



HOKKAIDO UNIVERSITY

Title	XAFS Studies on the Local Structure of Battery-Driven Gas Sensor
Author(s)	村田, 尚義
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第12308号
Issue Date	2016-03-24
DOI	https://doi.org/10.14943/doctoral.k12308
Doc URL	https://hdl.handle.net/2115/64805
Type	doctoral thesis
File Information	Naoyoshi_Murata.pdf



XAFS Studies on the Local Structure of Battery-Driven Gas Sensor

Naoyoshi Murata

Department of Quantum Science and Engineering
Graduate School of Engineering
Hokkaido University
2016

Contents

Chapter 1

General introduction	1
1. Introduction	2
2. Review of the SnO ₂ and the oxide type gas sensors	3
2.1. Rutile-type SnO ₂	3
2.2. A solid state oxide type gas sensor	4
2.2.1. A solid state electrolyte gas sensor	5
2.2.2. Catalyst combustion sensor	9
2.2.3. Semiconductor sensor	11
2.3. Sensing mechanism of semiconductor sensor	12
2.3.1. Electronic surface states and depletion charge layers	12
2.3.2. Electric conduction mechanism	15
3. Application of MEMS technique	19
and application of Pt doped SnO ₂	
3.1. Application of MEMS technique	19
3.2. Pt-SnO ₂ thin film gas sensor	20
4. XAFS technique	21
5. Outline of this thesis	22

Chapter 2

Experimental	51
1. Introduction	53
2. Catalytic preparation and characterization method	53
2.1. Catalytic preparation	53
2.2. Characterization of the catalyst	53
2.2.1. XRD and XPS measurements	53
2.2.2. XAFS measurement	53
2.2.3. Catalyst performance	54
2.2.4. TDS measurement	54
3. <i>in situ</i> cell	
for fluorescence X-ray absorption fine structure measurement	55
3.1. Structure of the <i>in situ</i> cell	55
3.2. Performance as <i>in situ</i> cell	55
3.2.1. Heating performance	55

3.2.2. XAFS measurements in and out of the cell	56
4. Discussion	57
5. Conclusions	58

Chapter 3

Characterization of Pt doped SnO₂ Catalyst for a high performance micro gas sensor	69
1. Introduction	70
2. Experimental	71
2.1. Catalyst preparation	71
2.2. Characterization of the catalysis	71
2.3. Catalyst performance	72
3. Results	72
3.1. Catalytic active of Pt/SnO ₂	72
3.2. Crystal structure Analysis of Pt/SnO ₂ by XRD	73
3.3. XAFS result of Pt/SnO ₂	73
3.3.1. XANES of Pt/SnO ₂	73
3.3.2. EXAFS spectra of Pt/SnO ₂	74
3.4. Surface Analysis of Pt/SnO ₂ by XPS	76
4. Discussion	77
4.1. Local structure of Pt species	77
4.2. The structure and activity	79
5. Conclusions	79

Chapter 4

Pd-local Structure of the Pd/Al₂O₃ – Pt/SnO₂ Model Thin Film for High-Performance Micro Gas Sensor	97
1. Introduction	98
2. Experimental	98
2.1. Sensor performance	98
2.2. Catalyst preparation	98
2.3. Characterization of the catalyst	99
3. Results	99
3.1. The structure of Pd in Pd/Al ₂ O ₃ of the fresh sample	99
3.2. The stable structure of Pd catalyst under sensor driven condition	100

4. Discussion	100
5. Conclusions	101

Chapter 5

***in situ* XAFS investigation of Pt doped SnO₂ Catalyst for a high performance micro gas sensor**

1. Introduction	111
2. Experimental	112
2.1. Sample preparation	112
2.2. <i>in situ</i> XAFS characterization of the catalyst	112
2.3. TDS characterization of the catalyst	113
3. Results	114
3.1. <i>in situ</i> XANES analysis	114
3.2. <i>in situ</i> EXAFS analysis	114
3.3. Stability of Pt-SnO ₂ structure as solid state	115
4. Discussion	116
5. Conclusions	117

Chapter 6: General conclusion

Acknowledgement

Chapter 1

General introduction

1. Introduction

The demand for natural gas is increasing because of the easy supply and of its eco-friendliness as an energy source.¹ However, the safety problem prevents the further utilization of the natural gas. For example, 665 cases of methane gas leakage incident were happened in 2010, Japan.² Sixty percent of them were occurred in the case of residential use. As past cases the gas explosion were happened in commercial buildings of Osaka prefecture in 1970 and underground shopping center of Shizuoka prefecture in 1980, thus an expansion of methane gas alarm diffusion is highly required. SnO₂ is n-type semiconductor and widely used as gas sensing materials.^{3,4} Oxygen atoms which adsorbed on the SnO₂ surface can be reacted with reductive gases at high temperature. After reduction reaction, trapped electrons are released into the electrode as carrier. Thus the conductivity of SnO₂ is highly depended on the partial pressure of revealed oxygen and reductive gases. The AC power-driven type SnO₂ sensors have been developed and widely used so far. In order to increase the number of home-use gas sensor, battery-driven type or wireless models are preferable because of their good appearance and their free installation. Longer lifetime at least five years for gas alarm device is required from the Japan gas association thus the low power consuming sensors have to be developed to realize cordless type gas alarm.

Methane, a main ingredient in natural gas, is the most inert gas in the hydrocarbons and thus the activation of methane is necessary for reduction reaction. At the same time high methane selectivity is necessary which is because the kitchen atmosphere contains many reductive components such as alcohol, grease and oil. If too sensitive sensor were made, the sensor will malfunction for the other gases. The strategy of our novel gas sensor design is to enhance the sensor activity and selectivity using several types of metal catalysts and to miniaturize the sensor to reduce the energy consumption. Yamazoe et al has studied the effects of additives on SnO₂ gas sensors.⁵ M.Labeau et al has demonstrated that Pd and Pt additives play important role in the electrical properties of SnO₂-thin film-based sensor.⁶ They conclude that noble metals enhance the sensitivity of SnO₂ sensors. From this standpoint of miniaturization, Suzuki et al. have developed SnO₂ thin film produced by MEMS (Micro Electro Mechanical System) method.^{7,8} Recently we found that the Pt-dope SnO₂ catalyst increases methane

sensitivity of SnO₂ thin film sensor device which will provide the new pathway to realize a low power consumption gas sensor. The required performance for methane gas sensor is the 12500 ppm methane concentration which is a four times lower than the methane explosion limit (53000 ppm) even after the 5 years. The mass production of the high performance sensors requires further clear understanding of the atomic structure of the gas sensors.

2. Review of the SnO₂ and the oxide type gas sensors

2.1. Rutile-type SnO₂

A rutile-type crystal has tetragonal system which is $P 4_2/mnm$ on space group in Figure 1.⁹ SnO₂ belongs to MO₂ type dioxide which is composed of an octahedral structure unit(MO₆).

This rutile structure was described by Vegard firstly.¹⁰ This structure was characterized by two parameters of c/a for axes ratio and x for anion position. The M was located at position of (0, 0, 0) and $\pm (1/2, 1/2, 1/2)$ within unit cell. The position of O anion was described at $\pm (x, x, 0)$.

Baur pointed out that oxygen packing of MO₂ type is tetragonal close packing(t. c. p) from a view a point of symmetry and coordination number.¹¹ Three different angle of 90 °, 135 °, 135 ° was found at M-O-M bond by West et al.¹²

Bolzan et al. has estimated detailed parameter of SnO₂ as rutile type as shown Figure 2 by neutron diffraction.¹³ They concluded as 4.73735 Å on a-axis, 3.18640 on c-axis in Table 1.

Many researchers have studied an electronic structure of SnO₂ on bulk^{14,15,16,17} and surface^{18,19,20,21} by first principle calculation. Figure 3 shows a band structure of tetragonal-SnO₂ by Barbarat et al. Space area of 0(the Fermi level) – 6 eV is a band gap. Band structure was formed in valence band as maximum at R-point and conduction band as minimum at Γ -point. Experimentally, the band gap value at 0 degree is known as 3.6-3.9 eV.^{22,23,24} In their calculation, the energy of indirectly transition of the $R \rightarrow \Gamma$ and directly transition of the $\Gamma \rightarrow \Gamma$ was associated as 3.6 eV and 4.0 eV, ca. The projection of DOS obtained by Barbarat et al. was shown in Figure 4. The Sn(s) on bottom of band, Sn(p), Sn(d) on top of band and O(p) orbital is in valence band between -7 and 0 eV, and the Sn(s) orbital is in conduction band between 3 and 9 eV. Moreover, they found by Crystal orbital overlap

population (COOP) that top part of valence band was formed by antibonding orbital Sn(d)-O and O-O interactions combined with bonding Sn(p)-O interactions.

The occurrence of the lowest energy indirect optical transition at the R→Γ transition was reported by Arlinghaus and Svane et al.^{25,26} Therefore, this material is limpidity in the visible light area. SnO₂ has conductivity when donor level under conduction band is taken by defect of oxygen atoms in lattice or additives as shown in Figure 5. Studies about efficiency for electron structure by changing the amount of oxygen defects were reported by various groups.^{27,28} Studies of electron structure by additive (Ir, Sb, Cu, Pt, In, Ti, Mn, Pb, Zn, Ru, Rh, Li, N, Mg, F, Co, Ag, ZnO, TiO₂, etc.) were also reported by many researcher.^{29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46} Yoneda et al. have also pointed that there is correlation between defect level and career density, while defect is scattering factor of career. Therefore conservation of crystalline state of SnO₂ is important for stabled performance of sensor.

Table 1. The detailed parameter of SnO₂ structure

Lattice parameters			Anisotropic displacement parameters / Å ² × 10 ⁻³					
			Sn			O		
a / Å	c / Å	x	U ¹¹	U ¹²	U ³³	U ¹¹	U ¹²	U ³³
4.73735 (9)	3.18640 (7)	0.30562 (9)	4.4 (3)	-0.4 (2)	3.1 (4)	6.6 (2)	-1.6 (2)	5.5 (4)

2.2. A solid state oxide type gas sensor

The oxide including SnO₂ is often utilized as gas sensor. The gas sensor has developed with the chemical industry. This sensor has widely diffused since 1960s for monitoring of the exhausted pollution gas (NO_x, CO, CO₂ etc) from automobile and industrial process mainly.⁴⁷ Three type's gas sensors of electrolyte, catalyst-combustion and semiconductor have developed for industrial measurement development. I review about these three 3 type sensors in the chapter below.

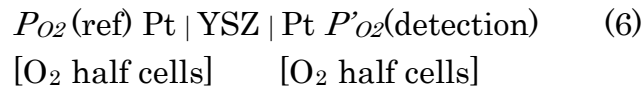
2.2.1. A solid state electrolyte gas sensor

Solid state electrolyte type's gas sensor detects signal from electrochemical reaction in electrolyte. An electrode with catalysis is attached on electrolyte. Pt, Au, oxide (ie SnO₂) and perovskite is often utilized as electrode material. We can measure electrochemical reaction in electrolyte as an electro motive force(EMF) following the Nernst law, an alternation of current and a change of impedance. I review a detection method for each signal in the below chapters.

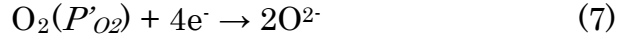
●An equilibrium potential type

Detection method of electro motive force(EMF) is classified in an equilibrium potential type and a mixed potential type. The former is often employed when a detect gas is one, the latter is used in case of the multiple gases. I review about a mixed potential type later.

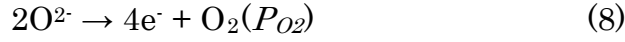
Solid state electrolyte material has tiny electrical conductivity but relatively major ionic conductivity in the temperature range from 773 to 1573 K.⁴⁸ Electrolysis cell is composed of this material used as barrier membrane with electrode which is often applied as gas sensor. The sensor utilized yttria-stabilized zirconia (YSZ) as electrolyte material is known commonly as management system for oxygen concentration control in steel and copper melts or combustion monitor of furnace, boiler, oil etc.^{49,50} Bias voltage is applied between electrodes which located at both ends of the electrolyte in high temperature. YSZ acts as oxygen ion conductor because of ion translates though oxygen ion vacancy which occurred by bias voltage. A cell based on this technique would develop as the galvanic cell was shown in Figure 6.^{51,52} Equation (6) explains structure of cell.



P_{O_2} is partial gas pressure of reference gas. P'_{O_2} is detection gas. Figure 6 is ZrO₂ oxygen sensor mounted an exhaust pipe on (a), for an automotive sensor on (b). The Pt electrode was coated at the end of electrodes which stabilized ZrO₂ (YSZ) pipe intercepted one side. Reaction of eq. (7) and (8) occurs in between of two electrodes of this cell.



and



EMF is generated according to Nernst law showing in eq. (9).

$$E = RT / 4F \times \ln \text{O}_2(P'_{\text{O}_2}) / \text{O}_2(P_{\text{O}_2}) \quad (9)$$

F is faraday constant, R is gas constant, T is temperature. E can measure by the EMF generated by reaction of eq. (7) and (8) on two electrodes though the YSZ electrolyte at a given T. EMF is proportional to logarithm of oxygen partial pressure. The oxygen partial pressure can convert to EMF from equilibrium electric potential of the detection side to combine O₂ half cells of left and right. P'_{O_2} can calculate if P_{O_2} is known value. However, in this method, the sensitivity is poor when the difference between P_{O_2} and P'_{O_2} is minor.⁵³

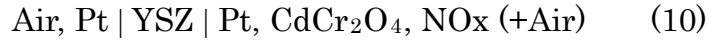
●A diffusion controlled limiting current type

New sensing method of diffusion controlled limiting current type based on YSZ to solve above limitation has developed. Figure 7 is structure of limiting current type oxygen sensor. Feature is the structure having a capped cover with pinhole onto sensor showed in Figure 6. Oxygen diffusion to detection electrode side (cathode) is limited on Fick's law by this pinhole. Electrochemical pumping to anode reaction eq. (8) from the cathode (7) occurs with a given voltage impression of low potential to cathode. Amplitude of pumping is increased with increasing of voltage, and is saturated with diffusion limitation of the supplied oxygen over time. Limiting current which is saturation value is proportional to oxygen concentration as shown in Figure 8.⁵⁴

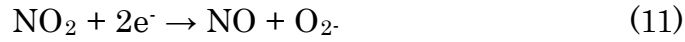
●A mixed potential type

This method has developed for the method to detect various gases in mixed gas (air and fuel etc.). If two or more electrochemical reaction was taken place at the same time, complex electrode potential, so-call mixed potential, based on the electrochemical reaction rate might be observed. Note that the relationship between EMF and Air/Fuel ratio must be ideal to Nernst law,

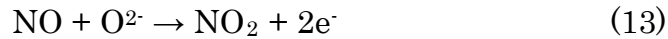
however the relationship is not follow Nernst law realistically.⁵⁵ Firstly, the sensor based on YSZ for this mixed potential detection was proposed by Fleming.⁵⁶ Currently, this method and an impedance type mentioned later have developed as sensor for vehicle diagnosis and environmental monitoring. Figure 9 is schematic of the NO_x sensing device of a mixed potential tubular type proposed by Miura et al..⁵⁷ This device has following electrochemical cell.



Left side of this cell is oxygen sensitive a half cell, Right side is NO_x sensitive a half cell. Right cell was composed by Pt electrode covered with CdCr₂O₄. We can detect signal by oppositely two electrochemical reactions following eq. (11) and (12) in Figure 10. These reactions occur at Pt/YSZ interface.



Opposite cathode reaction (11) and anode reaction (12) are generated at an equal rate. We can measure signal as mixed potential based on this two reaction. On the other hand, NO reaction can describe by eq. (13) and (14).



Moreover, gas phase reaction in Figure 10 occurs when reference gas is flowed in detection electrode. An incoming gas volume in the interface is determined by gas phase reaction. In order to improve the sensitivity and selectivity for the mixed potential sensor, selection of material which can control electrochemical reaction rate at interface is required.

●A complex impedance type

Recently, Miura et al. has proposed a complex impedance type as new gas detection method.^{58,59,60} Impedance at interface between of electrode and electrolyte changes by detection gas. We can detect gas concentration by measuring the change of impedance. A structure for YSZ sensor of this type

was shown in Figure 11. A sensitivity (S) against gas reaction on SE electrode in Figure 11 was calculated as Nyquist plot of eq. (15) using impedance value $|Z|$.

$$S = \left| \frac{|Z|^{base} - |Z|^{sample}}{|Z|^{base}} \right| \quad (15)$$

$|Z|^{base}$ and $|Z|^{sample}$ are impedance of base air and sample gas, Respectively. Nyquist plot of this impedance type YSZ sensor for NO_x (NO , NO_2) gas in air was shown in Figure 12 (a). Half a circular arch of low frequency side in NO_x gas(sample) compared with arch of air (base) is small. Diameter of this arch indicates resistance, or inverse of sensitivity (S) of reaction on interface, which means decreasing of resistance by NO_x reaction. A deference of this diameter is sensitivity (S). Moreover, equal deference between of NO and NO_2 maintains linear relationship against logarithm of NO_x concentration. Comparison of NO_x sensitivity on mixed potential and impedance was shown in Figure 13. While the signal of NO and NO_2 is revers in mixed potential type, the same direction in impedance with equally-sensitivity. This result indicates that electrode catalyst to convert to NO_2 from NO is necessary in case of mixed potential type, but not necessary in the case of impedance type.

Study of electrolyte gas sensor since 2000s was shown in Table 2.

Table 2. Study of Solid state electrolyte gas sensor since 2000s

method	Electrolyte	SE	Detection			Reference
			gas	concentration	temperature	
Current type	NASICON	WO_3+Pt	NO, NO_2	0.1 – 1 ppm	150 °C	61
	$2\text{Na}_2\text{O}-11\text{Al}_2\text{O}_3$	Au, Pt	NO_2	30 – 120 ppm	300 °C	62
Mixed potential type	YSZ	NiO, CuO	NO, NO_2	100– 500 ppm	700 °C	63
	YSZ	NiO+Au	C_3H_6	400 ppm	600 °C	64
	ACP	Pt/CB	CO CO ₂	400– 1000 ppm 400–2000 ppm	21 °C 30 °C	65
	YSZ	$\text{SnO}_2, \text{Cr}_2\text{O}_3$	CO, H ₂	50 – 100 ppm	450–700 °C	66
	YSZ	$\text{Ta}_2\text{O}_5, \text{ZnO}$	H ₂	100 – 400 ppm	500 °C	67

	NASICON	Pt(nBi ₂ O ₃)	CO	1 – 300 ppm	25–300 °C	68
Impedance type	YSZ	ZnCr ₂ O ₄	NO,NO ₂	50 – 400 ppm	600–700 °C	69
	YSZ	In ₂ O ₃	H ₂ O	70 – 30000 ppm	500–900 °C	70
	YSZ	ZnO	C ₃ H ₆	0.05 – 0.8 ppm	600 °C	71
	YSZ	Pt-WO ₃ ,ZrO ₂	NO,NO ₂	10 – 570 ppm	500 °C	72
	PYSZ, FYSZ	NiO,NiCr ₂ O ₄	NO,NO ₂	100 – 1000 ppm	550–620 °C	73
	YSZ	La _{0.8} Sr _{0.2} MnO ₃	NO ₂	50 – 800 ppm	500 °C	74
	LiSiPO	Li _{1-δ} Mn ₂ O ₄	CO ₂	1000-10000ppm	450 °C	75

YSZ : Yttria-Stabilized-Zirconia

2.2.2. Catalyst-combustion sensor

Catalyst-combustion sensor uses the detection method utilized the heat of reaction with gas on catalyst. A detector with this sensor was in particle use for flammable gas in England of the 1920's. However, it was not spread widely because of its high cost and large content. A gas leak alarm for household use has been developed to detect liquefied petroleum gas (LPG) in Japan of the 1960's, and has been become widely used. The structure of catalyst combustion gas sensor used in household was shown in Figure 14 (a).⁷⁶ Gas detection sensor was covered with noble metal catalyst such as Pt deposited on porous alumina support. This alumina was mounted on a platinum coil which works as not only sensing material, but also heater. This element was sintered and was the size of about 2 mm in length and 1 mm in diameter. Moreover, the element of Pt coil which covered with alumina without catalyst was prepared as a compensating sensor too. These elements were mounted on an insulated substrate as a pair device. This device was continuously heated upto about 523 – 723 K though current was passed to Pt coil. When gas reaches to element, it reacts on Pt coil. Combustion rate is high on Pt coil with catalyst, while is low on Pt coil without catalyst. This sensor detects the voltage by difference of combustion heat between Pt coil with catalyst and Pt coil without catalyst as compensating elements. Wheatstone bridge circuit as shown Figure 14 (b) was used for this sensing.⁷⁷ Resistance of the detecting and compensating

element is R_b and R_w , and R_0 is fixed resistance. The potential is maintained on equilibrium, because of resistance of R_b and R_w in air is equal. When combustion gas contacts on Pt coil, the R_b increases because of combustion heat is gave off by gas reaction, and potential difference (E) evolves.

$$E = U_0 \times \left[\frac{R_s + \Delta R}{R_s + R_w + \Delta R} - \frac{R_1}{R_1 + R_2} \right] \quad (16)$$

U_0 is bridge voltage, ΔR is variance of R_b , R_1 and R_2 is resistance on between of r - s point and q - s point. $R_1 \times R_w = R_2 \times R_s$ is satisfied on bridge circuit. Equation (17) is set based on this equilibrium. The (16) can replace to (18) by assignment of (17).

$$I_0 = \frac{R_2}{(R_1 + R_2) \times (R_s + R_w)} \quad (17)$$

$$E = I_0 \times U_0 \times \Delta R \quad (\Delta R \ll R_s, R_w) \quad (18)$$

The E and ΔR by eq. (18) is proportional. Moreover, ΔR can set following (19).

$$\Delta R = \lambda \times \Delta T \quad (19)$$

ΔT is temperature difference by combustion heat, λ is temperature coefficient on detecting element.

