parameter (V_{B0}) was obtained by the method of multiparameter fitting based on current–voltage (I–V) characteristics [24–26]. Nevertheless, for the porous sensing layer, the best way to describe the conduction process is to consider that the free charge carriers must overcome the grain boundary barriers, which is originated from the energy band bending at the surfaces of neighboring grains (see Fig. 1a) [12,27]. Therefore, the real situation of contacting between adjacent grains is necessary to receive adequate attention during the derivation of conduction model. For porous sensitive materials, the response would be influenced by the typical microstructural pattern with the porosity and necks since the carriers transport behaviors are limited. In fact, the porosity and neck can be described accurately by utilizing two morphological parameters: the average neck width W_n and the density of neck in unit area P_n. In a sense, W_n and P_n indicate that the proper physical meaning: the possibility of electrons flowing through the grain boundary, and the amount of conductive channels, respectively. For this reason, it is important for a practical conduction model to consider the impact on W_n and P_n in porous materials. In the present paper, a practical conduction model has been proposed, which is to describe the behaviors of carriers transport in the grain boundary, and further to investigate the gas sensing process. By using the conduction model for reference, and taking the real morphology feature of adjacent grains into consideration, a revised conduction model was derived by introducing two geometric microstructural parameters: W_n and P_n [26]. And thus the revised conduction model may illustrate the real situation of conduction in a porous sensing layer more convincing. In our work, zinc oxide (ZnO) porous films acted as the sensitive layers. The W_n and P_n were obtained statistically from field emission scanning electron microscope (FE-SEM) images. Besides, the electrical current–time (I–t) characteristics and I–V curves were acquired when the sensing layers were exposed to 300 ppm methanol, and then the barrier potential V_B was extracted by using multiparameter fitting from I–V curve measurements.

2. Derivation of conduction model for porous films

In general, for gas sensors based on n-type MOS, the conductive mode of the sensitive layer is crucial for the magnitude of the sensor signal [22]. The grain boundary contact consisting of the depletion layer is usually higher resistance than the bulk. The total conductance of a porous material is then determined by the transport path through the structural difference, which is always treated as an equivalent circuit with the low resistance of bulk grain in series with the high resistance of grain boundary contacts [9,12,28]. Especially the conductive mode may be controlled by necks and lead to lower potential barrier heights between grain boundaries for porous films. Naturally, the better results will be achieved if one is using thick porous films, because the carriers will pass through from one grain to the other by overcoming lower symmetric double Schottky barrier in grain boundary (see, Fig. 1a), leaving the result that the maximum impact of the surface changes onto the concentration of free charge carriers. This conceptually simple model has found a wide acceptance for the description of the transport properties in polycrystalline semiconductors [29]. In this work, only static and equilibrium state was discussed. Herein, the description of grain boundary potential was generally classified into two cases:

Case 1. *Symmetric back-to-back double Schottky barrier.* As depicted in Fig. 1a, the depletion width on both sides of the barrier is equal and meets a simple formula: $W_D = 2W_1$. If one assumes the Schottky approximation to be valid, *id est.* that all the electrons from the depletion layer are captured on surface levels, the electric field E and grain boundary potential V_B can be solved from the Poisson equation combined with the electroneutrality condition [12,28].

$$V_B = \frac{qN_B^2}{8\varepsilon N_d} \tag{1}$$

where N_B, N_d, ε represent for grain boundary charge density per unit area, donor density per unit volume and permittivity of sensing films, respectively. Based on Eq. (1) and the electroneutrality condition [34], the whole depletion width W_D can be estimated in Eq. (2).

$$W_D = 2\left[\frac{2\varepsilon V_B}{qN_d}\right]^{1/2} \tag{2}$$

where q is the magnitude of electronic charge.

Case 2. *Asymmetric Schottky barrier.* As shown in Fig. 1b, the depletion width on both sides of grain boundary is unequal, i.e. $W_1 \neq W_2$, when the bias voltage applied in the grain boundary, whereas the whole width of the depletion layer keeps invariant [26]. In addition, the energy band bending in grain boundary regions obeys the formula: $U_{\text{bias}} = V_1 - V_2$. Noticing that the Schottky approximation is used to deal with the density of electron which locates in depletion region, the electrical current density J passing through the grain boundary in one dimension obeys Eq. (3) in light of the classical drift-diffusion theory.

$$J = qD\frac{dn(x)}{d(x)} + q\mu n(x)E(x) \tag{3}$$

where D, n, μ, E represent for the diffusion constant of an electron, the electron density in the conduction band, the mobility of electrons and the electric field, respectively. The diffusion constant D can be estimated by using the Einstein relation $qD = \mu\, k_BT$. For the moment we will work with the hypothesis that there is no generation or recombination of charge carriers in the grain boundary regions, as well as the bias applied in single grain obeys $U_s = U/N_P$, the expression of the electrical current flowing though the sensing films is given

$$I = K(V_B)^{1/2}\exp\left(-\frac{qV_B}{k_BT}\right)\quad \sinh\frac{qU}{2k_BTN_p} \tag{4}$$

where $K = S\mu(2q^3N_d^3/\varepsilon)^{1/2}$, and S, k_B, T, U, N_P represent for the effective cross sectional area of gas sensitive film, Boltzmann constant, the operation temperature of sensor, the total bias voltage applied in grain boundary and the amount of potential barriers parallel to the direction of electrical current, respectively.

However, for porous thick film sensing layer fabricated by screen printing, the real contact situation may be complicated further because of the existence of necks between neighboring grains as well as distinct porosity in the bulk of the materials. Hence, the calculating methods of effective cross sectional area in Eq. (4) may be invalid, provided that the sensing films with distinct porosity and the sintering necks. For the sake of simplicity, the sensing layer is considered as cuboids with a in length, L in breadth, b in height as well as the cross section is constituted by spherical particles with necks (see Fig. 2b and c, grain size D, neck width W_n). Furthermore, the cross section (see Fig. 2b) which is perpendicular to the direction of the electrical current has specific physical significance that