Steady State and Transient Behavior of the
Pd-SnO_x MIS Oxygen Sensors

J.F. Xu*, W.P. Kang and B. Lalevic

Department of Electrical Engineering, Rutgers University,

P.O. Box 909, Piscataway, N.J. 08854

T. Poteat

AT&T Bell Laboratories, Murray Hill, N.J. 07978

ABSTRACT

Results on the device characteristics of the O₂ gaseous sensors are presented. These sensors are fabricated in the MIS configuration Pd-SnO_x-Si₃N₄-SiO₂-Si-Al with highly resistive SnO_x as oxygen adsorptive element. Partial pressures of O₂ below 0.1 torr can be detected at room temperature by these devices. Steady state and transient behavior are described as a function of O₂ partial pressure and temperature. Adsorption and desorption rates and time constants are determined. Activation energy for O₂ adsorption in SnO_x is found to be 1.6 k cal/mol.

INTRODUCTION

Since the first observation [1,2] on the conductivity change in metal-oxide resistor on gaseous adsorption, various types of gaseous sensors using semiconductor materials have been developed. Two principal types of gaseous sensors have emerged: a) Sensors based on the conductivity changes upon gaseous adsorption and b) MOS, MOSFET and Schottky diode sensors where the changes in metal work function upon gaseous adsorption are reflected in the I-V characteristics, change in the threshold voltage or a shift in flat band voltage [3,4,5].

Oxygen sensors based on resistivity change on oxygen adsorption have been fabricated with sintered blocks or sputtered, evaporated or oxidized thin films of TiO₂, ZrO₂, SnO_x, Nb₂O₅ and others [6,7]. Another group of oxygen sensors is made of the electrochemical ZrO₂ cell, with the EMF output related to the oxygen pressure [8]. Oxygen detection with the above devices, requires however higher operating temperatures (>250°C).

We report here on a new type of O₂ sensors based on different detection mechanism related to the changes in ionic charge of the adsorptive metal oxide in the MIS capacitor. The device is fabricated in the following MIS configuration: Pd-SnO_x-Si₃N₄-SiO₂-Si-Al with highly resistive SnO_x as oxygen adsorptive element. The increase in ionic charges in SnO_x upon O₂ adsorption is reflected in the depletion region of Si and thus produces a shift in the flat band voltage of the MIS capacitor. This effect is essentially the same as that of impurity ions in SiO₂ on MOS device characteristics. Since these new devices are based on the ionic charges in isolating layer of MIS capacitor where more than 10⁸ ions/cm³ can produce a shift in flat band voltage, they are much more sensitive than the devices based on resistance changes. This was confirmed by our experiments, which have shown device detection capability of <0.1 torr O₂ partial pressure at 300°K.

We report on compositional, structural and electronic properties of SnO_x films and on the following parameters characterizing the device: 1) pressure detection range as a function of temperature, 2) shift in the flat band voltage ΔV_{FB} as a function of pressure at a given temperature; 3) ΔV_{FB} as a function of temperature at various partial pressures of oxygen; 4) Adsorption and desorption rates and time constants as a function of pressure and temperature.

Further experiments were carried on the electro-adsorption process, detection mechanism and determination of ionic concentration in SnO_x upon oxygen adsorption.

Experimental Methods

Pd-SnO_x-Si₃N₄-SiO₂-Si-Al MIS capacitors were fabricated on <100> p-type Si, 5-10 Ω resistivity using standard procedures. A 50Å layer of SiO₂ is deposited first on Si wafer, followed by a deposition of 600Å thick Si₃N₄ layer. SnO_x adsorptive oxide layer 400-800Å thick was subsequently grown by deposition of Sn film and its thermal oxidation at $\approx$ 400°C. A thin $\approx$ 5Å catalytic Pd layer was deposited over SnO_x and an Au film 1000Å thick but of much smaller circular area than Pd layer was finally deposited.

