JOURNAL OF MATERIALS SCIENCE 25 (1990) 259–262

Sensing mechanism of SnO_2 gas sensors

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Studies have been made of the gas sensing properties of both steady and unsteady state SnO_2 thin film gas sensors in contact with CH_4 and H_2 in air from 400 to 500° C. The results suggest a new sensing mechanism model for SnO_2 semiconductor flammable gas sensors. This model is based on the following points: (i) Sensor conductivity is determined by the concentration of carrier electrons. (ii) Carrier concentration is controlled by surface unsaturated oxygen adsorption site concentration which is decided by the balance between oxygen adsorption and the surface reaction between oxygen adsorbate and flammable gases. (iii) The activation energy of the reaction is changed by the Fermi energy change for any change in sensor conductivity. This model explains all experimental results.

1. Introduction

It is known that the conductivity of n-type metal oxide semiconductors, for example SnO_2 and ZnO, changes when in contact with flammable gas [1, 2]. Seiyama [3] proposed using this property and such sensors were developed for commercial use by Taguchi [4]. As a result of these developments, this kind of sensor is now widely used for domestic gas leak alarm systems, and is one of the most important types of industrial gas sensor [5].

Ihokura *et al.* [6] suggested that changes in SnO_2 sensor conductivity are directly due to a change of the electronic potential barrier in the grain boundary of SnO_2 when flammable gas and oxygen adsorb or react on the surface. Morrison [7] suggests that the adsorption or reaction of flammable gas and oxygen on the grain surface causes a change in the grain Fermi level, and that the Fermi level determines the grain boundary potential barrier. Sakai *et al.* [8], think that the grain boundary area is like a neck area between grains, and that surface adsorption gases are individual negative oxygen adsorbates and positive flammable gas adsorbates. They suggest that the relationship between the concentration of flammable gas in air and the conductivity of a sensor is shown by the following relationship

$$\sigma_G^2 - \sigma_{AIR}^2 \propto P_G^n \quad n \simeq 1 \tag{1}$$

Sakai's suggestion is unfounded, however, because it does not take into account surface reaction or sensor properties in an unsteady state.

Recently, the authors have studied the properties of SnO_2 thin film gas sensors when in contact with methane or hydrogen in air from 400 to 500° C. The sensors were made by the reactive sputtering method. We have reported several results.

In this study, the authors conclude their recent results, and suggest a new sensing mechanism model for SnO_2 gas sensors. This model states that sensor conductivity is controlled by surface unsaturated oxygen adsorption site concentration, which is decided by the balance between oxygen adsorption and surface reaction between oxygen adsorbate and flammable gases.

2. Experimental results

2.1. Sensor properties in a steady state

The relationship between the concentration of flammable gas in air and the conductivity of this sensor is shown by the following relationship. The relationship established by Sakai was obtained, namely

$$\sigma_G^2 - \sigma_{AIR}^2 \propto P_G$$

The relationship between oxygen concentration and conductivity of this sensor is shown by the following relationship

$$\sigma_G \propto P_{O_2}^{-1/2} \tag{2}$$

where P_{O_2} is the oxygen concentration in a mixture of nitrogen and oxygen.

2.2. Dynamic properties of sensors

In our recent study, the transient response of SnO_2 thin film gas sensor conductivity to rapid change in gas concentration was examined. The results are as follows.

(1) In both hydrogen in air and methane in air, both transient properties and steady state properties can be explained by the following equation [9, 10]

$$d\sigma/dt = (aP_G + b - c\sigma^2)/\sigma \tag{3}$$

where σ is the sensor conductivity, P_G the flammable gas concentration in air and a, b, c are constants.

(2) The transient response rates in a change from flammable gas in air to pure air bear little relation to the type of flammable gas. However, the transient response rates in a change from pure air to flammable gas in air were determined by the type of flammable gas [10].

(3) The transient response rates in a change from pure air to hydrogen in a mixture of nitrogen and oxygen bear little relation to oxygen concentration in

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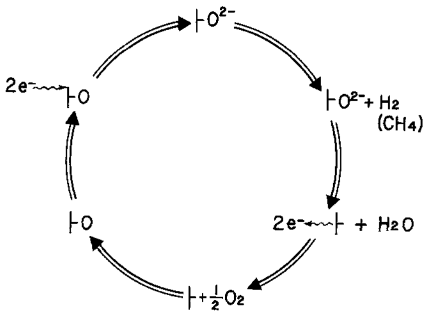

Figure 1 A reaction model on the SnO_2 surface.

the mixture. Therefore, we suggest that the oxidation reaction on the sensor surface is the reaction between flammable gas and surface oxygen adsorbate [11].

2.3. Hall effect measurement study of sensors

In our recent Hall effect measurement study of sensors, the sensor conductivity change for concentration of flammable gas in air is decided by sensor carrier concentration change. In other words, mobility in the sensor is not affected by the concentration of flammable gas in air [12].

3. Discussion about the model of sensing mechanism

In this paper, we describe the area which determines sensor conductivity as the grain boundary area.