Stuies of catalyst-combution gas sensor since 2000s are summerized in Table 3. Recently, a new type sensor used MEMS processing technology was studied instead of coil electrode type.

method	Catalyst	Detection			Reference
		gas	concentration	temperature	
Coil electrode type	SnO ₂ -In ₂ O ₃ -TiO ₂ (dopant: Pd, Al, Si)	CH ₄	200 – 1000 ppm	650 °C	78
	Pt-Pd/n-Ce-Al ₂ O ₃	CH ₄	400 – 10000 ppm	600 °C	77
MEMS type	Pd/γ-Al ₂ O ₃	VOCs	10 – 1000 ppb	200–400 °C	79
	Pt/γ-Al ₂ O ₃	H ₂	10 – 40000 ppm	100 °C	80
	Au-Pd/γ-Al ₂ O ₃	Ethanol	10 – 1000 ppm	450 °C	81

		Tolene n-Hexane			
--	--	--------------------	--	--	--

Table 3. Study of catalyst-combustion gas sensor since 2000s

2.2.3. Semiconductor sensor

The element of this sensor was fabricated by mainly n-type semiconductor material, particularly ZnO or SnO₂ was used widely. The resistance of that kind of materials is differentiated by changing partial pressure of oxygen and reductive gases.^{3,4} This type's gas sensor has been studied by Seiyama et al. in 1960's.^{82,83} Taguchi et al. proposed the gas leak alarm using this type^{84,85} The semiconductor sensor type developed by Taguchi has been become widespread since in practical use as TGS 109 from Figaro Co. Ltd. in 1970's.

Figure 15 (a) shows SnO₂ semiconductor type sensor proposed from Figaro Co. Ltd..⁸⁶ The element composed by SnO₂ was sintered between two Ir-Pd alloy wire electrodes. One electrode is heater, another is sensing the conductivity variance of SnO₂. Gases is reacted with oxygen adsorbed on SnO₂ surface varying conductivity at the temperature range of 300-673K applied by heater, and the variance depends on concentration gases (C). Relation between C and resistance (R) can express by eq. (20).

$$\log \frac{R_a}{R_g} = a + b \log C \quad (20)$$

R_a is resistance in air, R_g is resistance in reductive gases, a and b is constant. The b takes 0.3 or 0.5 defined experimentally, respectively. The a leads ratio R_a/R_g, corresponds approximately to sensitivity when C is 1. Figure 15 (b) shows electrical measuring circuit. V_C gives circuit voltage, V_H gives heater voltage. Resistance (conductivity) variance by the gas reaction was measured as a change in the voltage (V_{RL}) across load resistance (R_L).

Studies of catalyst-combustion gas sensor since 2000s were shown in Table 4.

Table 4. Study of semiconductor gas sensor since 2000s

Sensing type	Sensing Material	Additive	Detection			Reference
			gas	concentration	temperature	
N type	SnO ₂	Ti	CO	1500 – 2500 ppm	350 °C	87
		In	H ₂	100 – 40000 ppm	25 – 50 °C	88
		PdO	CO	200 ppm	300 °C	89
		Pt, Pd, Au	CO, H ₂	10 – 100 ppm	400 °C	90
			NO ₂	0.05 – 5 ppm	200 °C	
			CH ₄	5000-25000 ppm	470 °C	
		Mg	LPG	1000 ppm	350 °C	91
	WO ₃	Ag	SO ₂	800 ppm	450 °C	92
		Pt, Au, PtAu	H ₂ S	1 ppm	220 °C	93
		Pt, Cr	NH ₃	74 ppm	225 °C	94
		Fe	CO	100 – 1000 ppm	150 °C	95
		Ag	NO	2 – 15 ppm	150 – 250 °C	96
	ZnO	In	NO ₂	5 ppm	275 °C	97
		CeO ₂ (mixed)	CO	10000 ppm	380 °C	98
		Ti	Ethanol	50 – 1000 ppm	260 °C	99
		Pd	LPG	1500 – 5200 ppm	300 °C	100
		Pd	NH ₃	5 – 100 ppm	210 °C	101
		Ce	Acetone	10 – 2000 ppm	230 °C	102
	TiO ₂	MoO ₃ (mixed)	CO	25 – 400 ppm	300 °C	103
			NO ₂	0.5 – 2 ppm		
		–	NH ₃	500 – 1000 ppm	230 °C	104
		–	CO	1 – 25 ppm	200 °C	105
P type	TiO ₂	Cr	NO ₂	3 ppm	400 °C	106
				4 – 50 ppm	500 °C	107
P-N junction	SnO ₂	CuO	H ₂ S	250 – 2500 ppm	150 °C	108
	TiO ₂	CuO	CO, CH ₄	200 – 1000 ppm	600 °C	109
		NiO	CO	500 ppm	300 °C	110
			NO ₂	1 ppm		
			NH ₃	2 ppm		

2.3. Sensing mechanism of semiconductor sensor

2.3.1. Electronic surface states and depletion charge layers^{3,4}

The n-type semiconductor sensor detects the decrease of resistance by oxygen desorption react with a reductive gas against high resistance state by oxygen adsorption. Figure 16 shows energy schematic of n-type semiconductor. Conduction band (E_C) and valence band (E_V) is separated by energy gap (E_g) with form of Fermi level (E_F) as max level to occupation of Fermi particle (electron etc.) and donor level (E_D), occupied by electron, which expressed in chapter 2.1. Energy band near surface is modified by state on surface of semiconductor. It will occur by defects on surface or absorption/desorption of various molecules and ions which may form bond or dipole on surface. The charge transfer from molecule to the surface is occurred when molecules adsorb on the surface. Electric double layer on surface is formed by electron on conduction band which was named as space charge layer. Figure 17 shows the schematic of space charge layer. When surface is negatively charged by oxygen ion etc, the number of ionized donors is increased, and space charge layer spreads. On the other hands, when surface is positively charged by hydrogen ion etc, localized electron on surface increases. The depth to z vector of this space charge layer was estimated about $10^{-6} - 10^{-4}$ cm. Conductivity variation appears in result of change of this space charge layer by change of electron concentration. Eq. (21) is change of electron concentration (ΔN). Figure 17 (c) shows schematic of $n(z)$.

$$\Delta N = \int_0^{L_D} [n(z) - n_B] dz \quad (21)$$

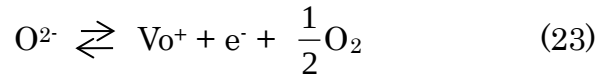
L_D is depth of space charge layer. Moreover, surface conductivity variation ($\Delta\sigma$) was defined as eq. (22).

$$\Delta\sigma = e \times \mu_s \times \Delta N \quad (22)$$

μ_s is surface mobility, e is elementary charge. $\Delta\sigma$ can express as difference of ΔN by the chemisorption which induce binding energy.

Because of $\Delta\sigma$ decreasing ΔN , identity of chemical state of oxygen adsorption is important. Yamazoe et al. has forecasted on the adsorption state of oxygen on the calcined powder SnO_2 surface (500 °C, 10h) by desorbing temperature of oxygen using TPD

(Temperature-Programmed-Desorption).¹¹¹ The sample was exposed to oxygen of 100 Torr at 600 °C following evacuation at the same temperature as pretreatment in apparatus. Then the sample was cooled to the three different temperatures, under oxygen atmosphere. TPD curve in Figure 18 was measured. When oxygen was adsorbed at RT after vacuum treatment, peak (α) around 100 °C was observed. On the other hand, peak α_1 (80 °C) and α_2 (150 °C) were appeared after adsorbed at 155 °C and RT, respectively. Moreover, samples treated at 400 °C in various oxygen pressure have peak near 520 °C (β and γ), and the intensity decreases corresponding to decreasing of oxygen pressure. They has identified by ESR (Electron Spin Resonance) that oxygen chemical state of each peaks is O^2 in α_1 , O_2^- in α_2 , O^{2-} in β and lattice oxygen into SnO_2 in γ . In particular, relation between this O^{2-} and defects on surface may be importance for gas reaction. Heiland has referred about equilibrium the defect diffusion at high temperature and O^{2-} under oxygen pressure (p).² He described following formula about thermal decomposition on surface, and proposed an exponent of oxygen pressure is -1/4. Vo^+ is defect on surface.



At equilibrium with $e^- = [n]$

$$[Vo^+] \times n \times p^{1/2} = \text{const} \quad (24)$$

With neutrality condition of $n \approx [Vo^+]$

$$\sigma \sim n \sim p^{-1/4} \quad (25)$$

Ohnishi et al. also studied the sensing mechanism by oxygen adsorption and desorption on SnO_2 thin film surface as shown in Figure 19.¹¹² They determined adsorbed state to be measured the electric conductivity (σ) from the carrier electron density (n) and the mobility (μ) using Hall effect.¹¹³ They reported that O^{2-} is dominant species on reaction with flammable gas, the balance between the rate of reaction A, B and C in Figure 19 is important. They propounded eq. (21) about the change of σ .

$$\frac{d\sigma}{dt} = \frac{\alpha P_G + \beta}{\sigma} - \gamma \sigma$$

$$(26)$$

P_G is flammable gas concentration, P_{O_2} is oxygen concentration, $\alpha = e^2 \times \mu^2 \times 2k_A \times K_{AO}[O^2]$, $\beta = e^2 \times \mu^2 \times 2k_B \times K_{BO}[O^2]$, and $\gamma = 4k_C \times P_{O_2}$.

Equation (27) for changing from pure air to flammable gas and (28) for changing from flammable gas to pure air was got by solving eq. (26).

$$\sigma^2 = \sigma_g \times (1 - \exp(-2\gamma t)) \quad (27)$$

$$\sigma^2 = \sigma_g \times \exp(-2\gamma t) + \sigma_{air}^2 \quad (28)$$

The σ_g is conductance in flammable gas, the σ_{air} is conductance in air.

SnO_2 layer is formed by a few nm to um sized polycrystalline domains. In SnO_2 thin film, the thickness of the whole film or the whole one grain does not exceed the extension of space charge layer.

2.3.2. Electric conduction mechanism

Shimano and Yamazoe have referred importance of three factors for enhancement of gas sensitivity as shown in Figure 20.¹¹⁴

(I) Receptor factor

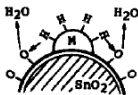
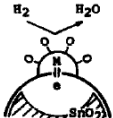
Receptor factor effects to sensitization of SnO_2 surface by dispersion of high activity material to SnO_2 surface. Yamazoe et al has studied the effects of additives on SnO_2 gas sensors. Figure 21 is sensitivity property for Pt- SnO_2 , Pd- SnO_2 and Ag- SnO_2 , and Table 5 is summary with involvement of other material. Sensitivity of SnO_2 with Pt, Pd, or Ag is higher than that of SnO_2 without additives. Two mechanism types about the enhancement by additive have proposed as shown in Table 6.¹¹⁵ One is chemical sensitization mechanism. This mechanism is explained by spillover effect of additive. The additive as promoter activates various gas to facilitate reaction on surface of SnO_2 . In the case, the promoter does not involve to change of resistance directly. This effect often appears in Pt etc. Another mechanism is electric sensitization by a direct electronic interaction between the additive and surface of SnO_2 . Change of state by oxidation or reduction reaction on the acceptor with surrounding atmosphere leads to change of resistance of SnO_2 , because of the electronic junction is formed

between the promoter and SnO_2 . This type often appears in PdO or Ag_2O . Figure 22 shows the electronic interaction of $\text{Ag}_2\text{O-SnO}_2$.⁵ The E_F of SnO_2 is pinned by the Ag^+ electrode potential of -5.3 eV under oxidation atmosphere, and the space depletion layer is formed. When it is exposed by reduction gas, E_F of SnO_2 shift up which is pinned at working function of Ag^+ (4.5 eV) because of state of Ag^+ changes to Ag^0 .

Table 5. Summary of sensitivity to the various additives [ref. 5]

Additive	0.02% CO	0.8% H_2	0.2% C_3H_8	0.5% CH_4
none	4 (200)	37 (200)	49 (350)	20 (450)
Mn (2.0%)	1	3 (300)	3 (300)	2 (450)
Co (2.0%)	1	3 (300)	2 (300)	2 (400)
Ni (2.0%)	7 (150)	169 (250)	67 (300)	9 (350)
Cu (0.5%)	7 (150)	98 (300)	48 (325)	20 (350)
Ru (0.5%)	2 (150)	63 (150)	67 (150)	3 (300)
Rh (2.0%)	1	11 (150)	4 (200)	3 (300)
Pd (0.5%)	12 (RT)	119 (150)	75 (250)	20 (325)
Ag (0.5%)	8 (100)	666 (100)	89 (350)	24 (400)
Pt (0.5%)	136 (RT)	3600 (RT)	38 (275)	19 (300)
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (2.0%)	34 (100)	184 (250)	71 (250)	9 (350)

Table 6. summary of additive effect. [ref. 115]

Type	Chemical	Electronic
Model		
Role of noble metal	Activation and spill-over of sample gas	Electron donor or acceptor
Origin of gas-sensitive properties	Change of adsorbed oxygen concentration	Change of oxidation state of noble metal
Example	Pt-SnO ₂	Ag ₂ O-SnO ₂ , PdO-SnO ₂

(II) Transducer factor

The sensing materials of SnO_2 or ZnO has a lot of joint parts named as neck shown as X in Figure 23 (a), because of these materials are the sintered ceramics body and particulate aggregation. Conductivity in particle can express in this X and crystallite size (D). Yamazoe et al., has reported

crystallite size (D) effect for gas sensitivity ($S = R_a/R_g$) as shown in Figure 26.^{115,116} Moreover, they have studied effect of the D for gas sensitivity of un-doped and doped SnO₂. Depth of space charge layer (debye length : L_D) can control by displacement at other atoms of cation in n-type semiconductor (Sn⁺⁴ in case of SnO₂). When the crystallite size (D) is 19 nm, it has high sensitivity in displacement at Al⁺³, while has low sensitivity in displacement at Sb⁺⁵. They have expressed these phenomena with L_D . In fact, L_D for Al-doped SnO₂ and pure SnO₂ was estimated about 90 nm and 3 nm, Sb-doped SnO₂ was estimated in lower value by measurement of Seebeck coefficients. They proposed the changing model of electron concentration in particle about relationship between S, D, X and L_D as shown in Figure 23. Electron concentration (n_e) is constant as $n_L(a)$ under air and $n_L(g)$ under gas in space charge layer, n_0 in center of particle. Following formula (29) about sensitivity was proposed based on this model.

$$S = \frac{R_a}{R_g} = \frac{(x-1)^2 + \frac{n_L(g)}{n_0} [x^2 - (x-1)^2]}{(x-1)^2 + \frac{n_L(a)}{n_0} [x^2 - (x-1)^2]} \quad (29)$$

where $x = 2L/X$. Neck size (X) was founded as approximately $X = 0.8 \times D$. Figure 23 (c) shows relationship between S and $X/2L$ in various $n_L(g)/n_L(a)$, a n_0/n_L was fixed. It describes that sensitivity drastically increases when $X \leq 2L$, so that means that proportion of particle size and space charge layer is for less than 2. Figure 24 shows the relationship between D and 2L. In $D \gg 2L$, conductance channel is wide though neck. Thus grain boundary parts control electrical resistance for gas sensitivity (S), where S is small as region of $X > 2L$ as shown in Figure 23 (c). When $D > 2L$ where space charge layer expands, neck parts control resistance. Finally, the space charge layer expands in whole of grains, when $D < 2L$. Grains share whole resistance, and controls S. They expressed that $n_g(r)/n_a(r)$ increases with decreasing of r, because of electron concentration in gas (n_g) and in air (n_a) inside space charge layer depends on distance (r) from surface.

Conductance between grains by Weimar et al., has been generally expressed as change of a double schottky barrier height (qV_s) formed by change of space charge layer under gas or air as shown in Figure 25.¹¹⁷ Recently Yamazoe et al., has proposed new conduction model.¹¹⁸ They have studied temperature property of resistance under various oxygen pressure of

SnO₂ film formed using spin coat or dip method which give no external force as shown in Figure 26. They represented that resistance is constant regardless of oxygen pressure in range of 150 °C-400 °C. Moreover Ippommatsu et al., has reported that electrical conductance doesn't change depending on temperature or atmosphere by hall measurement of thin film SnO₂ had average grain size of 20 nm. From here onwards, they proposed tunneling conduction model as shown in Figure 27, and was clear that the tunnel probability for electron is high with increasing of electron potential (E).

(III) Utility factor

Actual element is aggregate of secondary particle constructed by primary particle. Gas enters from surface of element, and diffuses to inside according to Molecular diffusion in macro-pore, Knudsen diffusion in meso-pore, surface diffusion in micro-pore. Yamazoe et al., has been examined this behavior of gas diffusion from point of both Knudsen diffusion and surface diffusion (distinction between two diffusion is cloud) using SnO₂ thin film (thick is 80-1000 nm) with grains of 20 nm in diameter.¹¹⁹ Knudsen diffusion is showed by eq. (30).

$$D = \frac{4r}{3} \times \sqrt{\frac{2RT}{\pi M}} \quad (30)$$

D is diffusion constant, r is pore size, R is gas constant, T is temperature, M is molecular weight. When elements are exposed in gas (A), diffusion equation (31) holds in attempt both Knudsen diffusion and surface diffusion.

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2} - k C_A \quad (31)$$

C_A is concentration of gas, t is time, x is depth from surface and k is rate constant. When state is steady, because of $\partial C_A / \partial t = 0$, general solution is eq. (32).

$$C_A = C_{A,s} \times \frac{\cosh\left((L-x) \times \sqrt{\frac{k}{D}}\right)}{\cosh\left(L \times \sqrt{\frac{k}{D}}\right)} \quad (32)$$

This equation shows that concentration of gas in film can indicate at D , k and L . Here $C_A = C_{A,s}$ at $x = 0$ on surface, $\partial C / \partial x = 0$ at $x = L$ on bottom of film. Figure 28 is distance dependence of diffusion concentration for gas ($C_A / C_{A,s}$) simulated from eq. (32) where film thickness is constant as $L = 300$ nm. When k/D is small, $C_A / C_{A,s}$ is about 1. $C_A / C_{A,s}$ decreases as k/D increase. This means the penetration depth of gas becomes small as k/D increases, the particle of inside of film contributes in no change of resistance. In particular, when gas molecular weight is large, D tends to small. Structure was reached gas till inside of film to take high sensitivity is importance, thickness is thin as possible, secondary particle is small, meso-pore is large, etc.

Ippommatsu et al., has been attempted investigation of the SnO_2 thin film using a sputtering technique for optimization of structure.¹²⁰ The TEM (Transmission Electron Microscope) for the SnO_2 thin film by sputtering method and sintered body of SnO_2 by TGS 109 made in Figaro. Co., Ltd. as shown in Figure 29. The SnO_2 thin film has column of 40 nm (primary particle size is 3 – 10 nm), while sintered body is aggregation of secondary particle by size of 20 - 40 nm. Gas until inside of SnO_2 for this equal column structure can diffuse. Moreover, a heat transfer to whole of SnO_2 is the superiority.¹²¹ Recently, Nonaka et al., reported about a long stability during using for this SnO_2 thin film.¹²²

3. Application of MEMS technique and application of Pt doped SnO_2

3.1. Application of MEMS technique

In order to increase the number of home-use gas sensor, battery-driven type or wireless models are important for their good appearance and their free installation. The battery-driven sensors should have longer life time than 5 years and thus the low power consuming sensors has to be developed with high selectivity for methane, which is a main ingredient in natural gas. From this standpoint of view, Suzuki et al. have developed SnO_2 thin film produced by MEMS (Micro Electro Mechanical Systems) method.^{7,8} The cross section of MEMS sensor by semiconductor type was shown in Figure 30. It has the layer structure of $\text{Pd-Al}_2\text{O}_3$ catalytic thick film/ SnO_2 thin film/Pt electrode/Thin film heater. $\text{Pd-Al}_2\text{O}_3$ is to enhance selectivity to gas other than methane. Recently we found that the Pt doping increases methane

sensitivity of SnO₂ thin film sensor device which will provide the new pathway to realize a low power consumption gas sensor with long life time.¹²³ The sensor can detect the 12500 ppm methane which is a 1/4 of the methane explosion limit (53000 ppm) even after the 5 years.

Recently, MEMS technique was also applied to catalyst combustion type sensor as shown in Table 3.

In this paper, I will discuss the Pt-SnO₂ thin film and its mechanism. First I need to clarify the structure of the sensor. However it is quite difficult to obtain the local structure of Pt in the SnO₂ gas sensors because it does not have long range order and diffraction techniques could not be applied. In this paper, I applied X-ray absorption fine structure(XAFS).

3.2. Pt-SnO₂ thin film gas sensor

I found as shown that the 5-9 at % Pt doping SnO₂ increases methane sensitivity of SnO₂ thin film sensor device which is layer structure will provide the new pathway to realize a low power consumption gas sensor with long life time.¹²⁴ Since Pt metallic cluster is a good catalyst for many reactions including the hydrogen and hydrocarbon oxidation reaction. There are several mechanisms to improve the sensor performance by the additives. One is an electronic effect and the other is a spillover effect. Yamazoe and Kocemba et al reported that Pt nanoparticles on the SnO₂ surface improve the performance by the spillover reaction.^{115,125} Thus Pt clusters deposited on the SnO₂ were expected to enhance the sensor sensitivity by the spillover reaction. In the previous papers about the characterizations of Pt-SnO₂ sensor, the oxidized Pt or Pt aggregates are present in SnO₂ substrate depending on the atmosphere and Pt concentration.^{3,126,127,128,129} On the other hand EXAFS techniques on the real gas sensor have suggested a quite different model where the Pt ion is located at the Sn position in the rutile structure on Pt-SnO₂.^{130, 131} However the information derived from the EXAFS was limited to the concentration as low as 0.2 wt% which is lower than the Pt content in our highest performance sample. In order to reveal the structure of Pt-SnO₂ and its mechanism for high performance, I carried out comprehensive studies on Pt-SnO₂ thin film in a wide concentration range using characterization techniques conventional fluorescence extended X-ray absorption fine structure (EXAFS) analyse in addition to structure analyses

such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), suggesting a different activation mechanism from spillover model or charge transfer model took place in the cosputtered Pt-SnO₂ thin film system.

