DOI 10.5162/IMCS2012/7.3.5

Proposal of Contact Potential Promoted Oxide Semiconductor Gas sensors

Noboru Yamazoe and Kengo Shimanoe
Kyushu University, 6-1, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan
Corresponding e-mail address (yamazoe@mm.kyushu-u.ac.jp)

Abstract:
Contact potential is generated always when an oxide semiconductor grain is contacted with another with different work function (hetero-contact). A novel type oxide semiconductor gas sensor making use of contact potential is obtained when grains of an oxide semiconductor (sensing oxide) are packed with grains of another (highly doped oxide or metal) to achieve such particular packing structure that allows the hetero-contact to act as a main path of electron transport. With a change in gas ambient, contact potential changes beside the surface electron density and hence the gas response can be promoted largely by the change of mobility of electrons as compared with the conventional devices.

Key words: contact potential, hetero-contact, work function, oxide semiconductor, gas sensor, pinning

Background and aim

Usually oxide semiconductor gas sensors are fabricated into a porous stack of a single oxide material, where constituent crystals (usually grains) are basically uniform and so exhibit the same gas response behavior on exposure to a gas. Recently we succeeded in establishing the theory of receptor function and transducer function for the sensors of this group [1~4]. When the grains identical in properties are brought into contact (homo-contact), the reduced resistance of each contact (r/r_0) and so that of the whole device (R/R_0) as well are determined by the surface density of conduction electrons ($[e]_S$) of each grain, where r_0 and R_0 stand for the values at flat band state. The drift mobility of conduction electrons (μ) through the contact remains constant and is cancelled out in the reduced quantities. When the contacting grains are different in size or other properties (hetero-contact), however, a totally different situation comes out. The hetero-contact inevitably involves generation of a contact potential, which attenuates μ. This means that if two kinds of sensing materials are mixed adequately to make use of the change of μ effectively, it is possible to enhance gas response in excess of that of the conventional device. This paper aims at exploring the way to a novel gas sensor in which gas response is promoted doubly, i.e., not only by the change of $[e]_S$ and but also by that of μ.

Homo-contact and hetero-contact

Let us consider two kinds of grains, 1 and 2, different in radius, donor density (N_D), kind of semiconductor or other properties. A homo-contact is formed when grains of the same group is paired, as shown in Fig.1. When free, each grain responds to the target gas exactly in the same manner, exhibiting the same Fermi level shift (p) or work function ($q\phi$). The term p is correlated with N_D, $[e]_S$ and reduced radius of grains ($n = a/L_D$, a; grain radius, L_D; Debye length).

$$N_D / [e]_S = \exp\{(1/6)\, n^2 + p\} \qquad (1)$$

Nothing particular happens in the energy band

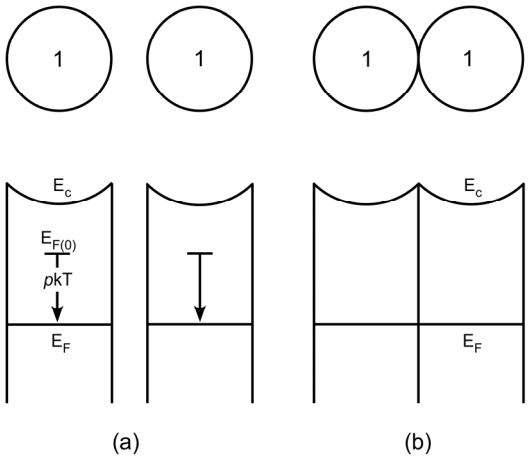

Fig. 1 Energy band diagrams of homo-contact (grains 1). (a) Free grains, (b) Contacting grains.