In pure air, we suggest that there is negative oxygen adsorbate on the grain boundary area surface. In an air and flammable gas mixture, surface oxygen adsorbate reacts with flammable gas, and a steady state appears on the surface with some unsaturated (open) adsorption sites. We suggest a reaction model on the grain boundary area surface shown in Fig. 1.

The structure of oxygen adsorbate has not been exactly determined but, from Nakamura's ESR measurements [13], we consider it to be O^{2-}.

The model uses the case of hydrogen for illustrative purposes in this paper, but it is applicable also to CH_4.

Fig. 1 shows that the surface oxygen adsorbate and hydrogen react to release carrier electrons to the semiconductor and to produce H_2O. The H_2O is desorbed to leave an open adsorbtion site. Atmospheric oxygen is adsorbed on the open site and reacts with carrier electrons from the semiconductor to produce O^{2-}.

In this steady reaction, sensor conductivity is determined by the carrier electron concentration in the semiconductor, because mobility is constant due to the Hall effect measurement. This concentration is determined by the balance between the release and recapture of electrons on the semiconductor surface.

In other words, sensor conductivity is determined by the concentration of the open adsorbtion sites on the grain boundary surface, which is decided by a balance between oxygen adsorption and surface reaction between oxygen adsorbate and flammable gas.

That the surface reaction is between the oxygen adsorbate, not atmospheric oxygen, and hydrogen is established by recent experimental results of sensor dynamic properties. That oxygen adsorption has no relationship to the type of flammable gas is established by recent experimental result. Our calculation of the carrier electron concentration was based on a number of assumptions.

(1) The SnO_2 semiconductor surface is almost covered with oxygen adsorbate, and the number of open adsorption sites is very much less than the number of sites of oxygen adsorbate.

(2) The electron carriers in the semiconductor are almost all captured by the energy level of the negative oxygen adsorbate. Consequently, the relationship between the concentration of open adsorption sites and the concentration of electron carriers in the semiconductor is shown by the following equation:

$$n = gS_{\text{open}} \tag{4}$$

where g is a constant, S_{open} the number of unsaturated (open) sites and n the carrier density.

(3) The rate-determining steps of these reactions are the reaction between flammable gas and oxygen adsorbate, and the adsorption of oxygen.

(4) Activated complex of the reactions is electronically neutral. Therefore, the activation energy of the reaction between surface oxygen adsorbate and flammable gas is related to the Fermi level in the semiconductor.

From these assumptions, the velocity of increasing carrier density in the semiconductor $(dn/dt)_I$ is described by the following relationship. Because the velocity is determined by surface reaction between oxygen adsorbate and flammable gas, and thermal desorption of oxygen adsorbate

$$(dn/dt)_I = 2k_1 S_{\text{close}}(P_G + b_1) \tag{5}$$

where k_1 is the reaction rate constant, P_G the concentration of flammable gas in air, S_{close} the concentration of oxygen adsorbate and b_1 the constance indicating the contribution of oxygen thermal desorption.

The velocity of the decreasing carrier density in semiconductor $(dn/dt)_D$ is described by the following relationship, because the velocity is determined by the oxygen adsorption from atmosphere to surface open sites

$$(dn/dt)_D = k_2 P_{O_2} S_{\text{open}} \tag{6}$$

where k_2 is the reaction rate constant, P_{O_2} the concentration of oxygen in air and S_{open} the concentration of open sites.

Therefore, the whole velocity of changing carrier density in the semiconductor is described by the following relationship derived from Equations 5 and 6.

$$\begin{aligned} dn/dt &= (dn/dt)_I - (dn/dt)_D \\ &= 2k_1 S_{\text{close}}(P_G + b_1) - k_2 P_{O_2} S_{\text{open}} \end{aligned} \tag{7}$$

By placing the assumed Equation 4 in Equation 7, and as S_{close} is a constant, the following equation is obtained

$$dn/dt = k_3(P_G + b_1) - k_4 P_{O_2} n \tag{8}$$

where $k_3 = 2k_2 S_{\text{close}}$, $k_4 = k_2 g$ and n is the carrier density.

As mobility is constant, we can obtain the following relationship from Equation 8

$$d\sigma/dt = k_5(P_G + b_1) - k_4 P_{O_2}\sigma \tag{9}$$

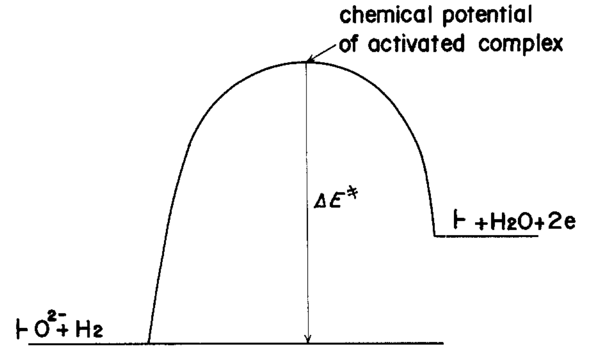

Figure 2 Energy diagram of surface reaction between flammable gas and oxygen adsorbate.

where $k_5 = k_3 n/\sigma$. By comparing Equation 9 with Equation 3, it should be possible to establish

$$k_3 \propto n^{-1} \qquad (10)$$

In the reaction between hydrogen and oxygen adsorbate, the reaction equation is described by

$$H_2 + \vdash O^{-2} \rightarrow H_2O + \vdash + 2e^- \qquad (11)$$

The reaction rate constant k_3 is described by the following relationship using the Arrhenius equation

$$k_3 = A \exp(-\Delta E/kT) \qquad (12)$$

where A is the frequency factor of the reaction, ΔE the activation energy, T the absolute temperature and k Boltzmann's constant. The energy diagram of the reaction is shown in Fig. 2.