4. XAFS technique

When X-ray enters a material, specific energy of X-ray was absorbed depending on existing elements in the material by influence of the photoelectron effect. Figure 31 (a) shows principle of the photoelectron effect drawn by Koningsberger et al.¹³² Electron is bound to inner shell which is excited by incident X-ray ($h\nu$). Hence kinetic energy (E_k) of electron is given in formula (33)

$$E_k = h\nu - E_b \quad (33)$$

E_b is binding energy to inner shell. The X-ray absorption coefficients($\mu(E)$) reflect the change of the transition probability ($\sigma_{i \rightarrow f}$) to a vacant orbital of inner-electron indicated by formula (34),(35).

$$\sigma_{i \rightarrow f} = \sum_f \left| \langle \psi_f | \mathbf{e} \cdot \mathbf{r} | \psi_i \rangle \right|^2 \quad (34)$$

$$\mu(E) = \sum_f \left| \langle \psi_f | \mathbf{e} \cdot \mathbf{r} | \psi_i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \quad (35)$$

ψ_i and ψ_f are the wave functions of initial and finish states, $\mathbf{e}$ is polarized vector, $\mathbf{r}$ is position vector. In this formula, the dipole transition is only allowed(dipole approximation) and thus the transition of electron is regulated from s to p orbital, or p from d or s orbitals. The transition from p to s is not so large as that of s to d.

Figure 32 showed results of Pt L₃ edge XAFS. This spectral has the precipitous rise by level excitation near 11600 eV followed by damping oscillation.as shown in Figure 32 (a). This structure near edge region is called as XANES (X-ray absorption near edge structure). He following oscillation structure was called as EXAFS (Extended X-ray absorption fine structure). The peak at the edge is especially called as white line. The XANES spectra have the information about electronic state. The EXAFS

oscillation is a phenomenon due to the interference between the exited electron by incident X-ray and the scattered electron by surrounding atoms as shown in Figure 31 (b).

EXAFS oscillation is theoretically expressed as follows

$$\chi(k) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} = \sum_j S_0^2 \frac{N_j F_j(k)}{k_j r_j^2} e^{-2k^2 \sigma_j^2} e^{-\frac{2r_j}{\lambda_j}} \sin(2kr_j + \phi_j) \quad (36)$$

$$k = \sqrt{\frac{2m}{\hbar^2} (h\nu - E_o - \Delta E)} \quad (37)$$

Where S_0^2 , N_j , r_j and σ_j are amplitude reduction factor, coordination number, bond distance, and Debye Wallar factor, of j -th coordination shell, respectively. λ is a mean free path. $F_j(k)$ and $\phi_j(k)$ are backscattering amplitude and phase-shift functions which can be obtained from FEFF (ver. 8.0).^{133,134,135}

The strong penetration power of X-ray allows investigators to perform *in situ* XAFS measurement in the presence of gas phase and allows the measurements under reaction conditions to reveal catalytic mechanisms.¹³⁶

Since the XAFS is a x-ray absorption spectrum which does not require the long range order, we can measure the local structure of metal species highly dispersed in media such as impurity in solid, solute in solution, and adsorbate on the substrate surface. The XAFS is suitable technique to investigate the Pt species in SnO₂.

5. Outline of this thesis

I need clearly that why Pt-SnO₂ is enhanced sensitivity of sensor, and life time. In this thesis I have studied sensor structure applying XAFS technique, and will discuss about structure and mechanism of Pt-SnO₂ with stability under reaction conditions. Moreover I will discuss about origin of high selectivity of sensor by *in-situ* XAFS analysis. I will be following a detailed content for each chapter.

Chapter 2

A specific cell design for *in situ* XAFS cell was described in chapter 2.

Chapter 3

Chapter 3 described about the structure of Pt-SnO₂ thin film which shows high sensitivity for methane gas. Platinum concentration dependency in the catalyst was also discussed.

Chapter 4

The moisture and/or reduction gas exists mainly in the home environment is driven this sensor. I will discuss in chapter 4 about the structure of Pd catalyst under those gases and the mechanism for degradation of methane selectivity.

Chapter 5

I will discuss in chapter 5 about the stability of the structure of the Pt-SnO₂ under reduction gas(hydrogen and methane), and the mechanism to enhance sensor performance.

Chapter 6

I will conclude about this paper in chapter 6.

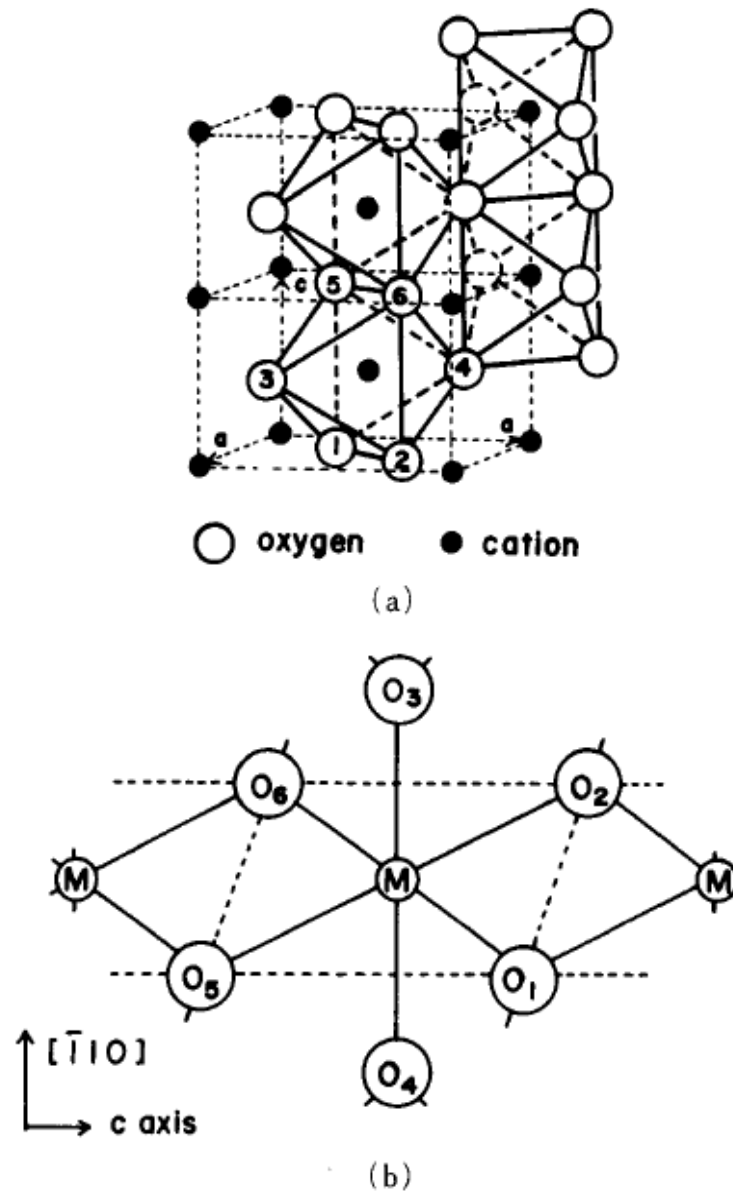


Figure 1. The rutile structure. (a) : Unit cells and parts of two columns of octahedral, (b) : Octahedron [ref. 9]

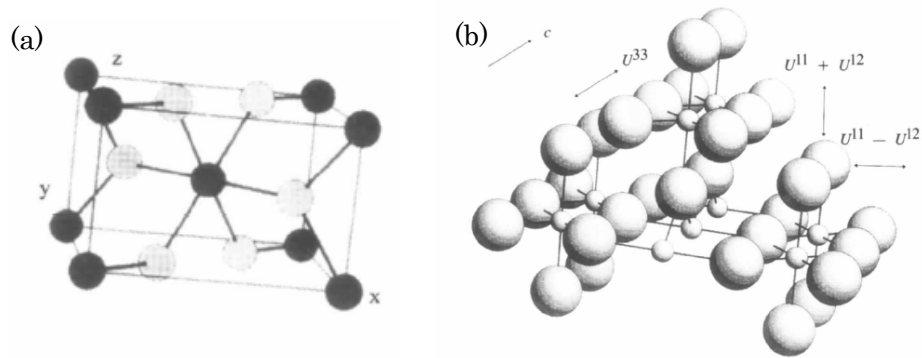


Figure 2. It is rutile structure was described by Bolzan et al. (a) as a unit cell was showed by black spheres as cation and white one as anion. (b) as a three-dimensional axes of vibration. The U^{33} is along c-axis. The small spheres is cation, big one is anion. [ref. 13]

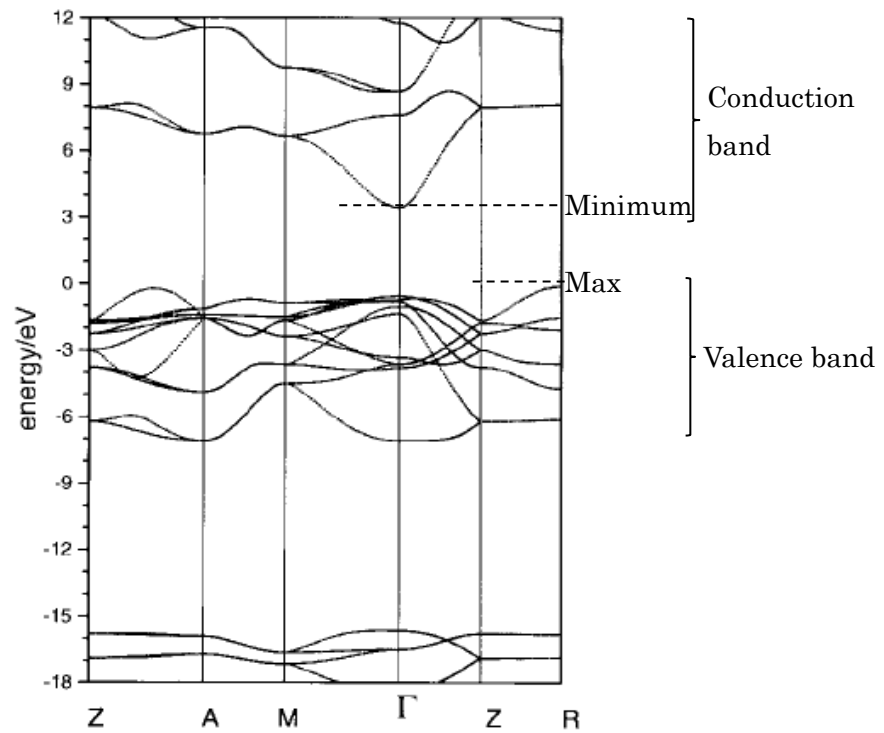


Figure 3. Band structure of SnO_2 was drawn by Barbarat et al.. [ref. 15]

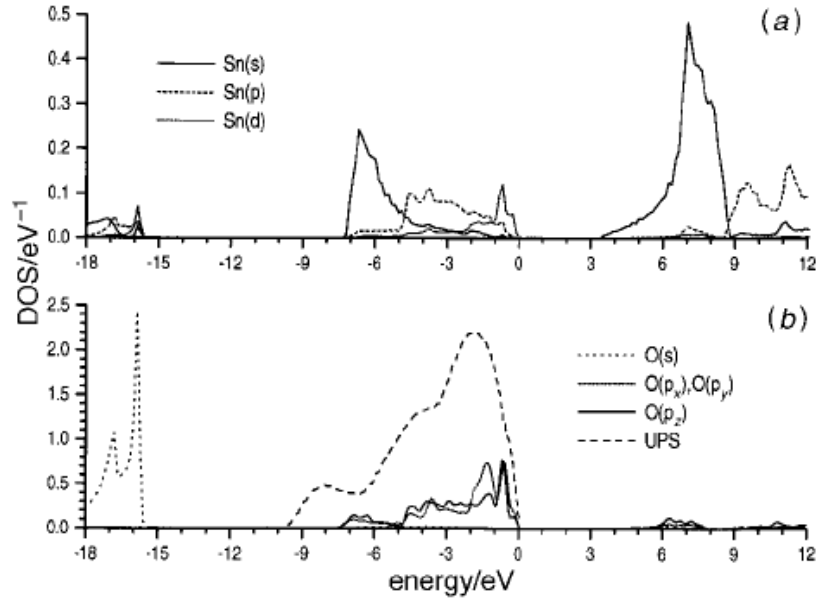


Figure 4. Partial density of state (DOS) for SnO₂ was drawn by Barbarat et al.. (a) : l-projected DOS for tin. (b): l- and Cartesian-projected DOS for oxygen with the Ultra Violet (UV) photoelectron spectroscopy (UPS) measurements . [ref. 15]

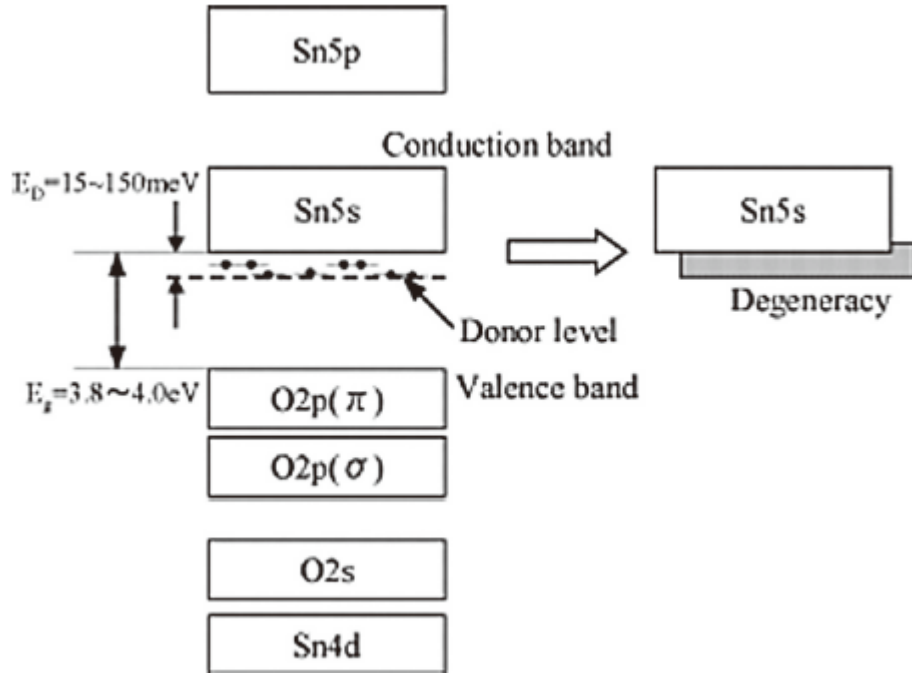


Figure 5. The band model of SnO₂ with donor level was drawn by yoneda et al.. [ref. 17]

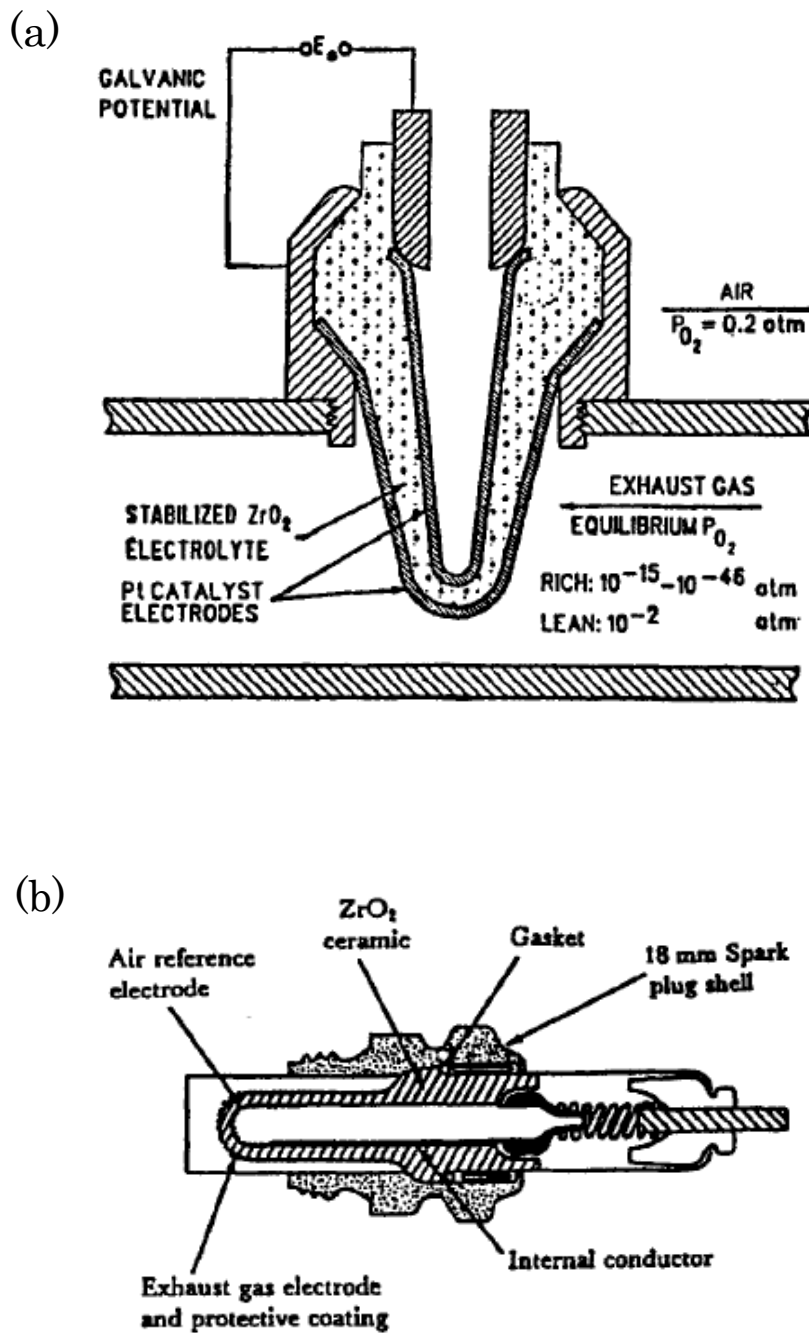


Figure 6. The graphic of a ZrO_2 oxygen sensor mounted in an exhaust pipe on (a) [ref. 51], and for an automotive sensor on (b) [ref. 52].

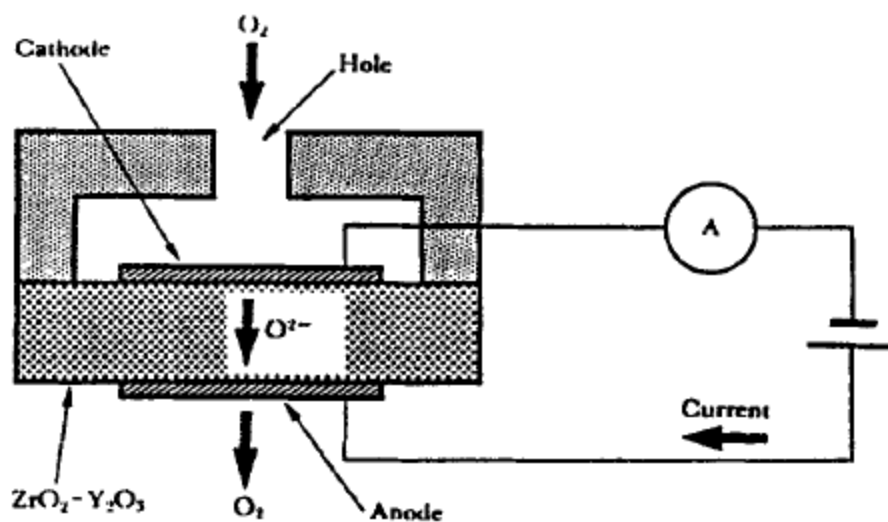


Figure 7. Structure of limiting current type oxygen sensor based on YSZ. [ref. 48]

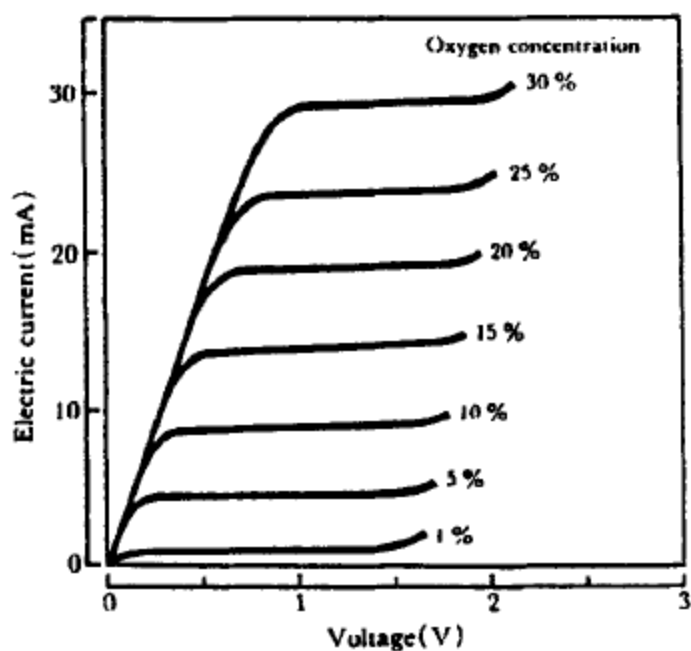


Figure 8. Characteristic of current type oxygen sensor in various oxygen concentrations in a $\text{N}_2\text{-O}_2$ mixed gas at 773 K. [ref. 54]