diagram when they are contacted. Conductance of the contact ($1/r_{11}$) is proportional to $[e]_S$, μ and the contact area and disproportional to the thickness of contact, while that at flat band state ($1/r_{11(0)}$) is similarly formulated [4]. As a result, the reduced resistance ($r_{11}/r_{11(0)}$) is given simply by

$$r_{11}/r_{11(0)} = N_D / [e]_S \qquad (2)$$

A pair of grains, 1 and 2, brought in a hetero-contact is illustrated in Fig.2, where grain 1, when free, is assumed to have larger Fermi level shift (p) than the other. When they are contacted under subjection to the pinning effect, this difference causes two particular phenomena to appear at the contact interface, i.e., conduction band edge difference (δ_{EC}) and contact potential ($q\,\delta_P$). The former is generated in order to establish exchange current across contact at equilibrium, while the latter is to compensate the difference in work function ($q(\phi_1 - \phi_2)$, $\phi_1 > \phi_2$) [4]. For the present particular case, these values are expressed as follows.

$$q\,\delta_P = \delta_{EC} = \{((n_1^2/6) + p_1) - ((n_2^2/6) + p_2)\}\,k\,T \qquad (3)$$

Since $q\,\delta_P$ is directional, it reduces the mobility of only those electrons running from grain 2 to 1, resulting in the directional resistance of the contact, i.e.,

$$r_{21} = r_{12} \exp(q\,\delta_P/k\,T) \qquad (4)$$

Suffix 21 means that electrons move across the contact from grain 2 to 1. Four kinds of contacting pairs are possible among two kinds of grains, 1 and 2, as shown in Fig.3. Under simplifying assumptions, r_{12} is further related to the resistance of homo-contact (r_{11}) by $r_{12} = r_{11} = r_{11(0)}\,N_{D1}/[e]_{S1}$, where N_{D1} and $[e]_{S1}$ are donor density and surface density of electrons of grain 1, respectively [4]. Thus one obtains

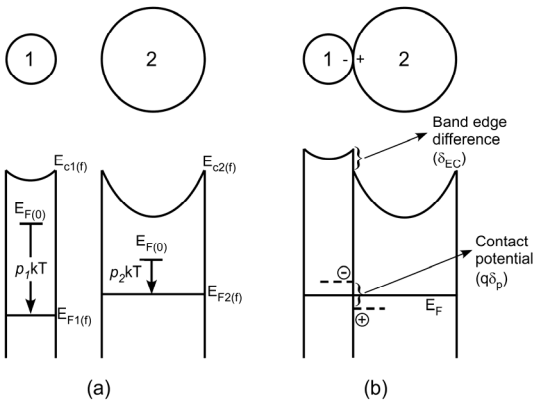

Fig. 2 Energy band diagrams of hetero-contact between grains 1 and 2.

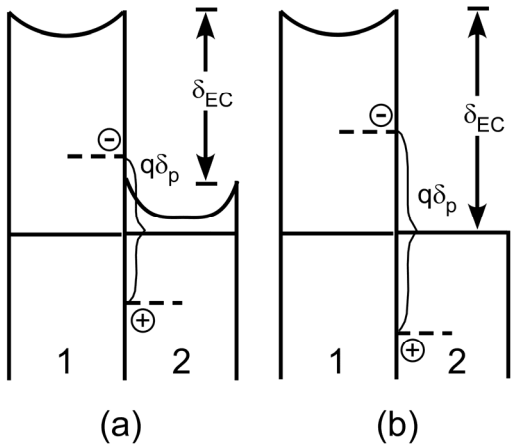

Fig. 3 Counter materials (grain 2) leading to large contact potentials. (a) Highly doped oxide (ITO), (b) Metal (Au).

$$r_{21} = r_{11(0)}\,(N_{D1}/[e]_{S1}) \exp(q\,\delta_P/k\,T) \qquad (5)$$

In this way, r_{21} is modulated doubly by the change of $[e]_{S1}$ and that of $q\,\delta_P$ (or μ) on changing gas ambient. $q\,\delta_P$ is enlarged when grain 2 is provided with a semiconductor of large N_D or a metal, as shown in Fig.4. When grain 2 is a metal, $q\,\delta_P$ can be equated to the change of work function of grain 1 so that this term can contribute to the change of r_{21} as comparably as the counter term, $[e]_{S1}$, does since $\exp(q\,\delta_P/k\,T) = (N_{D1}/[e]_{S1}) \exp(E_{FM}/kT)$ holds in this case E_{FM} is the Fermi level of the free metal.

