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Proposal of contact potential promoted oxide semiconductor gas sensor

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ABSTRACT

Contact between two oxide semiconductor grains different in work function (hetero-contact) is characterized by the generation of contact potential, which is sensitive to gases. The resistance of the hetero-contact is influenced by ambient gases dually, through a change in the surface density of carriers (receptor function of key grain) and through a change in drift mobility of electrons (contact potential effect), and hence not only it is more sensitive to gases than that of contact between grains of the same kind (homo-contact) but also it obeys different power laws. It is shown through explorations using device models that a novel composite oxides gas sensor making use of contact potential will be available if the two kinds of grains to be combined are selected properly and the structure the grains are packed in is designed properly. It is especially important to achieve such particular packing structure that allows hetero-contacts to be included in the main paths of electron transport.

1. Introduction

Oxide semiconductor gas sensors detect a reducing or oxidizing gas from a change in their electrical resistances. Since the pioneering works by Seiyama et al. [1] and Taguchi [2], the sensors of this group have traditionally been fabricated with a single oxide semiconductor such as SnO_2 and In_2O_3, except a few kinds of non-semiconductor materials such as alumina, silica and noble metals mixed together in practice. Usually the oxide semiconductor is synthesized into a fine powder consisting of tiny grains (crystallites) of 10–30 nm in diameter, which is then converted through ceramic processes into a porous resistor in the form of thick film, thin film or block. Endowed with excellences in sensitivity, durability, cost performance, compactness and so on, the sensors of this group have been adopted as safety devices in practice worldwide. Basic understandings of the sensors, however, have been left in the dark for a long time. For instance, it was found a long ago that sensor response to gases increases as the size of constituent oxide grains decreases (grain size effect) [3,4], but the effect could not be accounted for well by the double Schottky barrier theory advocated so far [5]. Rothschild and Komen were the first to point out its relevance with the surface area to volume ratio of the constituent grains [6], though their treatment was still empirical. Through a series of basic approaches, we recently succeeded not only in accounting for the grain size effect [7–11] but also in formulating the receptor function and transducer function separately [12]. These studies have shown that main features of the responses of a neat tin oxide sensor to gases under usual conditions can be explained fairly well by assuming the ionosorption of O^- ions, though, as found very recently, O^{2-} ions tend to form dominantly under very dry conditions [13,14].

As shown by these studies, transducer function is simple and rather formal when the device is fabricated with uniform grains, while otherwise it is affected by the contact potential appearing between non-uniform grains [12]. What is of interest in this regard is that the contact potential can possibly be utilized to promote gas response if two different groups of grains are mixed together adequately to form a composite device. This paper aims at exploring the possibility of such a contact potential-promoted gas sensor. Recently there are an increasing number of papers dealing with sensor devices fabricated with a mixture of oxide semiconductors such as SnO_2–WO_3, though the theoretical bases for forming the composites are not clear. It is believed that the present exploration will shed light on these composite devices.

2. Receptor function of a small grain

A small semiconductor grain is depleted of electrons in two steps of regional depletion followed by volume depletion with a progress of ionosorption of oxygen [8]. This is illustrated schematically for a spherical grain of radius a in Fig. 1, where O^- ions are assumed to be sole ionic adsorbates for simplicity. As shown by the energy band diagrams (top), depletion depth (w) increases in the initial stage (I) of ionosorption (regional depletion), while w extends up to the radius of grain at stage (II) (border) and then, at stage (III), the Fermi level has shifted down from the location at stage (II) by pkT while keeping the potential energy distribution profile unchanged (volume depletion). Here p stands for the extent of Fermi level shift expressed in units of thermal energy (kT) [12]. It is noted that a part

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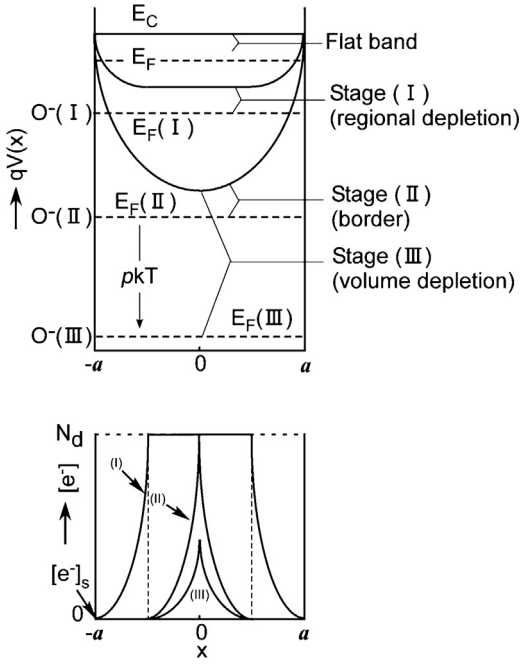

Fig. 1. Depletion of electrons for a small spherical grain (radius a) as expressed by energy band diagrams (top) and electron distributions (bottom). $qV(x)$; potential energy of electron, x; radial distance, E_C; conduction band edge, E_F; Fermi level, pkT; Fermi level shift as measure from the state (II), $[e^-]$ and $[e^-]_S$; density of electrons at x and at the surface ($x = a$).

of electrons are left behind in the depletion region, giving rise to the electron distribution tailing at each stage as shown in the bottom of Fig. 1, where N_D is the donor density of the oxide grain. The concentration of O^- ions, $[O^-]$, and the surface density of electrons, $[e^-]_S$, can be formulated for each stage of depletion [12] and are expressed for volume depletion as follows.

$$[O^-] = N_D L_D \left\{ \frac{n}{3} - A(n)\exp(-p) \right\} \quad (1)$$

$$[e^-]_S = N_D \exp\left\{ -\frac{1}{6}n^2 - p \right\} \quad (2)$$

Here L_D is Debye length for the oxide, n reduced radius defined by $n = a/L_D$, and $A(n)$ the residual electrons integral determined as a function of n.

