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An Oxygen Sensitive α-Fe_2O_3-Au Diode

Kenkichiro KOBAYASHI,* Minoru TAKANO,† and Shoichi OKAMOTO†
Faculty of Engineering, Ehime University, Matsuyama 790
†Faculty of Engineering, Technological University of Nagaoka, Niigata 949-54

The rectification characteristics of the α-Fe_2O_3-Au diode are significantly damaged at room temperature by applying the large reverse bias to the diode in Ar. The damage is recovered as the ambient O_2-partial pressure is increased. The diode can detect O_2 at more than 1000 ppm.

Electrochemical gas sensors,$^{1)}$ Pd-gate FET's,$^{2)}$ and Pd-Schottky diodes$^{3)}$ can be used at room temperatures. However, these gas sensors are unsatisfactory as gas sensors operating at room temperature, because the maintenance of the electrochemical gas sensors is not easy and the Pd-gate FET's or the Pd Schottky diodes are insensitive to gases other than hydrogen gas at room temperatures. On the other hand, solid-state gas sensors used as a detector for combustible gases are usually heated to about 300 °C to enhance the reaction rates on the semiconductor surface. Thus, a new method that enables the acceleration of the desorption rate without elevating temperature has been required to develop solid-state gas sensors operating at room temperatures. From the theoretical consideration of the desorption rate on the semiconductor surface, it has been predicted that the desorption of chemisorbed species takes place even at room temperatures when electrons transfer from the chemisorbed species to the semiconductor occurs by tunneling through the space charge layer of a semiconductor. The electron tunneling was confirmed experimentally in oxides such as SnO_2,$^{4)}$ α-Fe_2O_3,$^{5)}$ and ZnO.$^{6)}$ In this work, we examine the possibility of an oxygen sensor operating at room temperature by using a Schottky diode of α- Fe_2O_3.

The powder of α-Fe_2O_3 (99.99%) was cold-pressed at 1.96×10^7 Pa into a disk of 1 mm thick and 10 mm diameter, and then the disk was sintered at 1300 °C for 30 h in air. The sintered α-Fe_2O_3 comprised grains of 4-20 μm diameters and had a 95% density of the theoretical value. The disk exhibited the electric resistivity of 200 Ω·cm. An α-Fe_2O_3 Schottky diode having lattice-like pattern of Au electrode was fabricated by the following procedure. For a back-ohmic contact, Indium metal was deposited on one side of the α-Fe_2O_3 disk, and then a copper wire lead for electrical contact was attached to the In with a silver conductive paint. The back-ohmic contact was covered with epoxy resin. Photoresist was deposited on the other side of the disk. After the exposure and the solvent development, a negative photoresist image with lattice-like pattern was generated. The resulting bare α-Fe_2O_3 surface was then plated with gold by electrolysis in an aqueous solution of 0.03 M $HAuCl_4$ (M=mol dm^{-3}) for 20 h at the current density of 250 μA/cm^2. Neither rf sputtering nor vacuum evaporation of Au was useful to produce the rectification characteristics of the diode. After the electrochemical plating of Au, lift-off of the residual photoresist was accomplished by washing with acetone. The resulting Au electrode showed cross stripes of 0.01 mm width. The scanning electron microscopic observation of microstructure of the Au electrode showed that the Au electrode was composed of needle-like crystals twined with each other. Thus, it seems that gases can pass through the porous Au electrode.

Solid line (a) in Fig. 1 is a current-voltage(I-V) curve of the α-Fe_2O_3-Au diode in O_2. Although an appreciable leakage current is observed at a reverse bias voltage, the α-Fe_2O_3 diode exhibits the rectification characteristics. The leakage current at a reverse bias voltage is probably attributable to tunneling of electrons through the space charge layer of α-Fe_2O_3, because the I-V curve of this diode at 77 K is typical of a tunnel Schottky diode.$^{7)}$ A broken line (b) in Fig. 1 is the I-V curve after applying a bias voltage of - 2.6 V for 37 min in Ar. A large leakage current was observed at a reverse bias voltage. This indicates that the rectification characteristics of the diode were damaged significantly by applying a large reverse bias voltage to the diode in Ar.

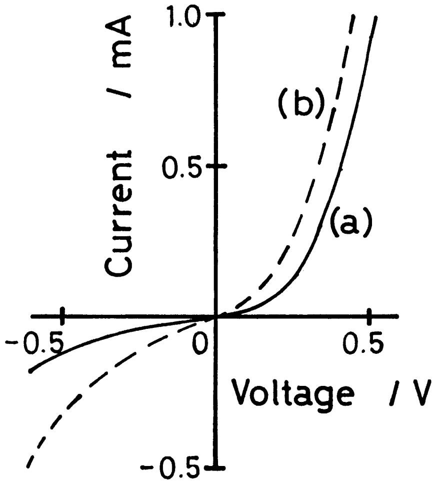

Fig. 1. I-V curves of α-Fe_2O_3-Au diode. (a):nontreated; (b): after applying bias voltage of -2.6 V for 37 min in Ar.