SnO_x composition depends on the oxidation temperature and time. Auger Electron Spectroscopy was used to determine SnO_x composition which shall give optimal device characteristics. So far the most promising composition seems to be SnO_{1.27}. Resistivity of SnO_{1.27} is about 4x10⁷ Ω -cm and relative dielectric constant is 4.9. SEM has shown a continuous SnO_{1.27} film with the grain size less than 1000Å.

The device under testing was placed inside a vacuum chamber, provided with heating stage. Oxygen alone or in a gaseous mixture was introduced into the chamber through a leak-rate valve. Subsequent shift, ΔV_{FB} , was measured at 1MHz from the C-V plot or by a constant capacitance voltage tracking circuit previously described. [4]

Results

As stated previously, oxygen adsorption or desorption by the device results in a shift in flat band voltage ΔV_{FB} which is determined from the C-V curves. Combined results of the observed ΔV_{FB} upon oxygen adsorption at a given temperature for various values of the O₂ partial pressure, and at a given pressure for different temperatures are given in Table I. It is seen in Table I

*Visiting Scientist, East China Normal University, Shanghai, PRC.

Table I

ΔV_{FB} Shift with O_2 pressure
at Several Ambient Temperatures

TABLE I

$T(^{\circ}C)$	$P(\mu m)$	$\Delta V_{FB}(mV)$	$P(\mu m)$	$\Delta V_{FB}(mV)$
	100		200	
26 $^{\circ}C$	5	20	32	40
75 $^{\circ}C$	20	30	59	79
100 $^{\circ}C$	39	52	72	81

that ΔV_{FB} increases with increasing temperature or pressure. At pressures below 1 torr, ΔV_{FB} increase linearly with increasing pressure. However in the measured pressure range from 1 to 60 torr, the linear relationship is replaced by a saturation trend where $\Delta V_{FB} \propto P^n$, with $n = 0.2$ for lower temperatures (20-35 $^{\circ}C$) and $n=0.12$ for higher temperatures (35-90 $^{\circ}C$).

Transient behavior of a device during O_2 adsorption process was studied in terms of the adsorption time rates and adsorption time constants. Adsorption rates are determined from the time rate of ΔV_{FB} i.e.

$$\frac{d\Delta V_{FB}}{dt} / \text{initial}$$

defined as the time necessary to achieve 90% of the total device response at a given O_2 pressure. These two parameters are investigated as a function of pressure and temperature. The experimental values for $\frac{d\Delta V_{FB}}{dt} / \text{initial}$ and τ for two ambient temperatures as a

function of O_2 partial pressure are given in Table II, while the dependence of $\frac{d\Delta V_{FB}}{dt} / \text{initial}$ and τ on temperature

at a given pressure is presented in Table III.

Table II

Rate of change of ΔV_{FB} and time constant τ as a function of pressure of 50 $^{\circ}C$ and 80 $^{\circ}C$.

TABLE II

$T(^{\circ}C)$	50 $^{\circ}C$		80 $^{\circ}C$	
$P(\text{torr})$	$\frac{d\Delta V_{FB}}{dt} (\frac{mV}{min})$	$t(\text{min})$	$\frac{d\Delta V_{FB}}{dt} (\frac{mV}{min})$	$t(\text{min})$
0.1	1.5	8.5	3.1	8.5
0.4	6	5.5	13	5.5
1	12	3	25.5	3.2
4	15	2.8	36.5	2.2
10	25	2	47.5	1.6
60	25	2	64.1	1.6

Table III

Time rate of ΔV_{FB} and adsorption time constant τ at different temperature for the O_2 pressure of 400 μm .

T	$\frac{dV_{FB}}{dt} (\frac{mV}{min})$	$t(\text{min})$
30 $^{\circ}C$	~1.2	6.5
45 $^{\circ}C$	~2.48	4.4
62 $^{\circ}C$	~4.45	4.7
77 $^{\circ}C$	~6.52	4.2
92 $^{\circ}C$	~9.80	4.6
106 $^{\circ}C$	~17.0	4.4

As seen in Table II, $d\Delta V_{FB}/dt$ increases initially with increasing pressure and levels off at higher pressures. The adsorption time constant decreases with increasing pressure and at higher remains at a steady value. Table III shows a sharp increase in $d\Delta V_{FB}/dt$ with increasing temperature at constant pressure, while τ remains essentially independent of temperature.