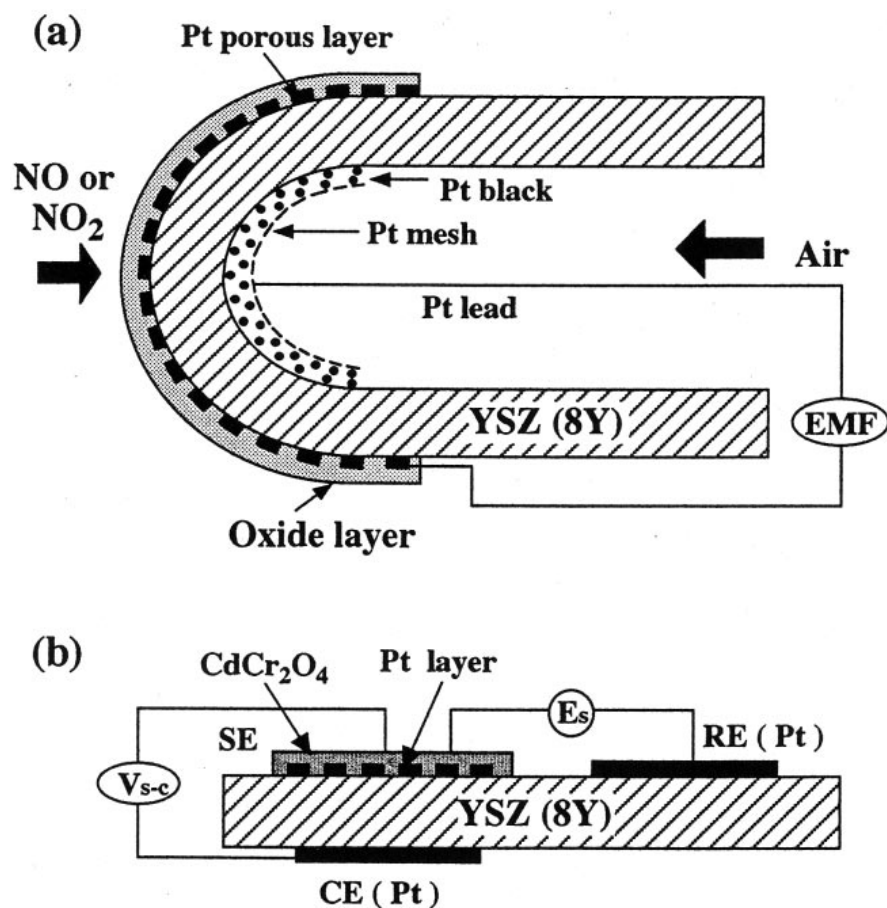


Figure 9. Structure of the NO_x sensing device (a): the mixed potential type tubular device, (b): the planar device with three electrodes. [ref. 57]

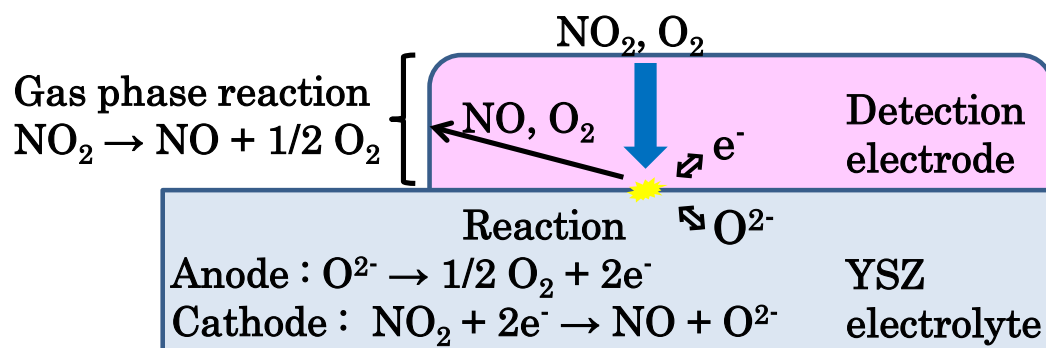


Figure 10. The sensing mechanism of mixed potential type.

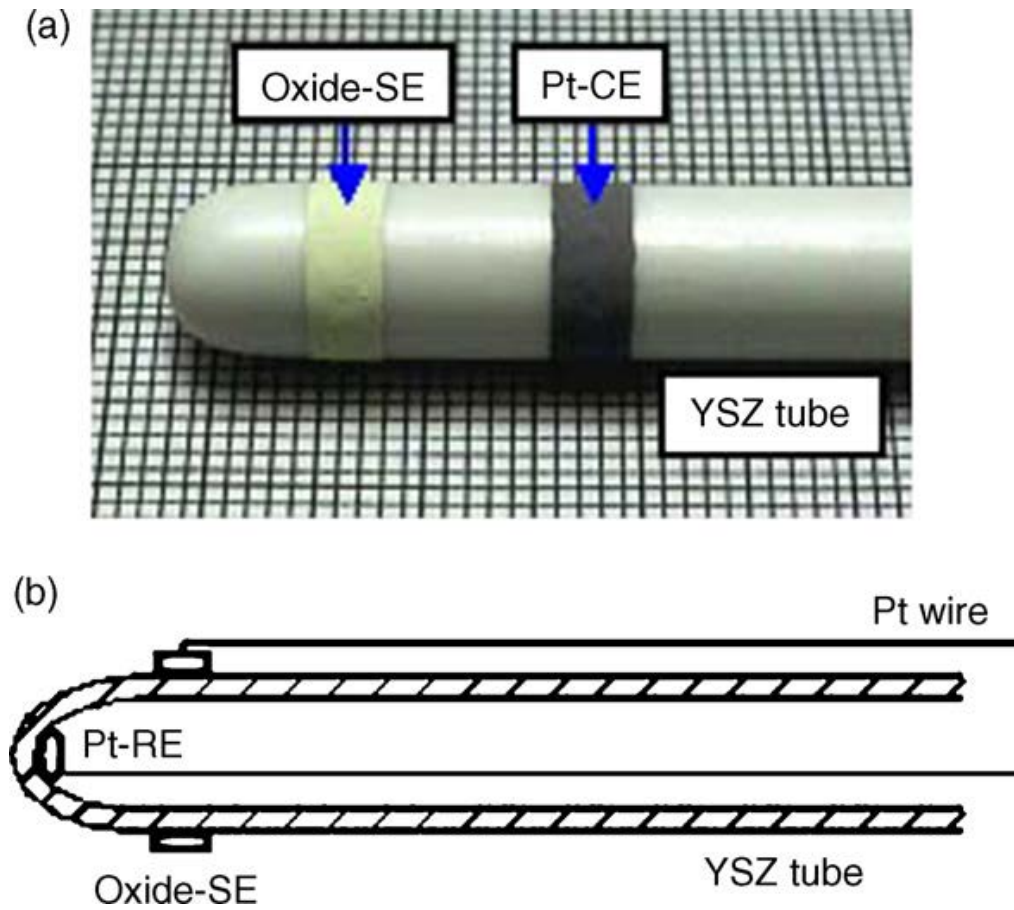


Figure 11. Structure of impedance method cell. (a): Photograph (b): Cross section. [ref. 59]

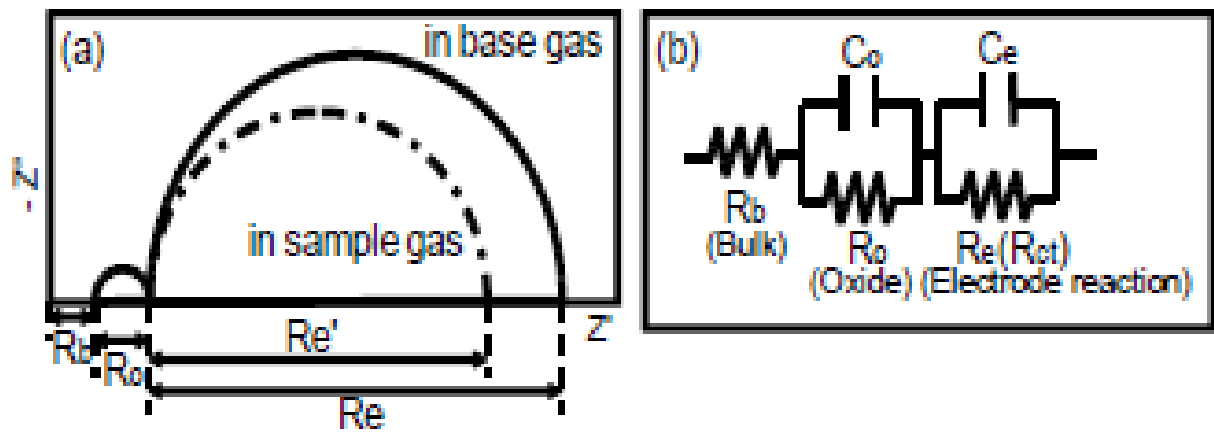


Figure 12. Nyquist plot (a) and circuit (b) of impedance type YSZ sensor. [ref. 60]

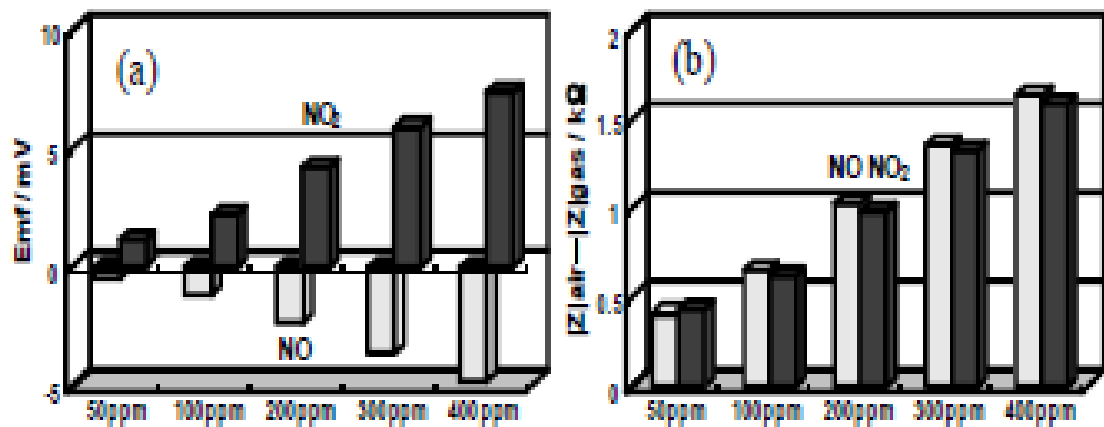
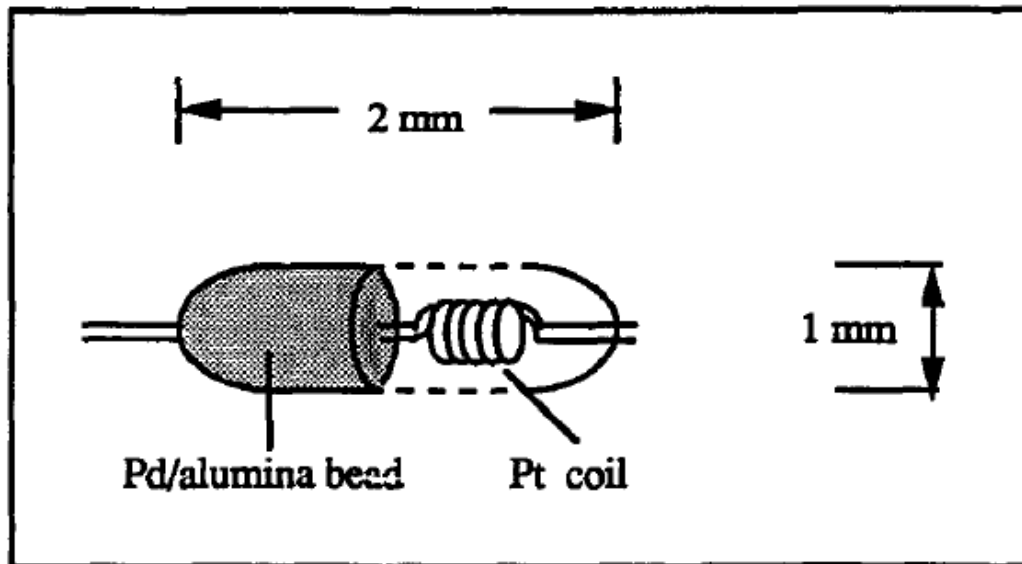


Figure 13. Comparison for sensitivity of between mixed potential and impedance type. [ref. 60]

(a)



(b)

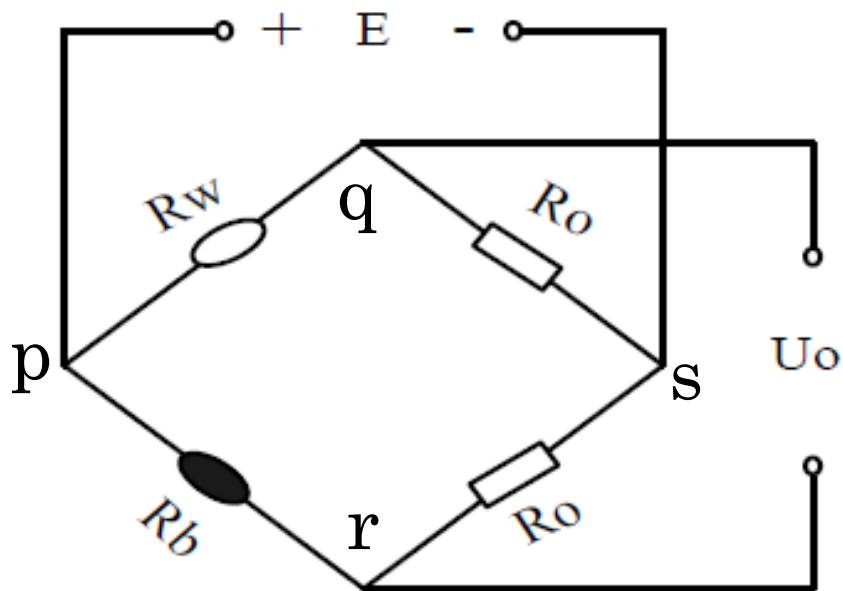


Figure 14. Structure of catalyst combustion type gas sensor (a) [ref. 76] and Wheatstone bridge circuit was used in this type (b) [ref. 77]. R_b is element to detect gas, R_w is compensating element.

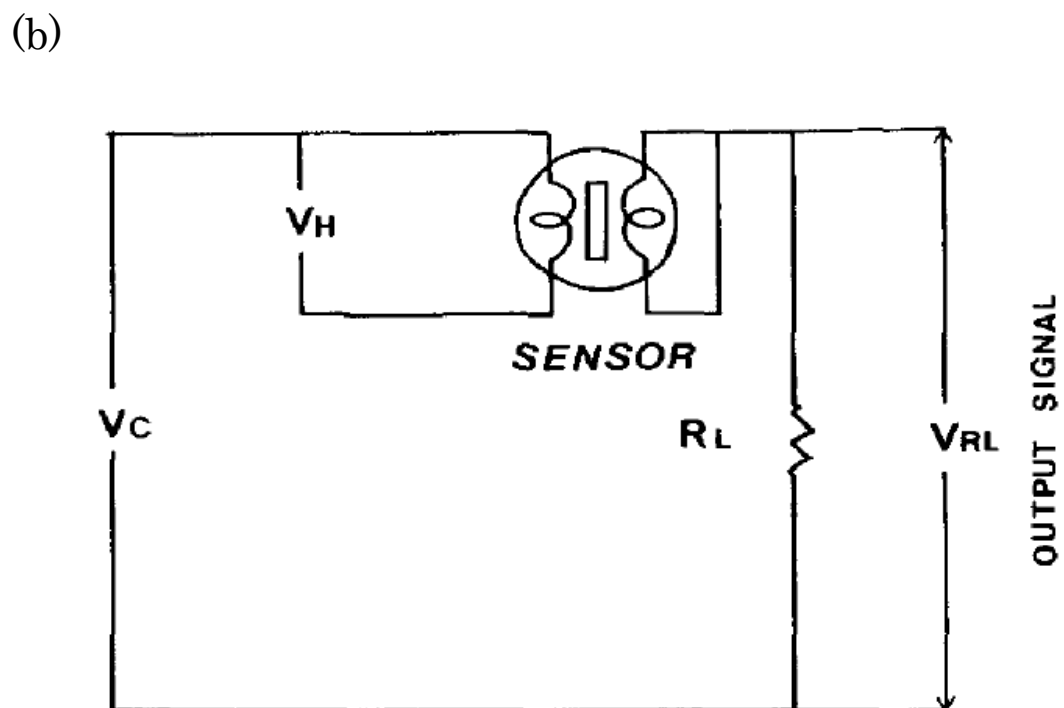
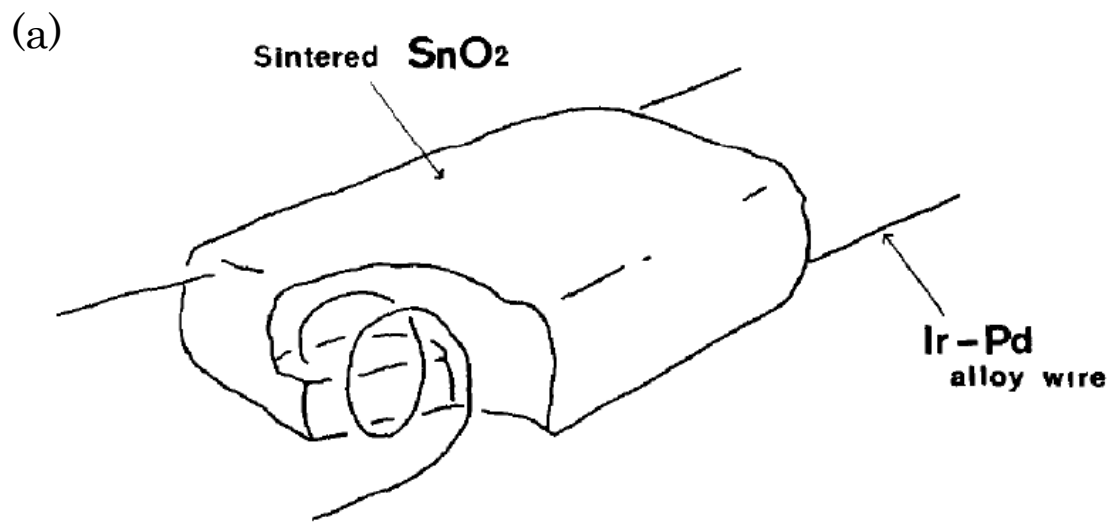


Figure 15. Structure of SnO_2 semiconductor type sensor in (a) and electrical measuring circuit in (b). V_H is heater voltage, V_C is circuit voltage, R_L is load resistance. [ref. 86]

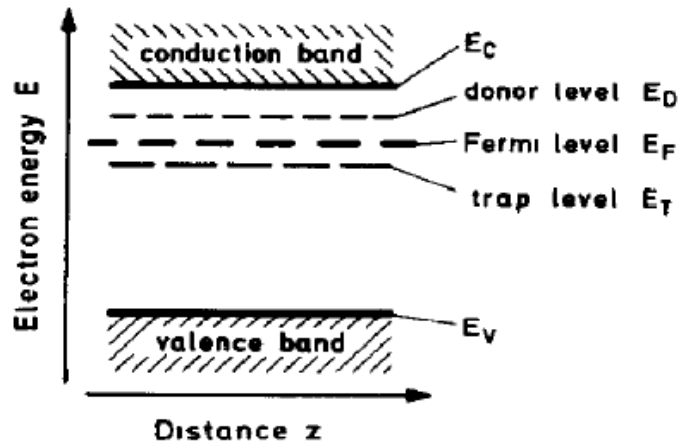


Figure 16. Energy schematic representation of flat band for bulk of n-type semiconductor. [ref. 3]

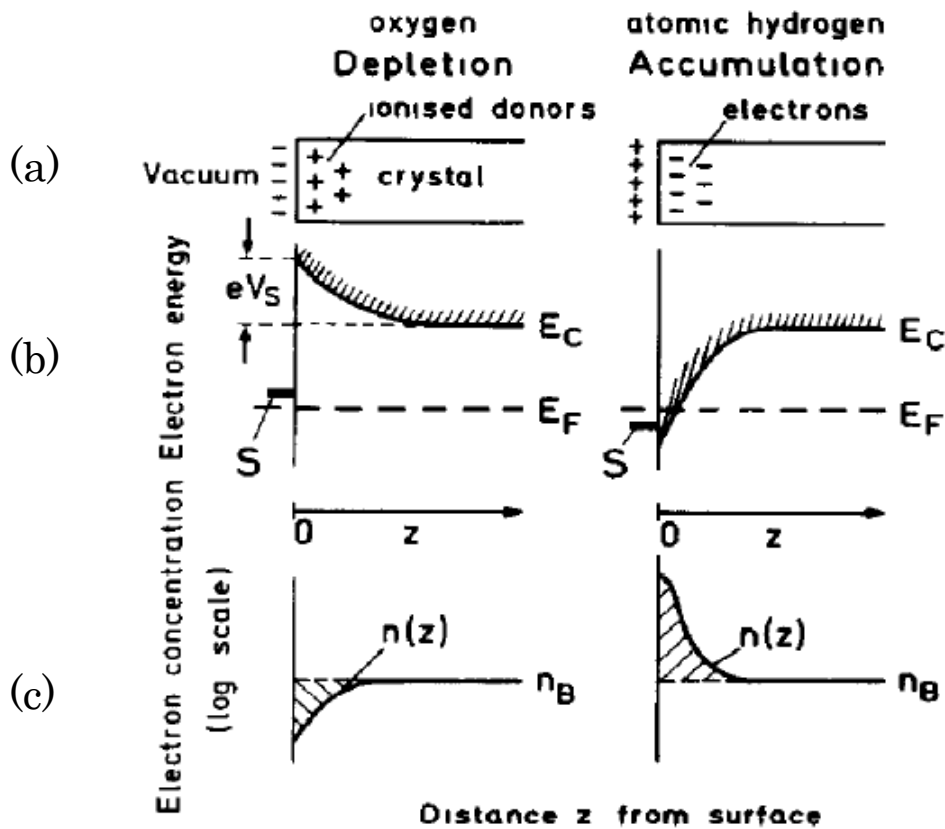


Figure 17. The change of band by gas absorption to surface of semiconductor. (a) is distribution of charges. (b) is near of conduction band. (c) is state of electron concentration. [ref. 3]