The change in the O_2 partial pressure has influence on the magnitude of the current at a large reverse bias voltage. The current variations with the ambient gases are shown in Fig. 2. The reverse current at a bias voltage of -2.8 V is increased in Ar but decreased in O_2 :their steady state values are 18.5 mA and 3.6 mA, respectively. The 90% response time, which is defined as the time required for the 90% of the total current change to be attained, was ca. 300 min for the ambient gas change from O_2 to Ar, and ca. 60 min from Ar to O_2. These response times measured by the d. c. current method are too long to be used as an actual oxygen sensor. It should be noted, however; that the capacitance method gives rise to a fast response. For instance, the 90% response time of the capacitance at 10 Hz was 15 s when the ambient gas was switched from Ar to O_2.

Figure 3 shows the O_2 concentration dependence of the current difference, $\Delta I = |I(Ar)-I(XO_2)|$, where I(Ar) and $I(XO_2)$ are the steady state currents in pure Ar and in a mixture of Ar and O_2(X ppm), respectively.

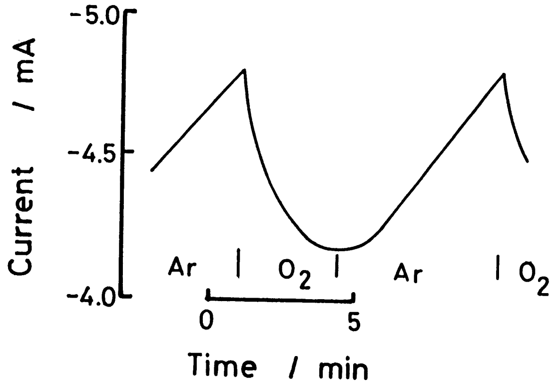

Fig. 2. Reverse current at -2.8 V as a function of time.

The relation of ΔI to the oxygen concentration is not linear. The O_2 sensitivity of the diode is not so high because the current difference ΔI approached zero at the oxygen concentration of ca. 1000 ppm.

Figure 4 shows the bias dependence of the currents in either Ar or O_2, together with the current difference $\Delta I = |I(Ar)' - I(O_2)|$. Here, $I(Ar)'$ is a current value at 10 min after the ambient gas is changed from O_2 to Ar (since the response of the current variation was very slow when the ambient gas was changed from O_2 to Ar, we took $I(Ar)'$ instead of the steady state value in Ar). The value of ΔI increased with the reverse bias, in contrast to a negligibly small change of ΔI in the forward bias range. This suggests that ΔI is not a result of the temperature rise of the α-Fe_2O_3 surface, which might be caused by current flow. The temperature of the α-Fe_2O_3 surface at -3.0 V was confirmed experimentally to be below 40 °C.

Figure 5 shows the current changes with time at -0.3 and -2.3 V in Ar, and that at -0.3 V in O_2. In an Ar atmosphere, the bias voltage was kept at - 2.3 V for 1 h and then was returned to - 0.3 V. The value of current at -0.3 V was about three times larger than the initial value. This current increase arises from the breakdown of the rectification characteristics of the diode as mentioned above. When the ambient gas was changed from Ar to O_2, the reverse current at -0.3 V began to decrease and approached the initial value. This indicates that the rectification characteristics are recovered by O_2 even at a small bias voltage.

In order to get information on the barrier height, the exchange current was estimated by extrapolating the relation of log i vs. V in the forward bias range to V=0. The estimated values of the exchange current are 13.9 μA for the solid line (a) in Fig. 1 and 18.1 μA for the broken line (b), respectively. Hence, the barrier height of

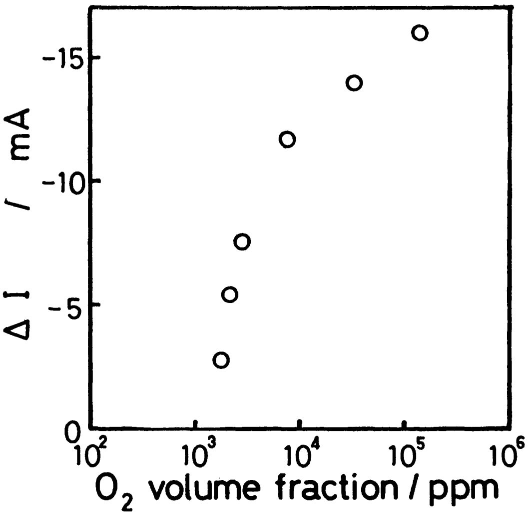

Fig. 3. O_2 sensitivity of α-Fe_2O_3-Au diode. The vertical axis is the current difference ΔI at -3.0 V.

