



New perspectives of gas sensor technology

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ABSTRACT

Two recent topics important for advancing gas sensor technology are introduced. Semiconductor gas sensors have been developed so far on empirical bases but now a fundamental theory has been made available for further developments. The theory reveals the roles of physical properties of semiconductors and chemical properties of gases in the receptor function. MEMS techniques have been applied to fabrication of micro-platforms for use in gas sensors. The micro-platforms appear to provide gas sensors with new innovative function.

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1. Introduction

Looking back its history, gas sensor technology was inaugurated when three kinds of pioneering gas sensors were put in practice in Japan, i.e., oxide semiconductor gas sensors for gas leakage alarms [1], solid electrolyte oxygen sensors for car emission control systems [2], and ceramic humidity sensors for automatic cooking ovens [3]. These sensors demonstrated dramatically how important it was to monitor a specific gas species *in situ*, in real time and continuously for ensuring safety from gas hazards, protecting environments, or making home appliances intelligent or friendly to users. Importance of such emerging technology was well recognized world wide when the first International Meeting on Chemical Sensors (IMCS) was held at Fukuoka, Japan, in 1983, under the leadership of the late Professor Seiyama [4]. Research and development was triggered off all over the world to seek new and/or better gas sensors.

Currently various kinds of gases including reducing ones (methane, propane, carbon monoxide, ammonia, hydrogen sulfide, etc.) and adsorptive ones (oxygen, nitrogen dioxide, ozone, etc.) have been made detectable with gas sensors using semiconductors, electrolytes or catalytic combustion. Yet there are various new demands to gas sensors ranging from detecting VOCs (Volatile

Organic Compounds) at very low concentrations (ppb levels) to constructing sensor network systems. Needless to say, even the established gas sensors are demanded for innovations towards better sensing performances, lower power consumption and more compact device structures. To meet these demands, semiconductor gas sensors are considered to be best suited because they have advantageous features such as simplicity in device structure and circuitry, high sensitivity, versatility and robustness. It is pointed out that most of the sensors in this group have been developed empirically from a lack of theoretical understandings. Fortunately, we recently succeeded in deriving theoretical equations to describe the response of these sensors to adsorptive or reducing gases quantitatively [5–7]. We expect that the new theory will provide useful guidelines on how to elaborate selection and processing of sensing materials and additives used as well as device structure and fabrication techniques to be used.

From such a standpoint, theory of semiconductor gas sensors is introduced here as a main topic. Another topic, MEMS-assisted gas sensors, is selected because those are likely to give rise to a new breakthrough in gas sensor technology.

2. Theory of semiconductor gas sensors

2.1. Overview of empirical information and problems

Semiconductor gas sensors detect a specific target gas from a change in the electric resistance of a sensing body which is a

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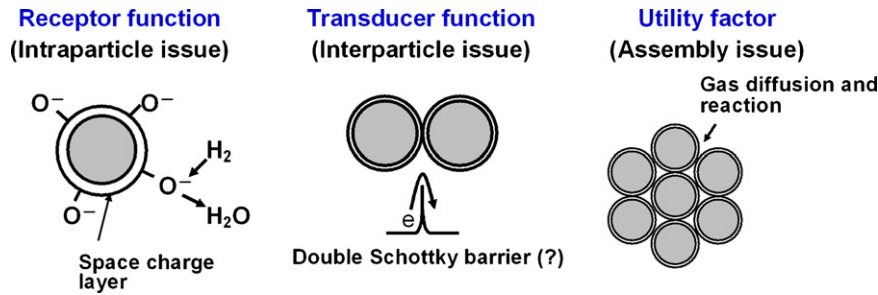


Fig. 1. Three basic factors controlling semiconductor gas sensors.

porous assembly of tiny crystals (particles) of oxide semiconductors such as SnO₂. Gas sensing properties have been accounted for by three basic factors, namely, receptor function, transducer function and utility factor, as schematically shown in Fig. 1 [6–10]. The first one is concerned with how each crystal responds to the stimulant gas in problem, while the second does how the response of each crystal is transduced into device resistance. The third one describes how the device response (resistance change) is attenuated in an actual porous sensing body due to a consumption of the stimulant gas during its diffusion inside. Among these factors, only the last one has been clarified theoretically [9,10]. As for the receptor function, it is known that oxygen is adsorbed on the crystals in air, presumably as O⁻, over the temperature range of interest [11] to form a depletion layer in them. Upon contact to a stimulant (H₂), the oxygen adsorbates are consumed more or less, causing the depletion layer to decrease. The transducer function can also be easily understood qualitatively based on the double Schottky barrier model so far assumed popularly.