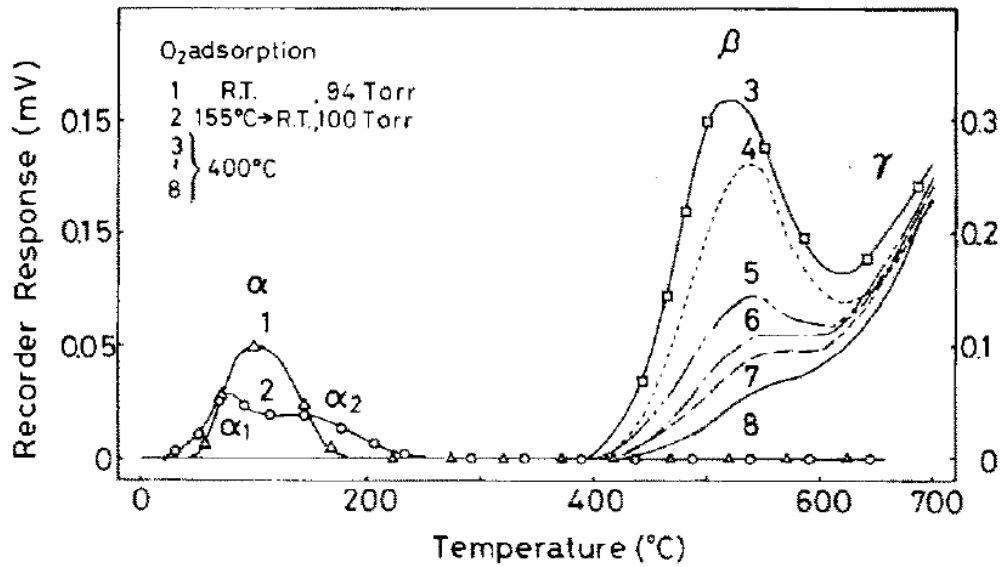


Figure 18. TPD chromatograms of oxygen of SnO_2 after oxygen adsorption under various conditions. Each sample conditions for oxygen adsorption after pretreatment is follow, Line 1 : exposure for 15 min in 94 Torr oxygen at R.T., Line2 : exposure for 15 min at 155 °C in 100 Torr oxygen following for 15 min at R.T. in 100 Torr oxygen, Line 3-8 : exposure for 15 min at 400 °C in oxygen pressure(line 3-8 : 99, 48, 16, 6, 3 and 2 Torr). [ref. 111]

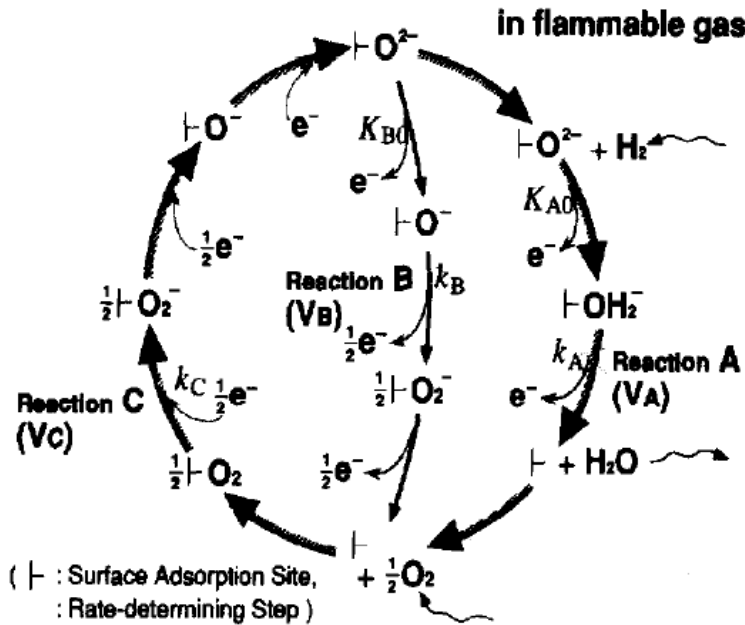
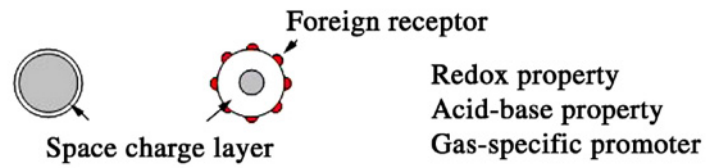
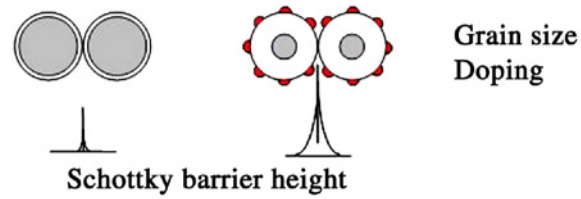


Figure 19. Sensing mechanism on surface of SnO_2 thin film. [ref. 112]

(I) Receptor function



(II) Transducer function



(III) Utility factor

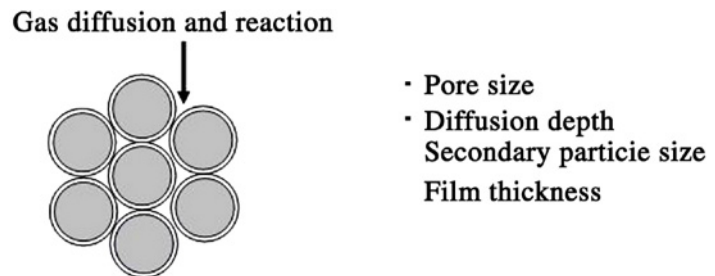


Figure 20. Factors for design of gas sensor was enhanced sensitivity. [ref. 114]

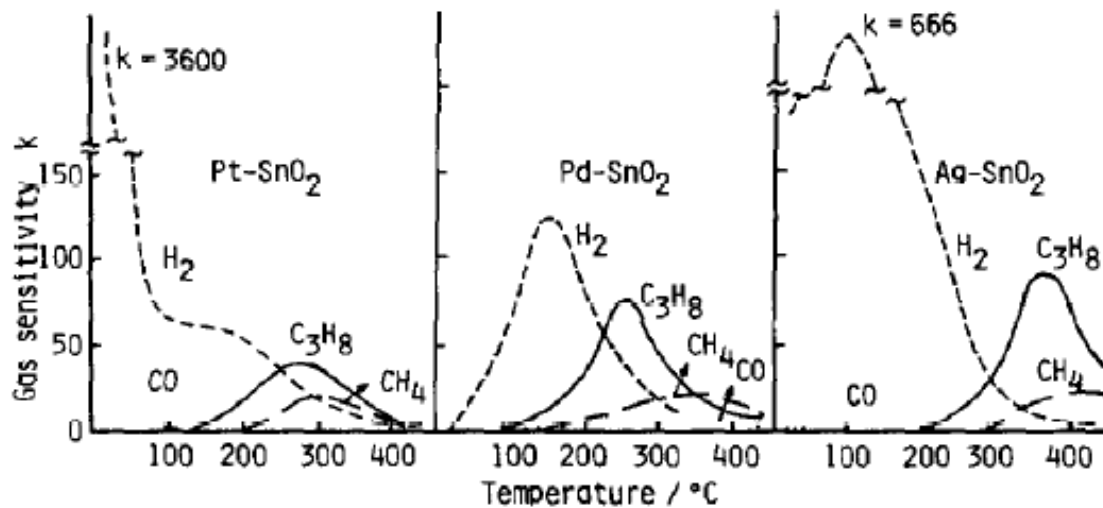


Figure 21. Sensitivity property for Pt-SnO₂, Pd-SnO₂, Ag-SnO₂. [ref. 5]

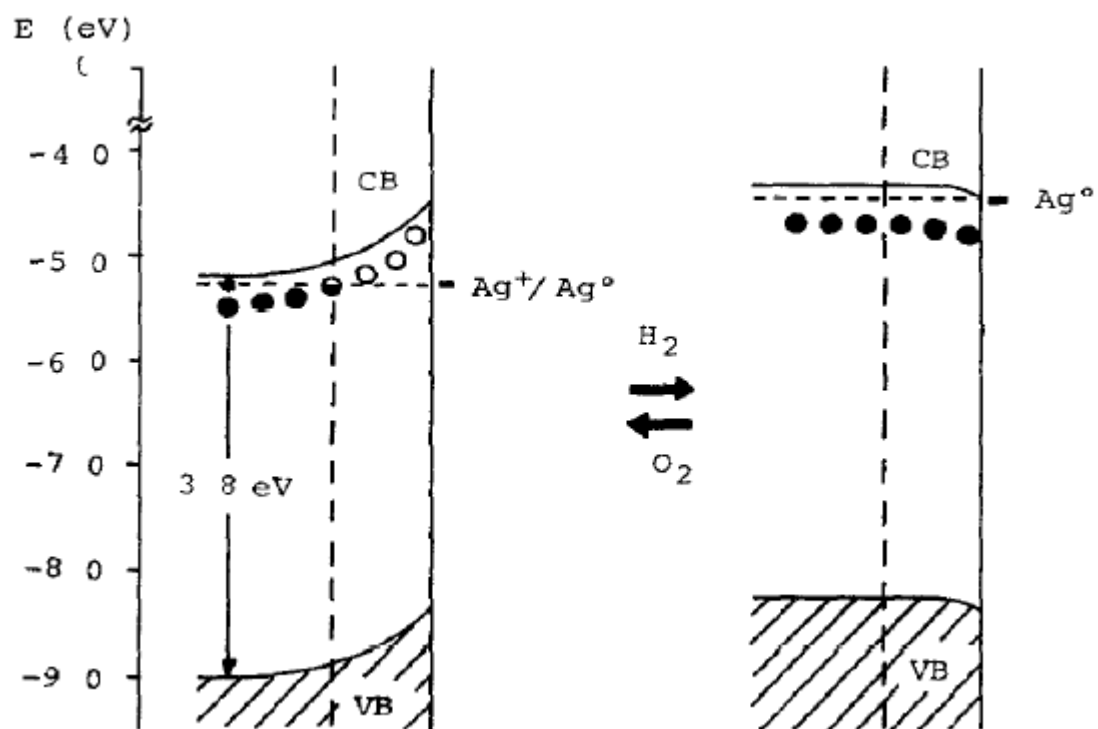


Figure 22. Electronic interactions between Ag and SnO₂. Left is under oxidation condition. Right is under reduction condition. [ref. 5]

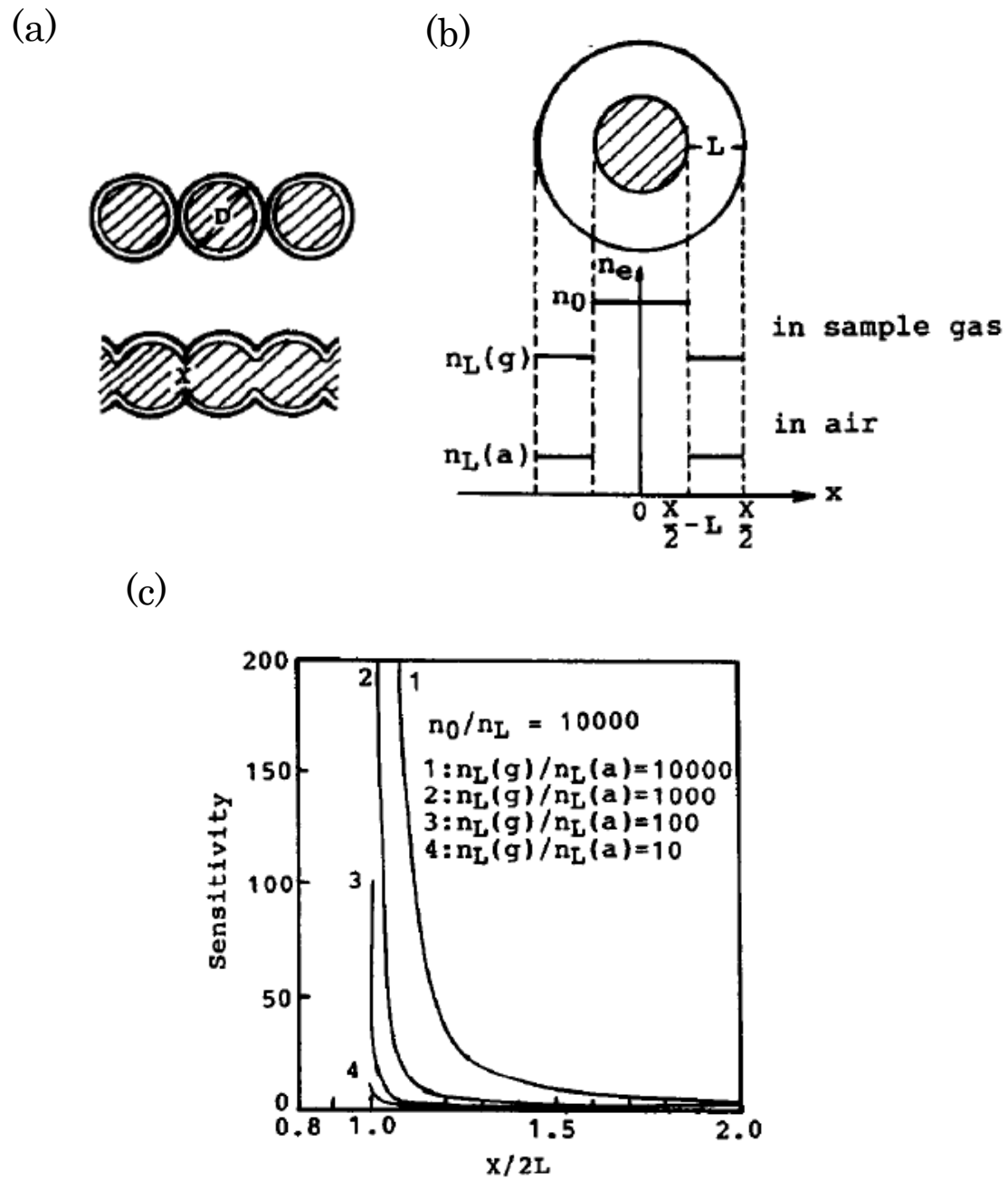


Figure 23. Change of electron concentration in neck (X). (a) is particle model, (b) is change of debye length (L) under aid and gas, (c) is simulation of correlation between $X/2L$ and sensitivity. [ref. 115]

$D \gg 2L$ (Grain boundary-control)



$D \geq 2L$ (Neck-control)



$D < 2L$ (Grain-control)



Figure 24. Schematic of grain size effect. Hatched region is core of low resistance, white region is space charge layer of high resistance. [ref. 115]

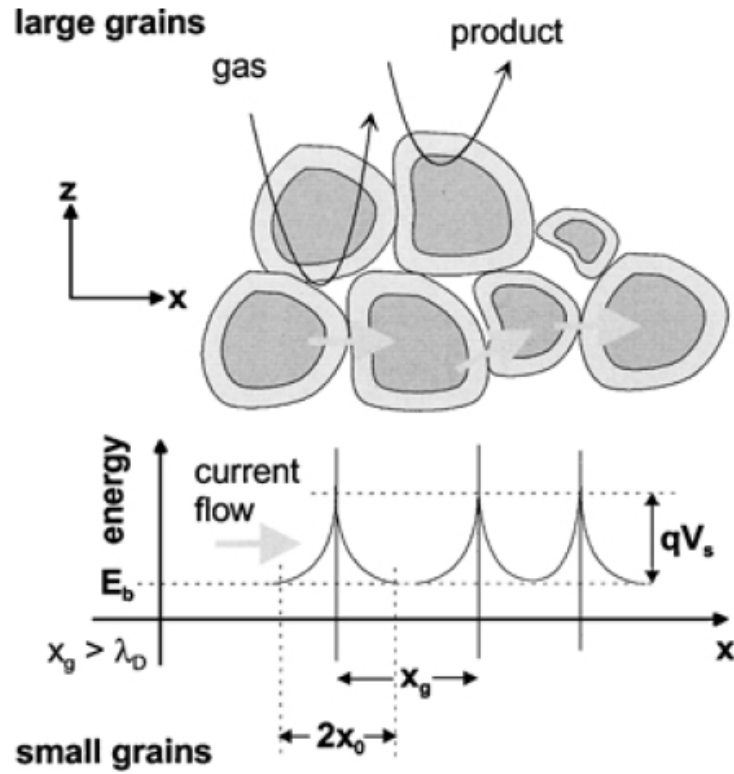


Figure 25. Schematic of schottky barrier height (qV_s) was formed on conduction band. Grain size is x_g , space charge layer length is $2x_0$. [ref. 117]

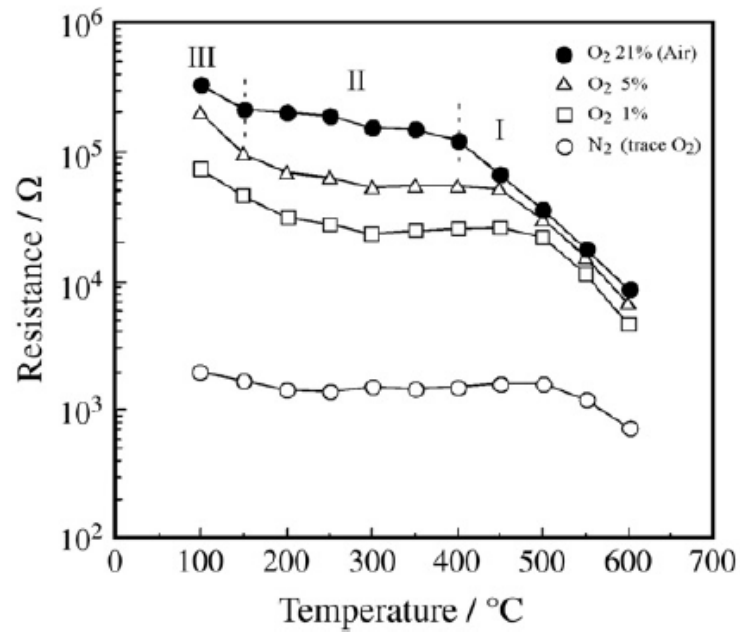


Figure 26. Temperature property under various oxygen pressure of SnO_2 film was formed by spin coat. [ref. 118]

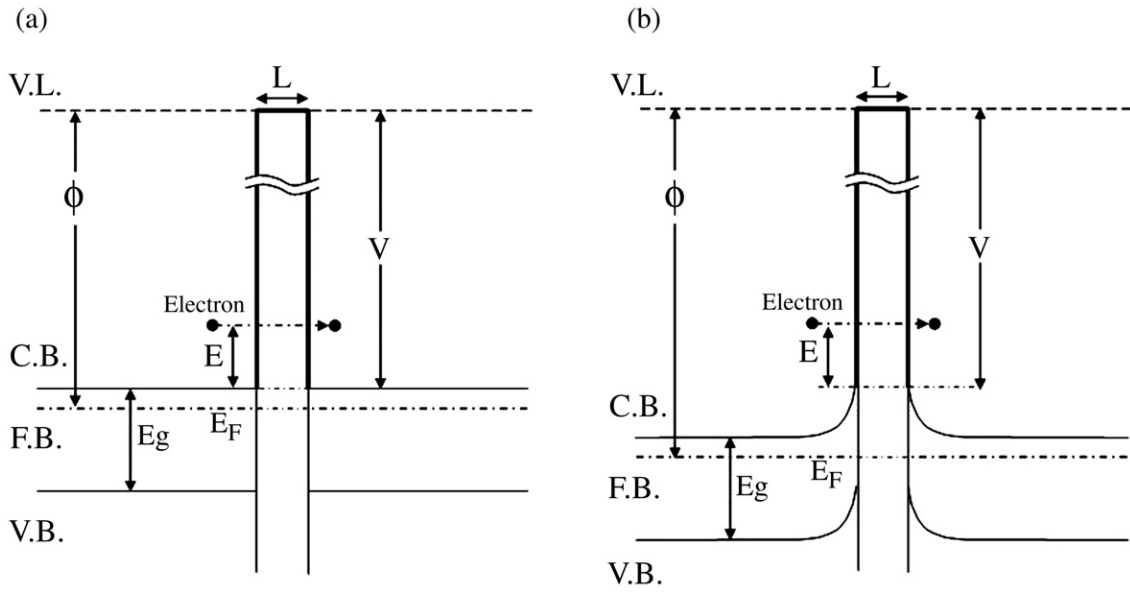


Figure 27. Tunneling conduction model [ref. 118]