We have now three quantities to determine, $[O^-]$, $[e^-]_S$ and p, while two equations are given above. The third equation is provided from surface chemistry. For example, let us assume that oxygen adsorption under exposure to oxygen takes place as follows.

$$O_2 + 2e^- = 2O^- \quad (3)$$

Its equilibrium can be expressed as follows.

$$(K_1 P_{O_2})^{1/2}[e^-]_S = [O^-] \quad (4)$$

K_1 and P_{O_2} are the equilibrium adsorption constant and the partial pressure of oxygen, respectively. The three quantities can now be determined uniquely by solving three simultaneous Eqs. (1), (2) and (4). Receptor function to oxygen is thus given for the volume depletion as follows [12].

$$\frac{N_D}{[e^-]_S} = c(n) + \left(\frac{3}{a}\right)(K_1 P_{O_2})^{1/2} \quad (5)$$

$$c(n) = \left(\frac{3}{n}\right)\exp\left(\frac{n^2}{6}\right)A(n) \quad (6)$$

It is worth noting that the receptor function is linear to the square root of P_{O_2}. Its slope (sensitivity) is proportional to the reciprocal of a (grain size effect). Receptor function to other gases can be formulated similarly as a function of the partial pressure of each gas. To H_2 in air, for instance, $[e^-]_S/N_D$ is shown to be approximately linear to the square root of P_{H_2} in the stage of volume depletion.

3. Electric resistances of contacts

Let us consider a case in which tiny grains as conventionally used (denoted grains 1) are mixed with other grains (denoted grains 2) different in radius, donor density, the kind of semiconductor or other properties. It is assumed for convenience that, under exposure to oxygen or other gases in air, grains 1 in isolation are in the stage of volume depletion and are more depleted of electrons than isolated grains 2; the Fermi level of grains 1 are located below that of grains 2. We can easily recognize four kinds of contacts between grains, 11, 12, 21 and 22, where 1 and 2 indicate the group each grain belongs to. It is noted that 12 and 21 are identical under non-biased condition but not identical under biased conditions, as mentioned later. Let us call the contacts between uniform grains (11 and 22) and non-uniform grains (12 and 21) homo- and hetero-contacts, respectively. Our task here is to derive the resistance of each kind of contact, denoted r_{11}, r_{12}, r_{21} or r_{22} in explicit form. To simplify the derivation, it is assumed that all contacts have the same contact geometry (area and thickness) and that isolated grains 1 and 2 have the same drift mobility of electrons (μ).

3.1. Homo-contacts

Fig. 2 illustrates how energy band structure behaves under exposure to oxygen or other target gases when free grain 1 is brought into contact with another grain 1. When isolated, each grain responds to the target gas exactly in the same manner, exhibiting the same Fermi level shift (p) or work function ($q\phi$), where q is the elementary charge of proton. As already mentioned, receptor function is determined uniquely once the gaseous condition is given; to oxygen in inert gas, for instance, it is given by (5) when only O^- ions are formed. Nothing particular happens in the energy band diagram on contacting the grains. It is shown that conductance of contact 11 is proportional to $[e^-]_S$ so that contact

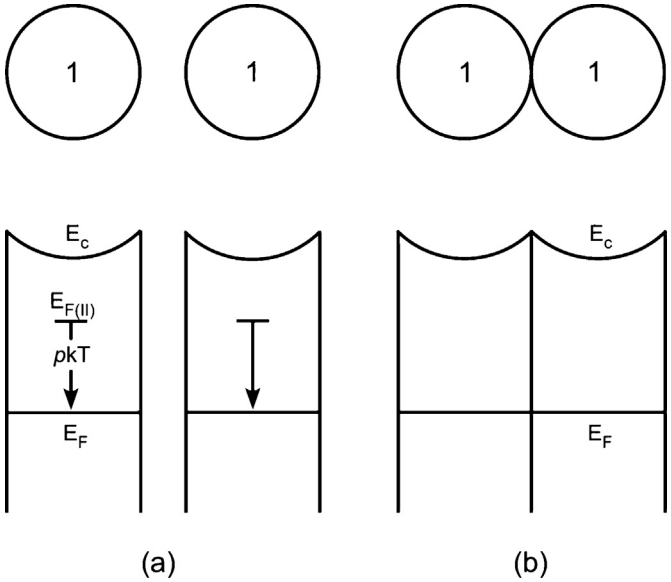

Fig. 2. Energy band diagrams of two identical grains in isolation (a) and in contact (homo-contact) (b).