It is remarked, however, that the double Schottky barrier model is nothing but estimated as an extension from other semiconductor devices. In fact, some sensor devices fabricated with wet-coating techniques have been found to exhibit temperature-independent resistance in air in disagreement with the model, and tunneling transport of electrons between adjacent crystals has been strongly suggested instead [8]. The scheme of receptor function above is also too qualitative, failing to account for many pieces of experimental information including grain size effects on sensitivity. Definitely quantitative approaches to the receptor function are badly needed. This is a main concern here in the first topic.

2.2. How to formulate receptor function

2.2.1. Scope of formulation

On each semiconductor crystal, adsorption and/or reactions of gases take place to capture or release electrons, while a corresponding redistribution of electrons takes place inside to achieve an electrostatic equilibrium. The surface chemical affair and the sub-surface physical one are not independent but united together, and this provides a base on which the receptor function is formulated as follows.

The chemical affair can be formulated easily. In an oxygen atmosphere, for instance, oxygen adsorption is expressed as follows:



$$(K_{O_2}P_{O_2})^{1/2}[e]_s = [O^-] \tag{1}$$

Here K_{O_2} and P_{O_2} are adsorption constant and partial pressure of oxygen, respectively, and $[e]_s$ and $[O^-]$ are surface densities of free electrons and O⁻, respectively. In the presence of a reducing gas

(H₂), O⁻ is consumed by the reaction:



By coupling with (R1), the following equation results in the steady state:

$$K_{O_2}P_{O_2}[e]_s^2 = [O^-]^2 + cP_{H_2}[O^-] \tag{2}$$

P_{H_2} is partial pressure of H₂, and c is a constant defined by $c = k_2/k_{-1}$, where k_2 and k_{-1} are rate constants of (R2) and reverse reaction of (R1), respectively. Eqs. (1) and (2) combine between $[e]_s$ and $[O^-]$ in the oxygen atmosphere in the absence and presence of H₂, respectively. Since the electrostatic equilibrium condition gives rise to another interrelation between $[e]_s$ and $[O^-]$ as stated later, the two variables can be determined uniquely if P_{O_2} , P_{H_2} and physical parameters of semiconductor crystals are fixed.

2.2.2. Electrostatic equilibrium for large crystals

Let us consider electrostatic equilibrium inside a semiconductor crystal. In case the crystal is large enough, depletion is limited in the shallow region from the surface. We can assume a flat surface for which the electrostatic equilibrium has been discussed well by using an energy band diagram as shown in Fig. 2. A location in the crystal is expressed by a depth from the surface, x . Under simplifying conditions of complete ionization of donors, no tailing of electron distribution, and no surface states other than O⁻, Poisson's equation

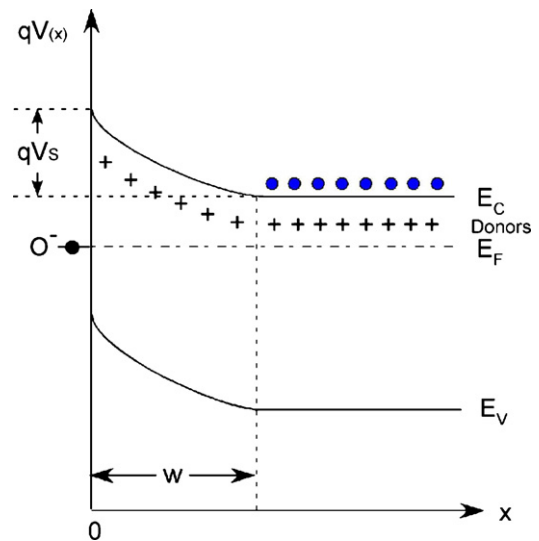


Fig. 2. Potential energy diagram for depletion in a large semiconductor crystal. Here $qV(x)$ is the potential energy of electron, qV_s surface potential energy of electron, x distance from the surface, w depletion depth, E_c conduction band edge, E_v valence band edge, and E_f is the Fermi level.

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