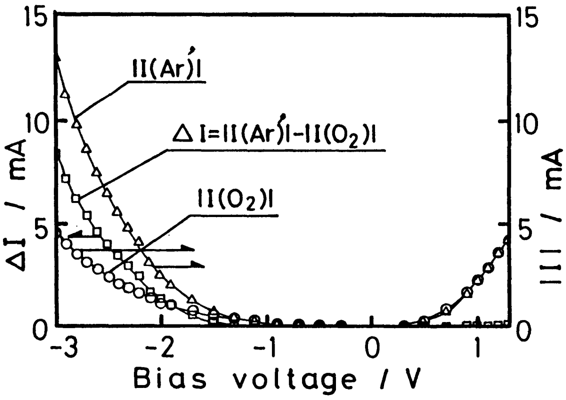

Fig. 4. Bias dependence of current difference ΔI. $I(Ar)'$ and $I(O_2)$ are currents in Ar and O_2.

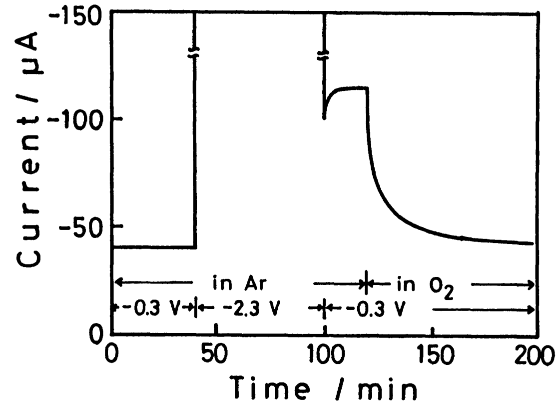

Fig. 5. Current changes in Ar and O_2 at different bias voltages.

the diode was reduced by applying a large reverse bias voltage to the diode in Ar and was increased in O_2 even at a small reverse bias voltage.

The sensing mechanisms of Pd-gate MOS transistors and Pd Schottky diodes have been related to the change in the work function of Pd metal. Such H_2 sensitive sensors can be also used as oxygen sensors in the presence of a small amount of H_2, because of reactions between H_2 and O_2 on the Pd surface. However, it is unlikely that the mechanism holds for the present α-Fe_2O_3-Au diode, because metal oxide-Au diodes are insensitive to hydrogen,8) and because the the bias dependence of the oxygen sensitivity shown in Fig. 4 was not observed in the Pd-Schottky diode.2,8) An alternative explanation is that the barrier height change is caused by the adsorption and desorption of oxygen on the α-Fe_2O_3 surface.9,10) In higher partial pressure of O_2, negatively charged chemisorption states of oxygen are formed on the α-Fe_2O_3 surface, and the positive charge is induced on the metal surface to compensate the negative charge. Consequently, dipoles produced at the interface of α-Fe_2O_3 and Au result in the increase in the barrier height of the diode. In lower partial pressure of O_2, the chemisorbed species of oxygen are removed by applying a large reverse bias, and thus the barrier height of the diode is lowered.

References

1) H. Dietz, W. Haecker, and H. Jahnke, Advances in Electrochemistry and Electrochemical Engineering, 10, 61 (1977).
2) I. Lundström, S. Shivaraman, C. Svensson, and L. Lundkvist, Appl. Phys. Lett., 26, 55 (1975); L.G. Petersson, H.M. Dannetun, and I. Lundstrom, Phys. Rev. Lett., 52, 1806 (1984).
3) N. Yamamoto, S. Tonomura, T. Matzuoka, and H. Tsubomura, J. Appl. Phys., 52, 6227 (1981); N. Yamamoto, S. Tonomura, and H. Tsubomura, J. Electrochem. Soc., 129, 444 (1982); K. Ito, Surf. Sci., 86, 345 (1979); L. Harris, J. Electrochem. Soc., 127, 2657 (1980).
4) K. Kobayashi, Y. Aikawa, and M. Sukigara, Bull. Chem. Soc. Jpn., 55, 2820 (1982).
5) F.M. Delnick and N. Hackerman, J. Electrochem. Soc., 126, 732 (1979).
6) B. Pettinger, H. R. Schöppel, T. Yokoyama, and H. Gerischer, Ber. Bunsenges. Physik. Chem., 78, 1024 (1974).
7) S.M. Sze, "Physics of Semiconductor Devices," John Wiley & Sons, New York (1981).
8) N. Yamamoto, S. Tonomura, T. Matsuoka, and H. Tsubomura, Surf. Sci., 92, 400 (1980).
9) J. Lagowski, E.S. Sproles, Jr., and H.C. Gatos, J. Appl. Phys., 48, 3566 (1977).
10) R. Jerisian, J.P. Loup, and J. Gautron, Thin Solid Films, 115, 229 (1984).

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