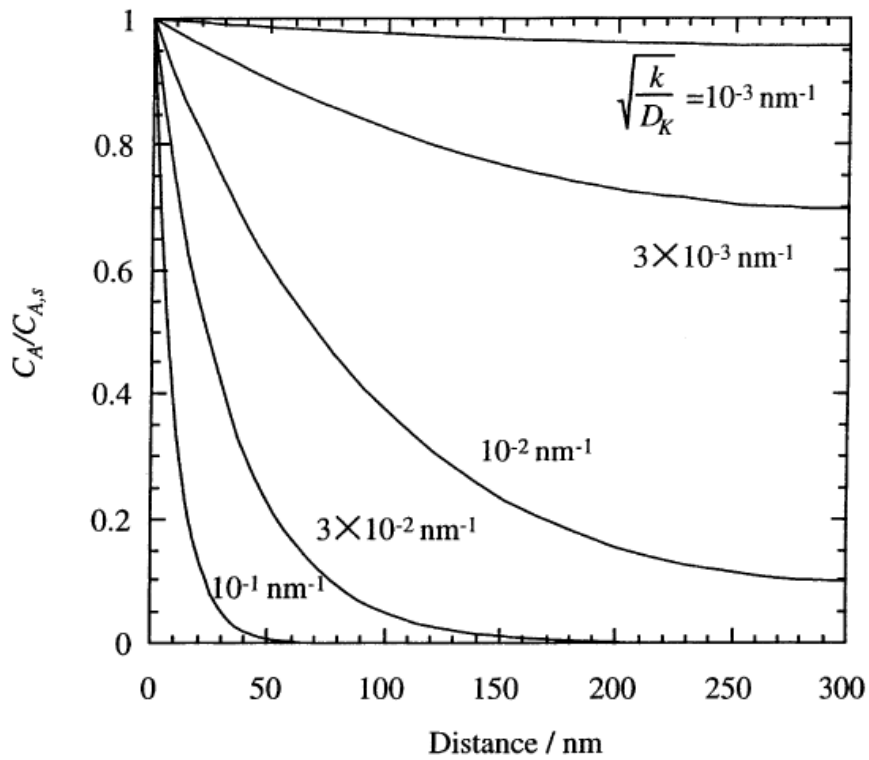


Figure 28. Distance dependence of diffusion concentration for gas ($C_A/C_{A,s}$) [ref. 119]

(a)



(b)

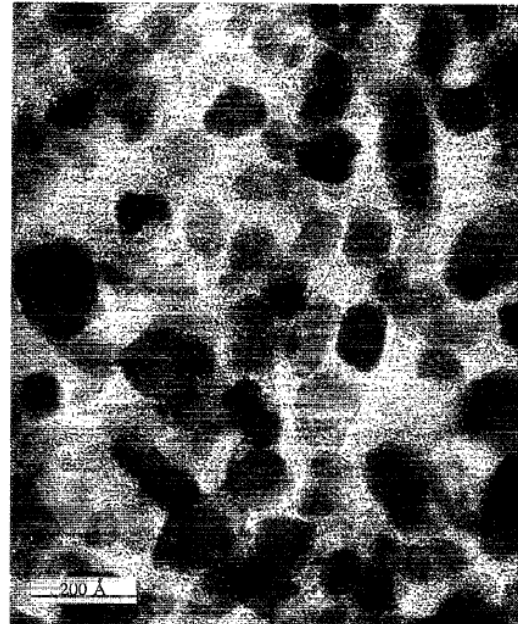


Figure 29. Micrograph by TEM of SnO₂ (a) Thin film SnO₂ by sputtering method, (b) Sintered body of SnO₂ of gas sensor, which is Figaro TGS 109 [ref. 113]

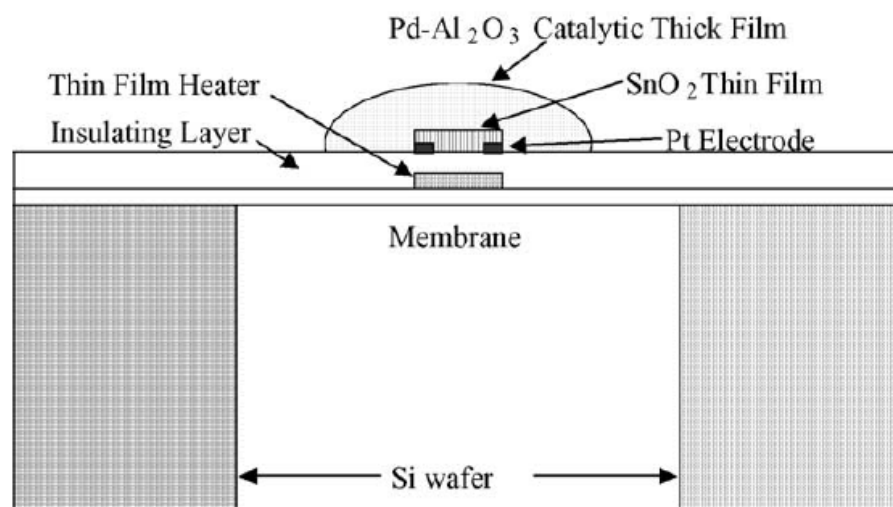


Figure 30. Cross section of MEMS sensor of semiconductor type by Suzuki et al., [ref. 7]

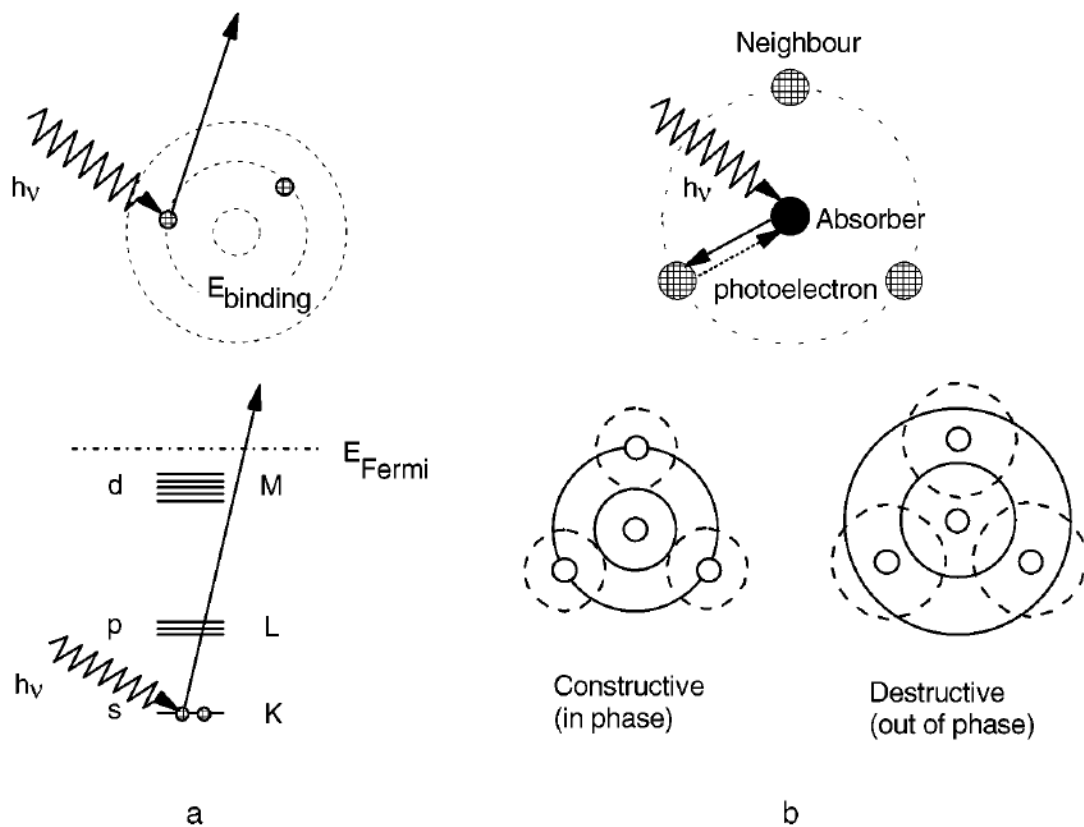


Figure 31. Schematic illustration of photoelectron effect in (a), phenomena of EXAFS oscillation in (b) [ref. 132]

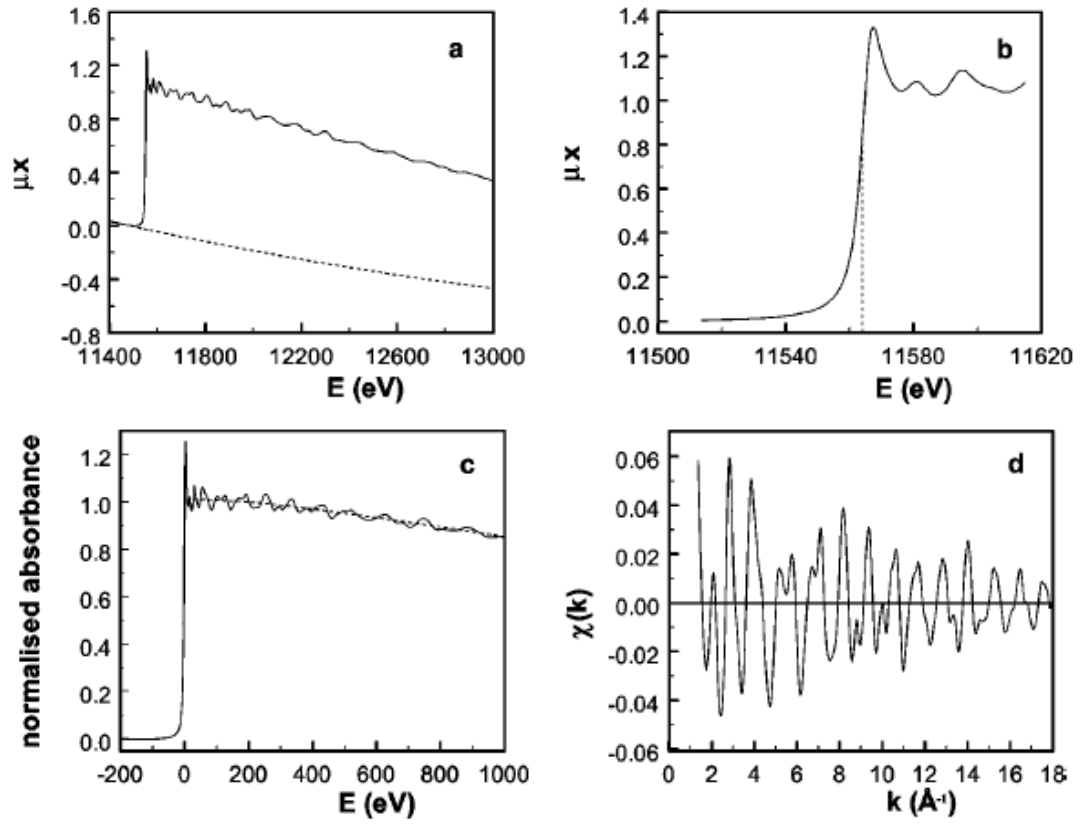


Figure 32. Schematic illustration for XAFS analysis [ref. 132]

- ¹ United Nations (UN), *2010 Energy Statistics Yearbook* United Nations, New York, 2014.
- ² Fire and Disaster Management Agency of Japan, “Statistical Table for explosion and leakage cases by gases and hazardous chemicals in 2011”
- ³ G. Heiland, *Sens. Actuators* **1982**, 2, 343.
- ⁴ N. Barsan, D. Koziej, and U. Weimar, *Sens. Actuators B: Chem.* **2007**, 121, 18.
- ⁵ N. Yamazoe, Y. Kurokawa, and T. Seiyama, *Sens. Actuators* **1983**, 4, 283.
- ⁶ A. V. Tadeev, G. Delabouglise, and M. Labeau, *Materials Science and Engineering*. **1998**, B57,76.
- ⁷ T. Suzuki, K. Kuniyara, M. Kobayashi, S. Tabata, K. Higaki, and H. Ohnishi, *Sens. Actuators B: Chem.* **2005**, 109, 185.
- ⁸ S. Tabata, K. Higaki, H. Ohnishi, T. Suzuki, K. Kuniyara, and M. Kobayashi, *Sens. Actuators B: Chem.* **2005**, 109, 190.
- ⁹ H. Seki, N. Ishizawa, N. Mizutani and M. Kato, *J. Ceram. Soc. Jpn.* **1984**, 92, 219.
- ¹⁰ L. Vegard, *Results of crystal analysis. Phil Mag, Ser 6.* **1916**, 32, 65.
- ¹¹ W. H. Baur, *Mater. Res. Bull.* **1981**, 16, 339.
- ¹² A. R. West and P. G. Bruce, *Acta Cryst.* **1982**, B38, 1891.
- ¹³ A. A. Bolzan, C. Fong, B. J. Kennedy and C. J. Howard, *Acta Cryst.* **1997**, B53, 373.
- ¹⁴ J. Robertson, *J. Phys. C* **1979**, 12, 4767-4776.
- ¹⁵ Ph. Barbarat, S. F. Matar, and G. Le Blevennec, *J. Mater. Chem.* **1997**, 7, 2547.
- ¹⁶ Qi-Jun Liu, Zheng-Tang, and Li-Ping Feng, *Comp. Mater. Sci.* **2010**, 47, 1016.
- ¹⁷ K. Yoneda, R. Satoh, Y. Iwata, H. Miyagawa, T. Isono, and K. Okamoto, *J. Jap. Welding Sci.* **2012**, 30, 86.
- ¹⁸ S. Munnix, and M. Schmeits, *Surface Sci.* **1983**, 126, 20.
- ¹⁹ S. Munnix, and M. Schmeits, *Phys. Rev. B* **1983**, 27, 7624.
- ²⁰ M. Meyer, G. Onida, A. Ponchel, and L. Reining, *Comp. Mater. Sci.* **1998**, 10, 319.
- ²¹ T. T. Tantal, T. S. Rantala, and V. Lantto, *Mater. Sci. Semicond. Process.* **2000**, 3, 103.
- ²² J. L. Jacquemin, and G. Bordure, *J. Phys. Chem. Solids*, **1975**, 36, 1081.
- ²³ T. Arai, *J. Phys. Soc. Jpn.*, **1958**, 15, 916.
- ²⁴ T. L. Credelle, C. C. Fonstad, and R. H. Rediker, *Bull. Am. Phys. Soc.*, **1971**, 16, 519.
- ²⁵ F. J. Arlinghaus, *J. Phys. Chem. Solids*, **1974**, 35, 931.
- ²⁶ A. Svane, and E. Antoncik, *J. Phys. Chem. Solids*, **1987**, 48, 171.
- ²⁷ J. Robertson, *Phys. Rev. B* **1984**, 30, 3520.
- ²⁸ K. G. Godinho, A. Walsh, and G. W. Watson, *J. Phys. Chem. C* **2009**, 113, 439.
- ²⁹ X. Wang, Q. Yin, Z. Tang, X. Liu, D. Tang, and W. Liu, *J. Eur. Ceram. Soc.* **2013**, 33, 3045.
- ³⁰ A. Boumeddiene, F. Bouamra, M. Rérat, and H. Belkhir, *Appl. Surf. Sci.* **2013**, 284, 581.
- ³¹ L. Shi, H. Dong, and G. Qi, *J. Mag. Mag. Mater.* **2013**, 345, 215.
- ³² T. S. Zyubina, A. S. Zyubin, Yu. A. Dobrovolskii, and V. M. Volokhov, *Russ. J. Inorg. Chem.* **2013**, 58, 311.
- ³³ M. N. Tripathi, K. Shida, R. Sahara, H. Mizuseki, and Y. Kawazoe, *J. Appl. Phys.* **2012**, 111, 103110.

-
- ³⁴ X. Xie, J. Jia, L. Han, X. Song, L. Zhong, Z. Liang, C. Fan, and P. Han, *Physica B* **2013**, 421, 132.
- ³⁵ N. V. Petrova, and I. N. Yakovkin, *Eur. Phys. J. B* **2013**, 86, 303.
- ³⁶ L. Shi, G. Qi, and H. Dong, *Mater. Sci. Semi. Proc.* **2013**, 16, 877.
- ³⁷ G. N. Leruth, G. Carchini, and N. López, *J. Chem. Phys.* **2013**, 138, 194706.
- ³⁸ G. Rahman, V. M. Suárez, and J. M. Morbec, *J. Mag. Mag. Mater.* **2013**, 328, 104.
- ³⁹ F. R. Sensato, L. Gracia, A. Beltrán, J. Andrés, and E. Longo, *J. Phys. Chem C* **2012**, 116, 16127.
- ⁴⁰ X. Sun, R. Long, X. Cheng, X. Zhao, Y. Dai, and B. Huang, *J. Phys. Chem. C* **2008**, 112, 9861.
- ⁴¹ N. Mazumder, A. Bharati, S. Saha, D. Sen, and K. K. Chattopadhyay, *Curr. Appl. Phys.* **2012**, 12, 975.
- ⁴² J. Xu, S. Huang, and Z. Wang, *Sol. State Comm.* **2009**, 149, 527.
- ⁴³ H. Wang, Y. Yan, Y. Su. Mohammed, X. Du, K. Li, and H. Jin, *J. Mag. Mag. Mater.* **2009**, 321, 337.
- ⁴⁴ J. Feng, B. Xiao, J. C. Chen, and C. T. Zhou, *Sol. State Sci.* **2009**, 11, 259.
- ⁴⁵ B. Cao, T. Shi, S. Zheng, Y. H. Ikuhara, W. Zhou, D. Wood, M. Al-Jassim, and Y. Yan, *J. Phys. Chem. C* **2012**, 116, 5009.
- ⁴⁶ A. Beltrán, J. Andrés, J. R. Sambrano, and E. Longo, *J. Phys. Chem. A* **2008**, 112, 8943.
- ⁴⁷ DieselNet : <http://www.dieselnet.com/standards>
- ⁴⁸ A. M. Azad, S. A. Akbar, S. G. Mhaisalkar, L. D. Birkefeld and K. S. Goto, *J. Electrochem. Soc.* **1992**, 139, 3690.
- ⁴⁹ R. A. Rapp, *Physicochemical Measurements in Metals Reserch Vol. IV, Part 1 and 2 of Techniques of Metals Reserch*, in: R. F. Bunshah (Ed.) Interscience Publ., New York, **1970**.
- ⁵⁰ K. S. Goto and W. Plaschkell, *Physics of Electrolytes vol2*, in: J. Hladik (Ed.) Academic Press, **1972**, 540.
- ⁵¹ C. T. Young, *Progress in Solid Electrolytes*, in: T. A. Wheat, A. Ahmad and A. K. Kuriakose (Ed.) *Energy, Mines and Resources, Ottawa on Canada*, **1983**, 549.
- ⁵² E. M. Logothetis, *Chemical Sensor Technology, Vol. 3*, in: N. Yamazoe (Ed.) Kodansya Ltd., Tokyo, **1991**, p. 89.
- ⁵³ T. Usui, A. Asada, M. Nakazawa and H. Osanai, *This Journal* **1989**, 136, 537.
- ⁵⁴ T. Takeuchi and I. Igarashi, *Chemical Sensor Technology, Vol. 1*, in: T. Seiyama (Ed.) Kondansya Ltd., Tokyo, **1988**, p. 79.
- ⁵⁵ W. J. Fleming, Paper No. 800,020, presented at the Society of Automotive Engineers Congress, Detroit, MI, **1980**.
- ⁵⁶ W. J. Fleming, *J. Electrochem. Soc.* **1977**, 124, 21.
- ⁵⁷ N. Miura, G. Lu and N. Yamazoe, *Sens. Actuators B: Chem.* **1998**, 52, 169.
- ⁵⁸ N. Miura, M. Nakatou and S. Zhuiykov, *Sens. Actuators B* **2003**, 93, 221.
- ⁵⁹ M. Nakatou and N. Miura, *Sens. Actuators B* **2006**, 120, 57.
- ⁶⁰ N. Miura, G-COE Program Kyushu University Novel Carbon Resource Sciences newsletter **2010**, 2, 11.
- ⁶¹ M. Ono, K. Shimanoe, N. Miura and N. Yamazoe, *Sol. State. Ionics* **2000**, 136-137, 583
- ⁶² N. Guillet, R. Lalauze, J. -P. Viricelle, C. Pijolat and L. Montanaro, *Mater. Sci.*

Engin. C **2002**, 21, 97.

⁶³ J. Parka, B. Y. Yoon, C. O. Park, W. -J. Lee and C. B. Lee, Sens. Actuators B **2009**, 135, 516.

⁶⁴ P. Elumalaia, V. V. Plashnitsaa, Y. Fujio and N. Miura, Sens. Actuators B **2010**, 144, 215.

⁶⁵ T. Hyodo, C. Ishibashi, K. Matsuo, K. Kaneyasu, H. Yanagi and Y. Shimizu, Electrochimi. Acta **2012**, 82, 19.

⁶⁶ G. Fadeyev, A. Kalakin, A. Demin, A. Volkov, A. Brouzgou and P. Tsiakaras, Int. J. Hydrogen. Energy **2013**, 38, 13484.

⁶⁷ S. A. Anggraini, M. Breedon and N. Miura, Electrochimi. Commun. **2013**, 31, 133.

⁶⁸ H. Takeda, T. Ueda, K. Kamada, K. Matsuo, T. Hyodo and Y. Shimizu, Electrochimi. Acta **2015**, 155, 8.

⁶⁹ N. Miura, M. Nakatou and S. Zhuiykov, Sens. Actuators B **2003**, 93, 221.

⁷⁰ M. Nakatou and N. Miura, Electrochimi. Commun. **2004**, 6, 995.

⁷¹ R. Wama, M. Utiyama, V. V. Plashnitsa and N. Miura, Electrochimi. Commun. **2007**, 9, 2774.

⁷² K. Shimizu, K. Kashiwagi, H. Nishiyama, S. Kakimoto, S. Sugaya, H. Yokoi and A. Satsuma, Sens. Actuators B **2008**, 130, 707.

⁷³ M. Stranzenbach and B. Saruhan, Sens. Actuators B **2009**, 137, 154.

⁷⁴ T. Ueda, T. Nagano, H. Okawa and S. Takahashi, J. Ceram. Soc. Jpn. **2010**, 118, 180.

⁷⁵ Y. Zhu, J. Zhang and W. Weppner, J. Solid State Electrochem. **2013**, 17, 1473.

⁷⁶ K. Angata and H. Furuta, in Proceedings of International Meeting on Chemical Sensors, Fukuoka, Japan, **1983**, p. 208.

⁷⁷ Y. Wang, M. M. Tong, D. Zhang and Z. Gao, Sensors **2011**, 11, 19.

⁷⁸ L. Sun, F. Qiu and B. Quan, Sens. Actuators B **2000**, 66, 289.

⁷⁹ T. Sasahara, H. Kato, A. Saito, M. Nishimura and M. Egashira, Sens. Actuators B **2007**, 126, 536.

⁸⁰ M. Nishibori, W. shin, N. Izu, T. Itoh, I. Matsubara, S. Yasuda and S. Ohtani, Int. J. Hydrogen. Energy **2009**, 34, 2834.