The value for the O_2 adsorption activation energy E_a in $SnO_{1.27}$ can be obtained from the above measurements. The initial rate of the adsorption process is related to the oxygen pressure by:

$$\left. \frac{d\theta}{dt} \right|_{\text{init}} = \frac{1}{\Delta V_{FB\text{max}}} \left. \frac{d\Delta V_{FB}}{dt} \right|_{\text{init}} = K_1 P_{O_2}$$

when K_1 is given by

$$K_1 = A e^{-E_a/RT}$$

Therefore, the slope of the plot of $\ln \left[\frac{1}{\Delta V_{FB\text{max}}} \left. \frac{d\Delta V_{FB}}{dt} \right|_{\text{init}} \right]$

vs $\frac{1}{T}$ is proportional to E_a . This plot is

shown in Fig. 1 for two different samples and the estimated value for E_a is about $1.6 \frac{kcal}{mol}$.

Fig.1 plot of $\frac{d\Delta V_{FB}}{dt}$ vs $10^3/T (K^{-1})$

Device transient behavior during oxygen desorption process was investigated as a function of O_2 partial pressure and temperature. The rates of desorption process $d\Delta V_{FB}/dt$ as a function of temperature for the O_2 adsorption partial pressure of 0.4 torr are given in Table IVa, while the data for $d\Delta V_{FB}/dt$ at $80^\circ C$ for different adsorption pressures are given in Table IVb.

Table IV

Desorption rate of change $d\Delta V_{FB}/dt$ at a) a constant O_2 adsorption pressure of 0.4 torr and b) at $80^\circ C$ for different adsorption pressures.

a) $T=80^\circ K$

$P(\text{torr})$	$\frac{d\Delta V_{FB}}{dt} / \text{init.} \left(\frac{mV}{min} \right)$
0.1	1.3
0.4	3.28
1.0	4.1
4.0	4.3
10.0	4.6

b) $P_{O_2} = 0.4 \text{ torr}$

$T(^{\circ}C)$	$\frac{d\Delta V_{FB}}{dt} / \text{init.} \left(\frac{mV}{min.} \right)$
51	1.4
80	3.28
100	3.76
122	4.7

The plot of $\frac{d\Delta V_{FB}}{dt}$ vs. P_{O_2} (torr) at 80° is given in Fig. 2. At lower pressure $\frac{d\Delta V_{FB}}{dt} / \text{init.}$ is directly proportional to pressure, while at higher pressure $\frac{d\Delta V_{FB}}{dt} \propto P_{O_2}^{0.17}$. As seen in Fig. 2 $\frac{d\Delta V_{FB}}{dt}$ levels at $\sim \frac{5 \text{ mV}}{\text{min}}$ for the adsorption pressure > 10 torr. The desorption rates increase almost linearly with temperature, at a given pressure, as shown in Table IVb.

Fig. 2 Plot of $d\Delta V_{FB}/dt$ vs P_{O_2} at $80^\circ C$

Conclusions

It has been demonstrated that Pd-SnO_x-MIS gaseous sensors can be effectively used for detection of oxygen at $300^\circ K$ at the operating pressure of O_2 below 0.1 torr. The characteristic device parameters and its steady state and transient response have been described as function of O_2 partial pressure and temperature in the region of interest.

Further experiments have been performed to clarify the detection mechanism, and they will be presented elsewhere. These experiments have confirmed the device operation is based on O_2 adsorption in SnO_x and subsequent effect at the ionic excess in SnO_x on the depletion region of the MOS capacitor. The number of the adsorbed ions at a given pressure and temperature has been determined by the triangular voltage sweep (TVS) measurements and found to be in agreement with theoretical calculation of ΔV_{FB} shift.

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