Next we consider the influence of the electron level in the semiconductor on the activation energy of the reaction ΔE. Fig. 3 shows the electron level model of the tin oxide semiconductor surface. We assume that the electron level E_0 is deep enough, and that the thermal-excitation from E_0 to conduction band E_c can be neglected. Furthermore, it is assumed that $E_c - E_0$, which is dependent on the adsorption state, is unrelated to E_F.

From Assumption 4 the energy of the activated complex is unrelated to the Fermi level E_F, and the energy of the electron trapped by the level of oxygen adsorbate is related to E_F, the following equation is deduced. Because activation energy from negative oxygen adsorbate to neutral one is $(E_0 - E_F)$, the total activation energy is related to $(E_0 - E_F)$

$$\Delta E = \Delta E_1 - (E_0 - E_F) \qquad (13)$$

where ΔE_1 is a constant which is unrelated to E_F. On the other hand, the electron density of the conduction band is described by the following equation using Boltzmann's distribution

$$n = N_c \exp(-E_c - E_F)/kT) \qquad (14)$$

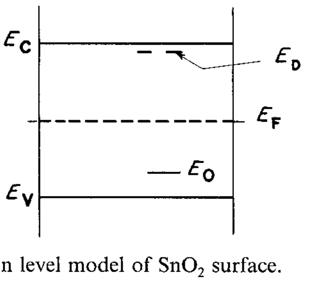

Figure 3 Electron level model of SnO_2 surface.

where N_c is the density of states in the conduction band. From a transformation of Equation 14

$$\begin{aligned} -kT \ln(n/N_c) &= E_c - E_F \\ &= (E_c - E_0) + (E_0 - E_F) \qquad (15) \end{aligned}$$

By inserting this in Equation 13

$$\Delta E = \Delta E_1 + kT \ln(n/N_c) - (E_c - E_0) \qquad (16)$$

Since $E_c - E_0$ is constant as shown in the assumptions

$$\Delta E_1 - E_c + E_0 = \Delta E_2 \qquad (17)$$

where ΔE_2 is a constant which is unrelated to E_F. By inserting this in Equation 16

$$\Delta E = \Delta E_2 + kT \ln(n/N_c) \qquad (18)$$

and by inserting this in Equation 12

$$\begin{aligned} k_3 &= A \exp\{-[\Delta E_2 + kT \ln(n/N_c)]/kT\} \\ &= N_c/nA \exp(-\Delta E_2/kT) \qquad (19) \end{aligned}$$

Since the parameters, except for n, are constant in the case of constant temperature and with no change in the type of gas, the following equations are deduced by inserting Equation 19 in Equation 8 (to obtain Equation 20) and, as the oxygen concentration is constant, by rewriting the constant (to obtain Equation 21)

$$\begin{aligned} dn/dt &= (aP_G + b)/n - k_4 P_{O_2} n \qquad (20) \\ &= (aP_G + b - cn^2)/n \qquad (21) \end{aligned}$$

where $c = k_4 P_{O_2}$. Thus we can prove Equation 3, which was obtained by our experimental results.

Seiyama *et al.* [14] suggested that the oxidation reaction of methane on the tin oxide surface is proportional to the root of the methane partial-pressure. Their results support Equation 20. In the case of $\sigma_G \gg \sigma_{AIR}$ in a steady state ($dn/dt = 0$)

$$n \propto P_G^{1/2} \qquad (22)$$

Therefore, the first term of Equation 20, which is determined by reaction rate, is described by

$$(aP_G + b)/n \propto P_G^{1/2} \qquad (23)$$

This equation is consistent with the experimental results. Furthermore, the relationship between sensor conductivity and oxygen concentration in a steady state in Equation 2 is deduced by inserting $dn/dt = 0$ in Equation 20.

4. Conclusion

We suggest the following model of the sensing mechanism of SnO_2 gas sensors. A diagram of this model is shown in Fig. 1. Sensor conductivity is determined by the concentration of carrier electrons which is decided by the balance between release of electrons by surface reaction between oxygen adsorbate and flammable gas, and recapture by oxygen adsorption.

Activation energy of the reaction between surface oxygen adsorbate and flammable gas is changed by the Fermi energy change for the change of sensor conductivity. This model is explained by the relationship shown in Equation 20, namely

$$dn/dt = (aP_G + b)/n - k_4 P_{O_2} n \qquad (20)$$

Using this relationship, we can explain that the relationship is described by Equation 21, and can understand the experimental results shown in Section 2.

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Received 25 July 1988
and accepted 4 January 1989