⁸¹ T. Hyodo, Y. Yuzuriha, O. Nakagoe, T. Sasahara, S. Tanabe and Y. Shimizu, Sens. Actuators B **2014**, 202, 748.

⁸² T. Seiyama, A. Kato, K. Fujiishi and M. Nagatani, Anal. Chem. **1962**, 34, 1502.

⁸³ T. Seiyama and S. Kagawa, Anal. Chem. **1966**, 38, 1069.

⁸⁴ N. Taguchi, United States Patent 3,631, 436, July 4th, **1970**.

⁸⁵ J. Watson and D. Tanner, Radio and Electronic Engineer **1974**, 44, 85.

⁸⁶ S. Yasunaga, S. Sunahara and K. Ihokura, Sens. Actuators **1986**, 9, 133.

⁸⁷ J. S. Chen, H. L. Li and J. L. Huang, Appl. Surf. Sci. **2002**, 187, 305.

⁸⁸ S. Shukla, S. Seal, L. Ludwig and C. Parish, Sens. Actuators B **2004**, 97, 256.

⁸⁹ M. Yuasa, T. Masaki, T. Kida, K. Shimanoe and N. Yamazoe, Sens. Actuators B **2009**, 136, 99.

⁹⁰ E. Y. Sevastyanova, N. K. Maksimovaa, V. A. Novikovb, F. V. Rudovb, N. V. Sergeychenkob and E. V. Chemikova, Semiconductors **2012**, 46, 801.

⁹¹ B. Thomas and B. Skariah, J. Alloys Compd. **2015**, 625, 231.

⁹² Y. Shimizu, N. Matsunaga, T. Hyodo and M. Egashira, Sens. Actuators B **2001**, 77, 35.

⁹³ W. -H. Tao and C. -H. Tsai, Sens. Actuators B **2002**, 81, 237.

-
- ⁹⁴ M. D'Arienzo, L. Armelao, C. M. Mari, S. Polizzi, R. Ruffo, R. Scotti and F. Morazzoni, *J. Am. Chem. Soc.* **2011**, 133, 5296.
- ⁹⁵ M. Ahsan, T. Tesfamichael, M. Ionescu, J. Bell and N. Motta, *Sens. Actuators B* **2012**, 162, 14.
- ⁹⁶ D. Chen, L. Yin, G. B. Fan, R. Zhang, J. Sun and G. Shao, *Sens. Actuators B* **2013**, 185, 445.
- ⁹⁷ R. Ferro, J. A. Rodríguez and P. Bertrand, *Thin Solid Film* **2008**, 516, 2225.
- ⁹⁸ M. F. Al-Kuhaili, S.M.A. Durrani and I. A. Bakhtiari, *Appl. Surf. Sci.* **2008**, 255, 3033.
- ⁹⁹ K. Zheng, L. Gu, D. Sun, X. Mo and G. Chen, *Mater. Sci. Engin.* **2010**, 166, 104.
- ¹⁰⁰ K. V. Gurav, P. R. Deshmukh and C. D. Lokhande, *Sens. Actuators B* **2011**, 151, 365.
- ¹⁰¹ Y. Zeng, Z. Lou, L. Wang, B. Zou, T. Zhang, W. Zheng and G. Zou, *Sens. Actuators B* **2011**, 156, 395.
- ¹⁰² G. X. Wan, S. Y. Ma, X. B. Li, F. M. Li, H. Q. Bian, L. P. Zhang and W. Q. Li, *Mater. Lett.* **2014**, 114, 103.
- ¹⁰³ K. Galatsis, Y. X. Li, W. Wlodarski, E. Comini, G. Faglia and G. Sberveglieri, *Sens. Actuators B* **2001**, 77, 472.
- ¹⁰⁴ B. Karunakaran, P. Uthirakumar, S. J. Chung, S. Velumani and E. –K. Suh, *Mater. Charact.* **2007**, 58, 680.
- ¹⁰⁵ J. –Ah. Park, J. Moon, Su. –J. Lee, S. H. Kim, T. Zyung and H. Y. Chu, *Mater. Lett.* **2010**, 64, 255.
- ¹⁰⁶ Y. Li, W. Wlodarski, K. Galatsis. S. H. Moslih, J. Cole, S. Russo and N. Rockelmann, *Sens. Actuators B* **2002**, 83, 160.
- ¹⁰⁷ A. Ruiz, A. Cornet, G. Sakai, K. Shimanoe, J. R. Morante and N. Yamazoe, *Chem. Lett.* **2002**, 31, 892.
- ¹⁰⁸ M. Choudhary, N. K. Singh, V. N. Mishra and R. Dwivedi, *Mater. Chem. Phys.* **2013**, 142, 370.
- ¹⁰⁹ N. Savage, B. Chwieroth, A. Ginwalla, B. R. Patton, S. A. Akbar and P. K. Dutta, *Sens. Actuators B* **2001**, 79, 17.
- ¹¹⁰ A. Wisitsoraat, A. Tuantranont, E. Comini, G. Sberveglieri and W. Wlodarski, *Thin Solid Films* **2009**, 517, 2775.
- ¹¹¹ N. Yamazoe, J. Fuchigami, M. Kishikawa and T. Seiyama, *Surf. Sci.* **1979**, 86, 335.
- ¹¹² H. Ohnishi, H. Sasaki, T. Matsumoto and M. Ippommatsu, *Sens. Actuators B* **1993**, 13-14, 677.
- ¹¹³ M. Ippommatsu, H. Ohnishi, H. Sasaki and T. Matsumoto, *J. Appl. Phys.* **1991**, 69, 8368.
- ¹¹⁴ N. Yamazoe, K. Shimanoe and C. Sawada, *Thin Solid Films* **2007**, 515, 8302.
- ¹¹⁵ N. Yamazoe, *Sens. Actuators B* **1991**, 5, 7.
- ¹¹⁶ C. Xu, J. Tamaki, N. Miura and N. Yamazoe, *Sens. Actuators B* **1991**, 3, 147.
- ¹¹⁷ N. Barsan and U. Weimar, *J. Electroceram.* **2001**, 7, 143.
- ¹¹⁸ N. Yamazoe, K. Shimanoe and C. Sawada, *Thin Solid Films* **2007**, 515, 8302.
- ¹¹⁹ G. Sakai, N. Matsunaga, K. Shimanoe and N. Yamazoe, *Sens. Actuators B* **2001**, 80, 125.
- ¹²⁰ M. Ippommatsu and H. Sasaki, *J. Electrochem. Soc.* **1989**, 136, 2123.
- ¹²¹ A. Nonaka, T. Nakajima, H. Ohnishi, M. Okamura, N. Murata and T. Suzuki, *Proc.*

-
- The 57th Chem. Sensor Sym. **2014**, 30 Sup. B
- ¹²² A. Nonaka, T. Nakajima, H. Ohnishi, M. Okamura, N. Murata and T. Suzuki, Proc. The 58th Chem. Sensor Sym. **2015**, 31 Sup. B
- ¹²³ T. Suzuki, M. Okamura, N. Murata, A. Nonaka, T. Nakajima and H. Ohnishi, Proc. The 57th Chem. Sensor Sym. **2014**, 30 Sup. B
- ¹²⁴ T. Suzuki, M. Okamura, N. Murata, A. Nonaka, T. Nakajima and H. Ohnishi, Proc. The 57th Chem. Sensor Sym. **2014**, 30 Sup. B
- ¹²⁵ I. Kocemba, J. Rynkowski, Sens. Actuators B: Chem. **2011**, 155, 659.
- ¹²⁶ M. Gaidi, M. Labeau, B. Chenevier, and J. L. Hazemann, Sens. Actuators B: Chem. **1998**, 48, 277.
- ¹²⁷ L. Mädler, T. Sahm, A. Gurlo, J. -D. Grunwaldt, N. Barsan, U. Weimar, S. E. Pratsinis, Journal of Nanoparticle Research **2006**, 8, 783.
- ¹²⁸ A. Kowal, M. Li, M. Shao, K. Sasaki, M. B. Vukmirovic, J. Zhang, N. S. Marinkovic, P. Liu, A. I. Frenkel, and R. R. Adzic, Nat. Mater. **2009**, 8, 325-330.
- ¹²⁹ M. Gaidi, J. L. Hazemann, I. Matko, B. Chenevier, M. Rumyantseva, A. Gaskov, and M. Labeau, J. Electrochem. Soc. **2000**, 147, 3131-3138.
- ¹³⁰ Hübner, M.; Koziej, D.; Bauer, M.; Barsan, N.; Kvashnina, K.; Rossell, M.D.; Weimar, U.; Grunwaldt, J.-D. Angew. Chem. Int. Ed. **2011**, 50, 2841 –2844.
- ¹³¹ Hübner, M.; Bârsan, N.; Weimar, U. Sens. Actuators B **2012**, 171-172, 172-180.
- ¹³² D. C. Koningsberger, B. L. Mojet, G. E. van Dorssen and D. E. Ramaker, Top. Catal. **2000**, 10, 143.
- ¹³³ M. Newville, J.J. Kas, J.J. Rehr, Journal of Physics: Conference Series **2009**, 190, 012023.
- ¹³⁴ J.J. Rehr, J.J. Kas, M. P. Prange, A. P. Sorini, Y. Takimoto, F. Vila, Comptes Rendus Physique **2009**, 10, 548-559.
- ¹³⁵ J. J. Rehr, Radiation Phys.Chem. **2006**, 75, 1547-1558.
- ¹³⁶ D. Bazin, H. Dexpert, and J. Lynch, X-ray Absorption Fine Structure for Catalysts and Surfaces, edited by Y. Iwasawa, pp. 113 (1996). Singapore: World Scientific.

Chapter 2

Experimental

1. Introduction

Fluorescence X-ray absorption fine structure (XAFS) is a powerful technique for determining the local structure in a dilute system.^{1,2} When X-ray absorption occurs with the core electron emission as a photoelectron, the created core hole is filled by a transition from the outer shell electrons accompanied with an emission of a fluorescence X-ray. Consequently, if the sample is dilute or in a thin film, the fluorescence X-ray intensity becomes proportional to the absorption coefficient. Because the fluorescence X-ray emission occurs in a 4π sr, the use of a large solid-angle detector, such as a multielement solid state detector (SSD)³ or a Lytle detector⁴, is desirable. Recently, in case of samples including energy-ray of other element or scattering-ray in the nearby fluorescence energy of target element, the high-energy resolution fluorescence-detected (HERFD) XAFS which improves an energy resolution by arrangement of a crystal analyzer to front of the detector is often used.⁵

The strong penetration power of an X-ray allows investigators to perform *in situ* XAFS measurement under reaction conditions to reveal catalytic mechanisms.⁶ Numerous *in situ* fluorescence XAFS experiments have been performed.^{5, 7–14 15 16 17 18 19 20 21 22 23 24 25 26} *In situ* fluorescence XAFS cells require a large fluorescence window at a position sufficiently close to the sample to secure a large solid angle. When the polymer window is used for the *in situ* fluorescence XAFS measurements it is difficult to realize the large solid angle because the fluorescence window temperature raises easily even if the peripheral region of the window is cooled by water flow owing to low thermal conductivity of polymer window material. Kappen and Grunwaldt et al. used a thin quartz tube as an incident and fluorescence X-ray window^{7,8} where the quartz window can be in contact with the sample because the quartz window is a temperature proof material. Another alternative is to decrease the power supply by decreasing the sample size. High-brilliance synchrotron radiation is now available, and the X-ray can be focused to an area less than a few mm² for the small samples to be used. In this study, I selected this option so that the distance between the window and the heater could be as short as 35 mm. The window temperature reached only 373 K without any cooling, even when the sample was heated to 703 K. The cell used in this study enables us to measure the *in situ* fluorescence XAFS of flat substrate and powder samples. In this paper I measured the fluorescence

XAFS spectra of a Pt-SnO₂ thin film on a Si substrate as model sensor catalyst under the working conditions.

2. Catalytic preparation and characterization method

2.1. Catalytic preparation

Pt doped SnO₂ thin layer with 400 nm thickness (denoted as X% Pt-SnO₂ where X indicates the atomic % of Pt) was prepared by the sputtering method on the p-type Si substrate covered with naïve SiO₂ film (600 nm) followed by annealing at 803 K. Pt and SnO₂ ratio was controlled by the loading ratio in the targets and finally the concentration of Pt in the film was determined by the ICP(Inductively Coupled Plasma) by dissolving the film using hydrochloric acid.

7 wt % Pd catalysts were supported on γ -Al₂O₃ (confirmed using XRD) by impregnation. It was followed by the calcination at approximately 803 K in air. The Pd/Al₂O₃ catalyst was deposited on Pt-SnO₂ film on the Si wafer by a screen printing method.

2.2 Characterization of the catalyst

2.2.1. XRD and XPS measurements

XRD patterns were recorded by using a Cu K α from RIGAKU ATX-G with X-ray tube voltage = 50 kV and X-ray tube current = 300 mA. XPS spectra were measured in ULVAC Phi Quantum-2000 using monochromated-Al K α X-ray operated at 15 kV-15 mA.

2.2.2. XAFS measurement

Pt L₃-edge XAFS spectra were measured at BL-12C of KEK-PF using a Si(111) monochromator in a fluorescence mode^{27,28}, and the Sn K, Pd K edge XAFS spectra were measured at the NW-10A of KEK-PF-AR equipped with a Si(311) monochromator also in a fluorescence mode.²⁹ XAFS spectra were analyzed with REX2000 (Ver. 2.5, RIGAKU).^{30,31,32} The backgrounds of all XAFS spectra were removed by a spline smoothing method with Cook and Sayers criteria and normalized by the edge height.³³ The k^3 -weighted EXAFS oscillations were Fourier-transformed to k -space over $k = 14 - 148$ nm⁻¹ for Pt L₃-edge spectra, over $k = 23 - 144$ nm⁻¹ for Sn K-edge spectra. The each peak in the Fourier transforms was filtered and inversely Fourier transformed to the k -space for the curve fitting analysis. I carried out the

non-linear least square curve fitting using the following equations.

$$k^3 \chi(k) = \sum_j S_0^2 \frac{k^2 N_j F_j(k)}{r_j^2} e^{-2k^2 \sigma_j^2} e^{-\frac{2r_j}{\lambda_j}} \sin(2kr_j + \phi_j)$$

$$k = \sqrt{\frac{2m}{\hbar^2} (h\nu - E_0 - \Delta E)}$$
(1)

where S_0^2 , N_j , r_j , and σ_j are amplitude reduction factor, coordination number, bond distance, and Debye Waller factor, of the j-th coordination shell, respectively. λ is a mean free path. $F_j(k)$ and $\phi_j(k)$ are backscattering amplitude and phase-shift functions which were obtained from FEFF (ver. 8.0).^{34,35,36} E_0 is the absorption edge energy tentatively determined as the inflection points and energy shift ΔE is adjusted during the fitting process.

The errors were estimated by Hamilton test on R-factor with a significance level over 90 %.³⁷

2.2.3. Catalyst performance

I evaluated the catalyst performance with a flow reactor (Okura Riken Co) with a space velocity of 16800 SV [h⁻¹]. Two catalytic combustion reactions of 5000 ppm CH₄ or 5000 ppm H₂ balanced with O₂ were performed with the products being analyzed by gas chromatography.

2.2.4. TDS measurement

A TDS (Thermal Desorption Spectroscopy) was measured as M/z = 32 to evaluate oxygen desorption from Pt-SnO₂ or SnO₂ using the equipment manufactured by Electron Science Co., Ltd.. Detector used mass spectrometer. Sample was measured up to temperature of 1000 K by the infrared heat lamp into vacuum chamber of ~10⁹ Pa. Temperature of sample surface was monitored directly by the K type thermocouple.

Sample of layer of Pt-SnO₂ (~400 nm)/SnO₂ (~400 nm) which was annealed for 4 hours under air (20 % oxygen) at about 703 K was prepared for TDS measurement. Pt concentration was deposited at 8 at% (and 4 at% as only TDS measurement) which take solid solution.

3. *in situ* cell for fluorescence X-ray absorption fine structure measurement

3.1. Structure of the *in situ* cell

Figure 1 shows a photograph and schematic sketches of the *in situ* cell. To install the cell more easily at any beam line, the cell body was made of aluminum to increase its portability. The cell weight was just 2.4 kg. In addition, local heating of the cell body could be avoided because of Al's high thermal conductivity. The volume of the cell is about 1.3 L in order to keep the volume / sensor area ratio in the same order of the real sensor which was 4×10^3 cm and 1.3×10^3 cm for real and model sensors, respectively. The cell body had gas flow ports and an incident X-ray window. I used a 200- μ m-thick Kapton (DuPont, USA) for the incidence and fluorescence X-ray windows, which were fixed to the body using an epoxy adhesive. I made a large fluorescence Kapton window with an area of 116 mm².

The cell body had a sample stand with electric feedthroughs for heating the sample. The pyrolytic graphite heater was wrapped with pyrolytic boron nitride (PBN) (HTR1001; Adcap Vacuum Technology Corporation, Japan) and was used to heat the sample to 873 K. The heater size was 25 mm². Temperature was controlled in a proportional–integral–derivative (PID) manner using the temperature controller designed especially by the Sakaguchi Electric Heating Corporation. This temperature controller measured temperature by a chromel–alumel thermocouple attached to the back of the sample. Its temperature sampling time was as short as 25 ms. It controlled the temperature by another chromel–alumel thermocouple attached to the sample holder, as shown in Fig. 2. The heater was fixed to the sample holder. The sample was fixed at two corners with jigs and clinchers to ensure good contact with the heater. The sample holder and jigs were made of Al₂O₃ to reduce heat dissipation. The angle between the X-ray direction and the sample stage was set at 25° as no diffraction from the Si substrate was detected at this angle empirically. The length from the sample to the window was approximately 35 mm. I did not use a water-cooling system. With this configuration, I can guarantee a large half-cone angle of 56°.

3.2. Performance as *in situ* cell

3.2.1. Heating performance

Although the sample and sample heater in this study were small, the

power of the heater and the heat capacity of the sample were sufficiently large for temperature stability. I actually achieved the stable sample temperature using the temperature controller in a current-control mode with well-tuned PID parameters. Figure 3 shows the heating performance of the *in situ* cell. The temperature was linearly raised to 703 K at the sample position. The sample surface reached this temperature in approximately 3 minutes, as shown by the dashed line. The temperature overshoot was only 5 K, and the temperature was controlled to within 2 K for a long time. In the off-line experiment, I measured the fluorescence window temperature at its center by a thermocouple directly attached to the window. Note that the Kapton window was kept at 373 K because of the small power input, by a dotted line as shown in Fig. 3(a), despite the sample temperature at 703 K. However, the problem was the life of the heater; a very large power supply can readily damage the small heater. Therefore, I installed a safety circuit to prevent the current from being exceeded more than desired one (5 A). I then slowly increased the power to extend the life for a few days, which was sufficient for one experimental run. Figure 3(c) shows the XAFS spectra at room temperature, 613 K and 703 K in dry air flow. I could find little structure change of the Pt local structure at different temperatures.

3.2.2. XAFS measurements in and out of the cell

Pt-SnO₂ thin film on a 1 cm² Si substrate was loaded in the cell for confirmation of performance of cell. Figure 4 shows the XAFS spectra of Pt-SnO₂ thin film measured in and out of the cell at room temperature. Both spectra were very similar up to $k = 14 \text{ \AA}^{-1}$. This implies that the data can be accurately analyzed under *in situ* conditions using this cell. Figure 5 shows XANES spectra measured at the temperature increasing process to 703 K under a flow of dry air and 1% H₂-containing air (flow rates = 200 ml/min). The sensor resistivity was measured in this XAFS measurement cell. Figure 5(b) showed the resistivity at each temperature where XANES spectra were measured as shown Fig. 5(a). There is no difference in sensor resistance when the X-ray beam was on / was off. The most reduced state in Pt gave the lowest resistivity. Figure 6 showed XAFS spectra to 703 K under a flow of dry air and 1% H₂-containing air. I observed small changes in the X-ray absorption near-edge structure (XANES) region in Fig. 6(a). The edge peak (called as white line) decreased when the sample was exposed

to the H₂-containing air at a high temperature (703 K). The white line peak was assigned to the 2p_{3/2}→5d transition.³⁸ The decrease in the white line peak indicated an increase in the d-electron density of Pt, which was probably because of the loss of the first nearest-neighbor oxygen atoms and/or the formation of Pt nanoparticles. Identifying the change in the original EXAFS oscillation ($k^3\chi(k)$) was difficult, as shown in Fig. 6(b) so that we calculated its difference before and after contact with the H₂-containing air, as shown in Fig. 6(c). The difference EXAFS ($k^3\Delta\chi(k)$) showed the oscillation clearly. I performed a Fourier transform, as shown in Fig. 7, where one peak appeared at 0.18 nm, corresponding well with Pt–O. This does not necessarily mean that there was an increase in the Pt–O coordination because Fig. 7 shows only the absolute part of the Fourier transform, which does not contain phase information. Figure 8 shows the imaginary and real parts of the Fourier transform of $k^3\chi(k)$ together with absolute part for the Pt–SnO₂ in dry air at 703 K. Compared with the imaginary parts, the phase of the Pt–SnO₂ peak in Fourier transform of $k^3\Delta\chi(k)$ was π rad different from the Pt–SnO₂ before the H₂-containing air flow, indicating a decrease in the main oscillation arising from Pt–O. I did not find any notable peak above a noise level in the range of 0.2–0.3 nm, which showed little Pt–Pt formation. Thus, I concluded that Pt metal nanoparticles were not produced with H₂-containing air at high temperature, but a partial reduction of Pt ions occurred with the loss of the oxygen maintaining the location at the lattice position of SnO₂.