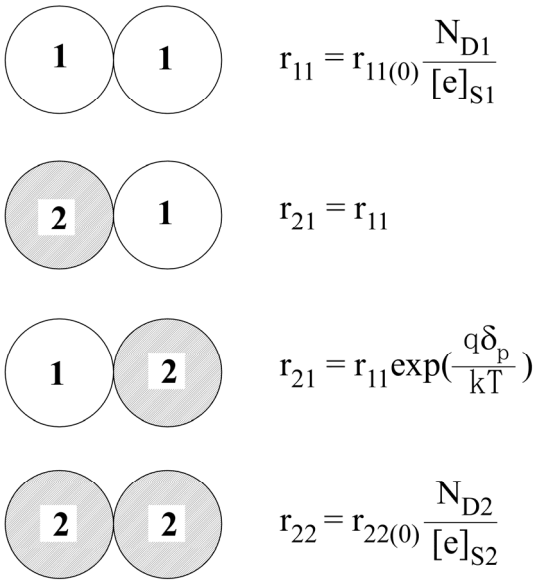

Fig. 4 Four contacting pairs given by two kinds of grains 1 and 2, and resistances of resultant contacts under approximations.

Linear chains (hypothetical model)

Fig. 5 shows two chains consisting of grains 1 only (a) and of alternate grains 1 and 2 (b). The resistance of chain (a) is given by eq. (2) times the number of grain contacts (2m).The reduced resistance is thus given by

$$R/R_0 = N_D / [e]_S \quad (6)$$

In (b), a half of the contacts have the resistance given by eq. (2), while another half has one by eq. (5). When m is the number of grains 1 and 2 each,

$$R = m\, r_{11(0)}\, (N_{D1} / [e]_{S1})\, x$$
$$(1 + \exp (q\, \delta_P / k\, T)) \quad (7)$$

When $q\, \delta_P/kT$ is sufficiently large,

$$R = m\, r_{11(0)}\, (N_{D1} / [e]_{S1}) \exp (q\, \delta_P / k\, T) \quad (8)$$

When grains 2 are provided with a metal, this reduces to

$$R = \text{const.}\, (N_{D1}/[e]_{S1})^2 \quad (9)$$

Comparison with eq.(6) indicates that the resistance is now proportional to the square of N_{D1} /$[e]_{S1}$. In the conventional device, the resistance under varying partial pressure of oxygen (P_{O2}) is usually proportional to $P_{O2}^{1/2}$, while the conductance under contact with an inflammable gas (H_2) is roughly proportional to $P_{H2}^{1/2}$. In contrast, the chain of alternate grains above is shown to exhibit resistance and conductance in proportion to P_{O2} and P_{H2}, respectively, owing to the contribution by contact potential. It is reserved, however, that such a chain can hardly be fabricated in practice.

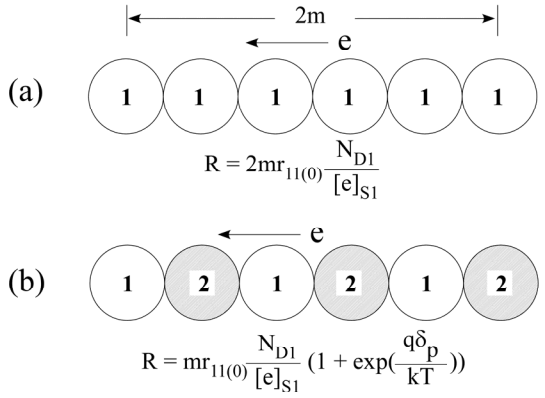

Fig. 5 Resistances of chains of grains.
(a) Homogeneous chain of grains 1
(b) Heterogeneous chain of alternate grains 1 and 2.

Practical grains packing structure

When a three dimensional device is fabricated by randomly packing grains 1 and 2, however, it is not possible to make use of contact potential, because the contacts involving contact potential (21, most resistive) are buried among those not involving contact potential (11, 12 and 22, more conductive). It is thus imperative to design the packing structure in such a way that the hetero-contacts are included in the major pathway of electron transport. For instance, layer by layer packing structure (Fig.6 (a)) fulfills this requirement, though this structure is not always easy to fabricate. Among others, the packing structure shown in Fig.6 (b) seems to be the most feasible in practice. To fabricate this structure, for instance, insulator (e.g. silica) balls are first covered with a layer of highly doped oxide semiconductor (e.g. ITO) or gold (grain 2) and then with a layer of small oxide semiconductor (grain 1) in succession through

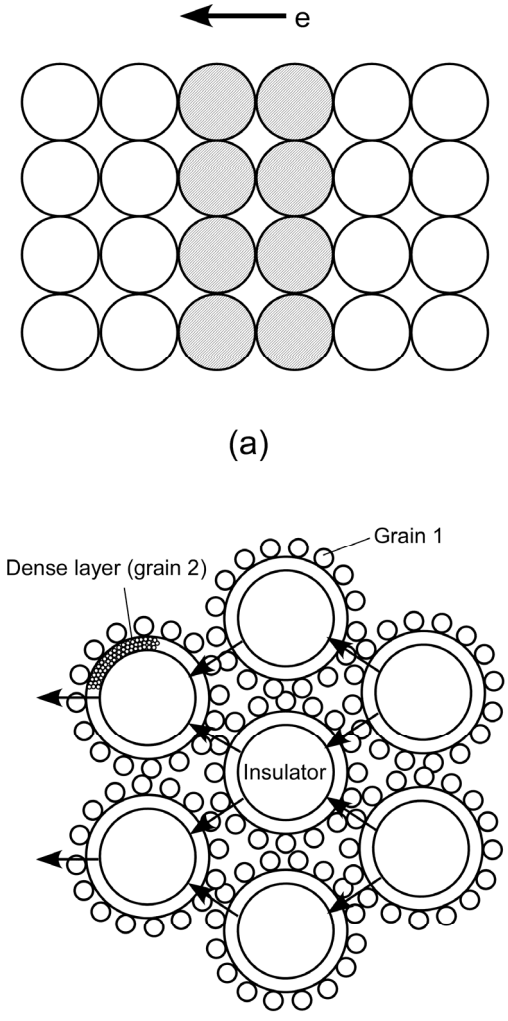

Fig. 6 Composites of grains, 1 and 2, packed in particular structures. (a) Layer by layer structure, (b) Thick film assembly of layer by layer- packed composite deposited on insulator balls.

wet processes, and the resulting balls are screen-printed on a substrate. There will be also other ways to fabricate such a unique packing structure. The most resistive contacts are those between grains 2 and 1, which are included in the major pathway of electrons. With such a structure, the device will serve as a novel gas sensor in which the resistance and conductance will change linearly with a change in P_{O2} and P_{H2}, respectively, though this is yet to be confirmed experimentally.

References

[1] N. Yamazoe, K. Shimanoe, *J. Electrochem. Soc.*, 155(4), J85-J92 (2008); doi:10.1149/1.2832655

[2] N. Yamazoe, K. Shimanoe, *J. Electrochem. Soc.*, 155(4), J93-J98 (2008); doi:10.1149/1.2832662

[3] N. Yamazoe, K. Shimanoe, *Sens. Actuators B Chem.*, 138, 100-107 (2009)

[4] N. Yamazoe, K. Shimanoe, *Sens. Actuators B Chem.*, 160, 1352-1362 (2011); doi: 10.1016/j.snb.2011.09.075