4. Discussion

There have been many reports about *in situ* cells for the fluorescence XAFS. Cells are classified into two types. The first type of cell is a tubular type. The fluorescence X-ray is measured through an incident window made of quartz.^{7–10} These materials are stable at high temperatures and are thus allowed to have direct contact with the sample. This cell type can provide large half-cone angles. Its drawback is the scattered X-rays from the quartz tube, which increases the background.

The second type of cell is the one that has the sample and windows separated from each other. Different X-ray incidence and fluorescence windows are used for X-ray scattering to be largely reduced. When a thin polymer window is applied, the window temperature has to be kept low. As

such, the distance between the window and the sample must be long and/or window size is small enough for effective cooling of the window both of which sacrifice a large fluorescence yield. D. Koziej *et al.* have reported a cell for a gas-phase reaction, where the sample is heated by a built-in small heater. They have studied the structure and behavior of Pt in Pt-SnO₂ based sensor with this cell.^{14,15} A. Gurlo *et al.* have reported also a cell for research of mechanism of sensor with small heater.^{16,17} With these arrangement, the sample can be effectively heated, and the power supply can be reduced to prevent undesired window heating. These cells have a large half cone angle without any water-cooling system, although measurements are limited to those systems with samples that can have a built-in heater. In this paper I used a small sample and a small separate heater. Consequently, the window is not heated up, even with its large window size (116 mm²) at a close distance (approximately 35 mm). As a result I have had a large half cone angle¹ of 56° by minimizing the sample heater size (25 × 35 mm²). This cell also has no water-cooling system because the Kapton window temperature was kept at less than 373 K due to the high thermal conductivity of Al, even at a sample temperature of 703 K. The system can be applied to reaction analysis of solid oxide or bimetallic catalyst for fuel cells¹⁹⁻²² or *in situ* analysis of WO₂ was used as photo / electrochromic materials.³⁹ In particular, it's interesting to study effect of humidity of WO₂.⁴⁰ Moreover, this may be able to apply to investigation for corrosion was formed on metallic film etc.²³⁻²⁶ These samples are loaded into a small container made of BN or graphite and fixed to the heater. The cell is thus universally applicable to many systems in the measurements of fluorescence XAFS under the reaction conditions.

5. Conclusions

I have developed a new type of *in situ* fluorescence XAFS cell, which has a large solid angle, a half-cone angle of 56°, and no water-cooling system. The sample is locally heated using a small heater, which prevents the unwanted heating of system components other than the sample. I obtain a good S/N ratio of *in situ* fluorescence XAFS signal under the reaction conditions, which allows data analysis by difference spectra to elucidate minute changes in XAFS oscillations during reactions.

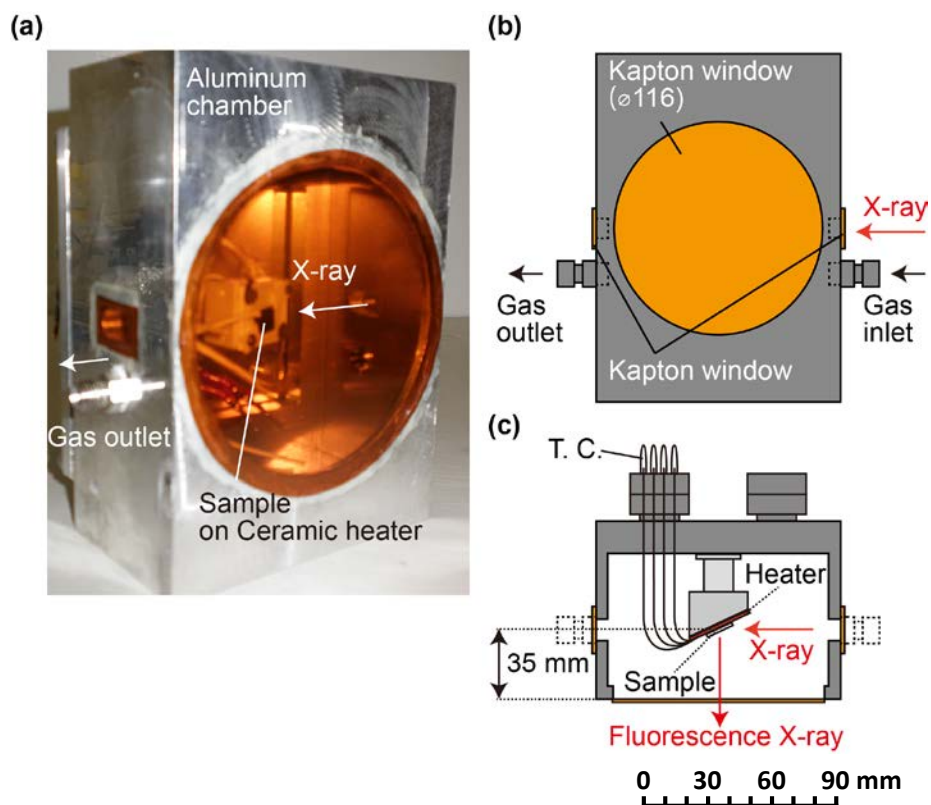


Figure 1. A photograph and schematic drawings of the *in situ* cell. It is (a) photograph (b) top view (c) side view.

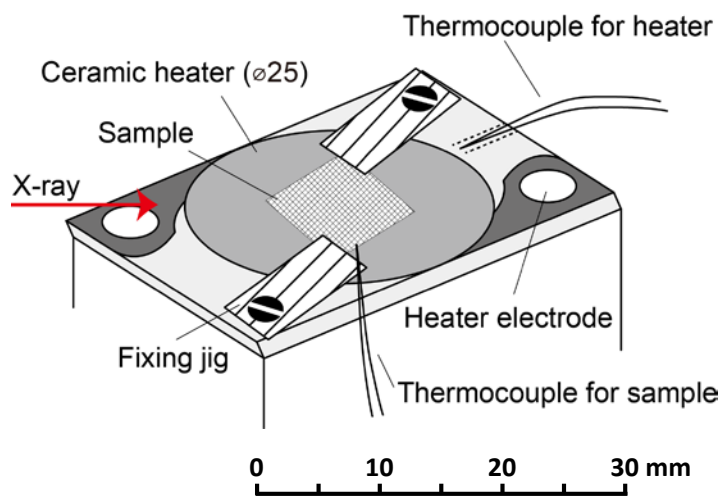


Figure 2. Sample holder with ceramic heater and thermocouples on the sample stand.

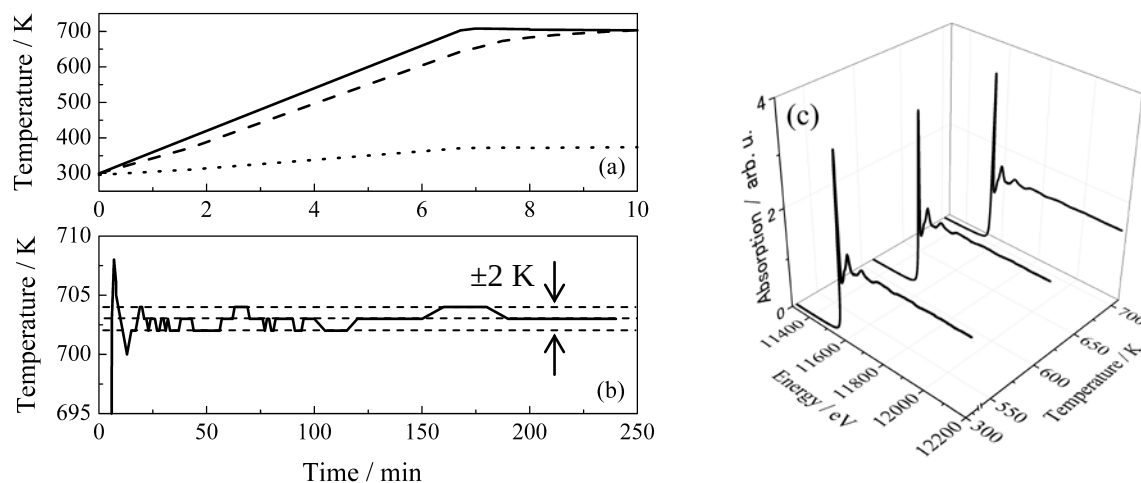


Figure 3. The heating performance of the cell. (a) The increasing temperature process at the holder (solid line), at the sample (broken line), and at the Kapton window (dotted line). (b) Stability of the temperature for 4 hours at the sample position. (c) XAFS spectra at 303, 613, and 703 K under the dry air flow.

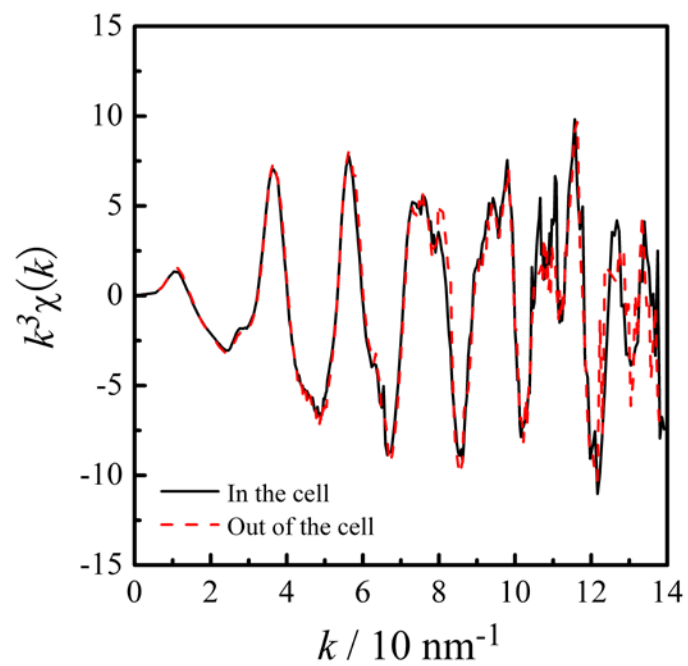


Figure 4. Comparison of EXAFS oscillation of a Pt–SnO₂ thin film in the cell (solid line) and out of the cell (broken line) at room temperature.

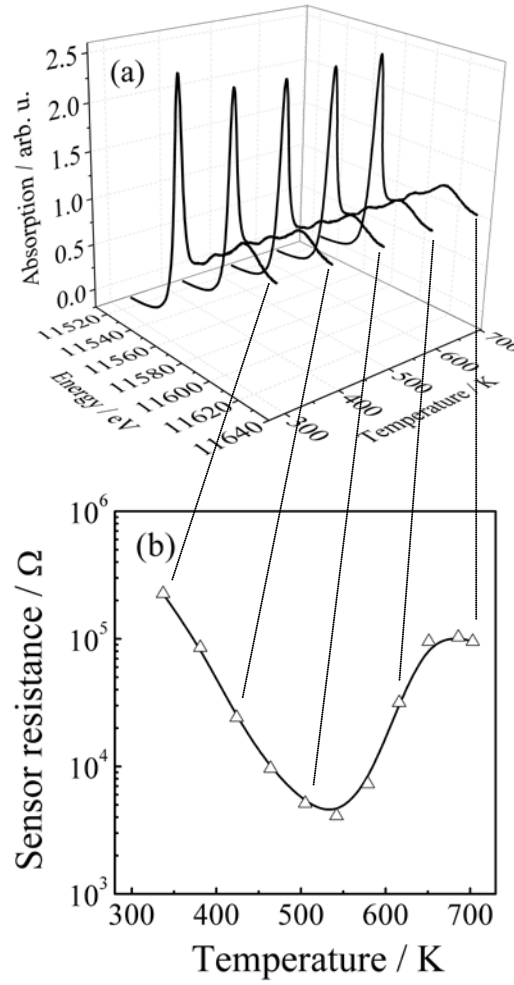


Figure 5. XANES spectra at the temperature increasing process to 703 K under a flow of dry air and 1% H₂-containing air (flow rates = 200 ml/min) in (a). Sensor property on model sample under the hydrogen based the dry air flow in (b).

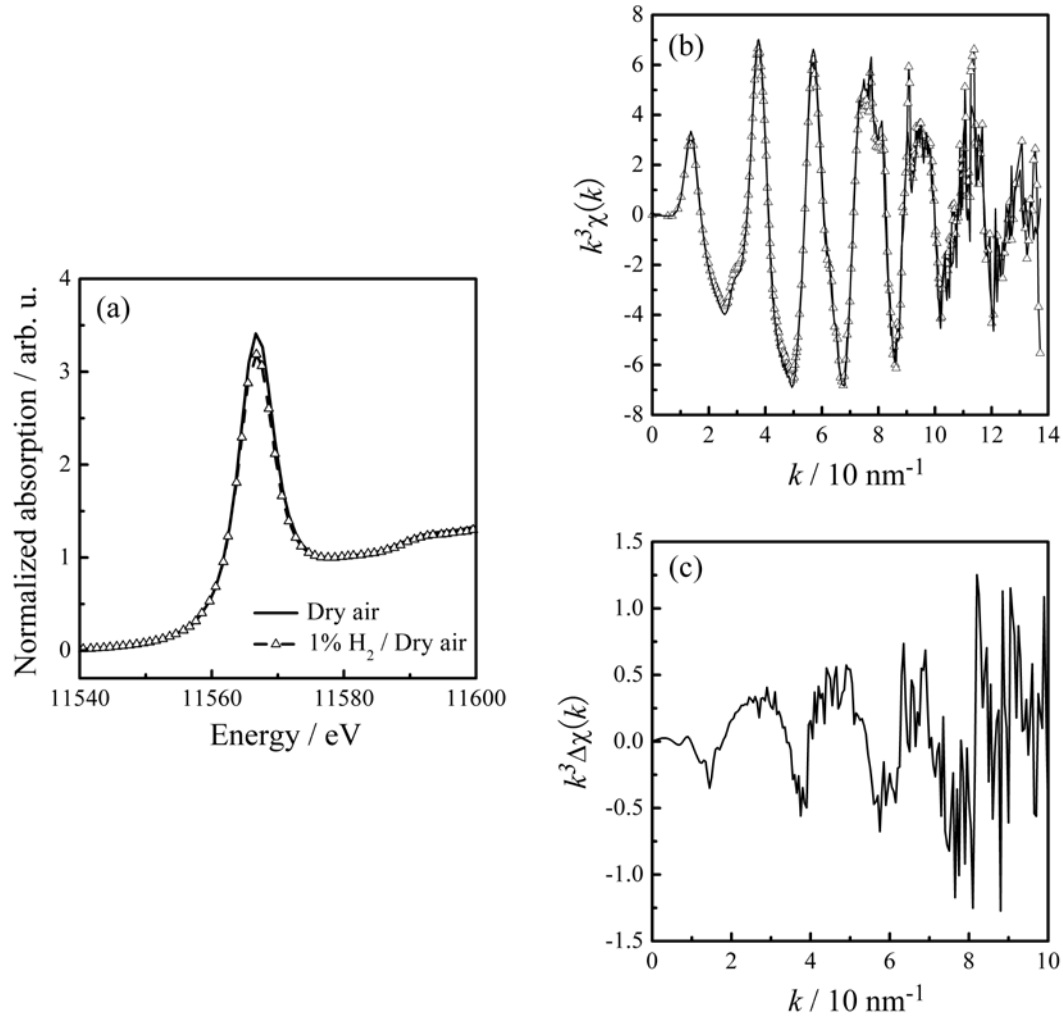


Figure 6. Pt L₃-edge XANES (a) and EXAFS (b) spectra to 703 K under a flow of dry air (solid line) and 1% H₂-containing air (triangle with broken line). (a) XANES spectra, (b) k^3 -weighted EXAFS oscillations, and (c) their difference spectrum $k^3\Delta\chi(k)$.

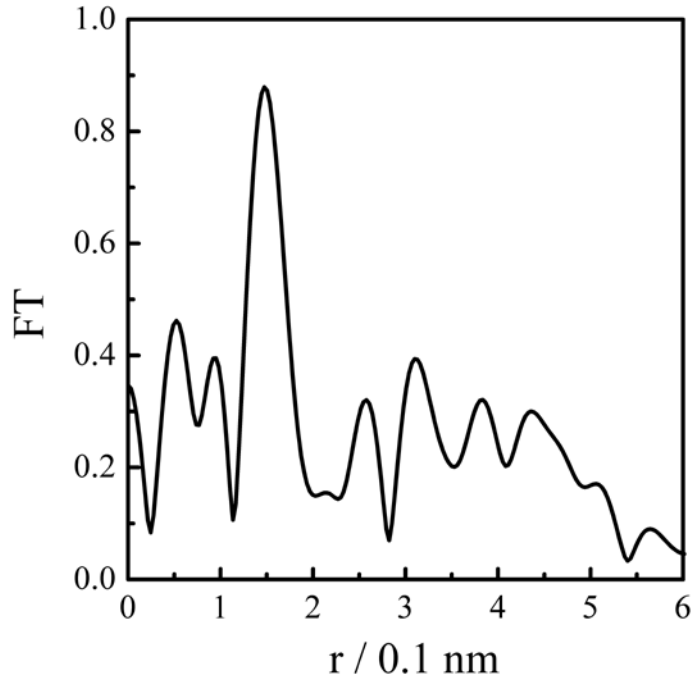


Figure. 7. Fourier transform of the difference spectrum $k^3\Delta\chi(k)$.

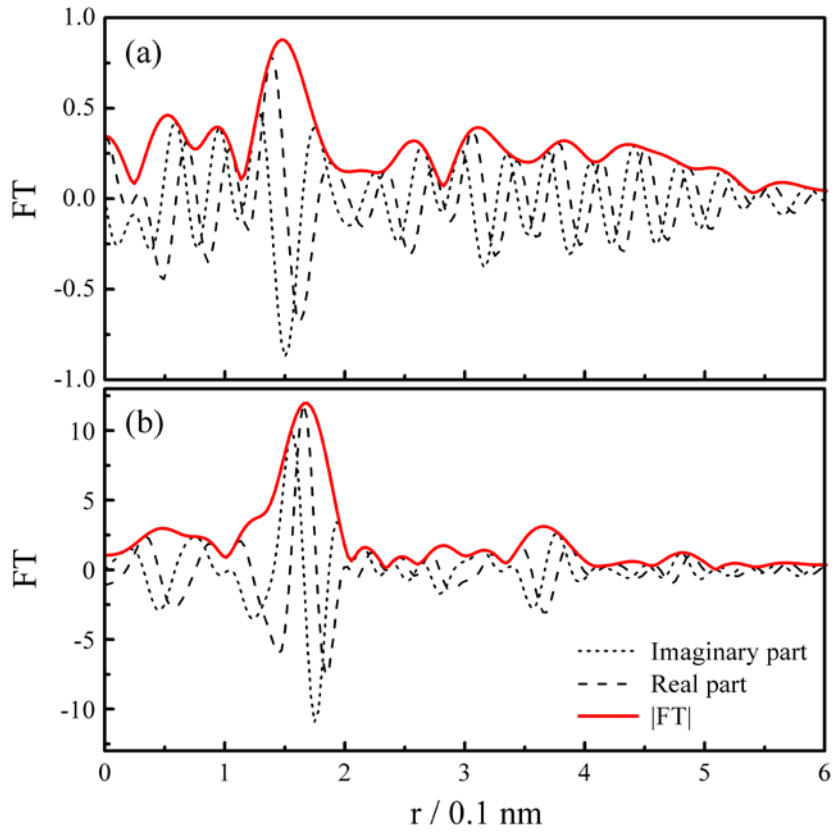


Figure 8. The Fourier transforms. (a) the difference spectrum $k^3\Delta\chi(k)$ (b) dry air at 703 K. Dotted, broken, and solid red lines indicated imaginary, real, and absolute parts, respectively.

-
- ¹ J. Jaklevic, J. A. Kirby, M. P. Klein, A. S. Robertson, G. S. Brown, and P. Eisenberger, *Solid State Commun.* **1977**, 23, 679.
- ² K. Asakura, *Catalysis* edited by J. J. Spivey and M. Gupta (RSC publishing, Cambridge) **2012**, 281, 281.
- ³ H. Oyanagi, A. Tsukada, M. Naito, N. L. Saini, M.-O. Lampert, D. Gutknecht, P. Dressler, S. Ogawa, K. Kasai, S. Mohamed, and A. Fukano, *J. Synchrotron Rad.* **2006**, 13, 314.
- ⁴ F. W. Lytle, R. B. Gregor, D. R. Sandstrom, E. C. Marques, J. Wong, C. L. Spiro, G. P. Huffman, and F. E. Huggins, *Nucl. Instrum. Methods A* **1984**, 226, 542.
- ⁵ O. V. Safonova, M. Tromp, J. A. Bokhoven, F. M. F. de Groot, J. Evans, and P. Glatzel, *J. Phys. Chem. B* **2006**, 110, 16162.
- ⁶ D. Bazin, H. Dexpert, and J. Lynch, *X-ray Absorption Fine Structure for Catalysts and Surfaces*, edited by Y. Iwasawa, pp. 113 (1996). Singapore: World Scientific.
- ⁷ P. Kappen, L. Tröger, G. Materlik, C. Reckleben, K. Hansen, J.-D. Grunwaldt, and B.S Clausen, *J. Synchrotron Rad.* **2002**, 9, 246.
- ⁸ J.-D. Grunwaldt, P. Kappen, L. Basini, and B.S Clausen, *Catal. Lett.* **2002**, 78, 13.
- ⁹ T. Kubota, N. Hosomi, K.K. Bando, T. Matsui, and Y. Okamoto, *Phys. Chem. Chem. Phys.* **2003**, 5, 4510.
- ¹⁰ S.R. Bare, G.E. Mickelson, F.S. Modica, A.Z. Ringwelski, and N. Yang, *Rev. Sci. Instrum.* **2006**, 77, 023105.
- ¹¹ N. Weiher, E. Bus, B. Gorzolnik, M. Möller, and R. Prins, J.A. van Bokhoven, *J. Synchrotron Rad.* **2005**, 12, 675.
- ¹² C. L. Fontaine, L. Barthe, A. Rochet, and V. Briois, *Catal. Today* **2013**, 205, 148.
- ¹³ D. Koziej, M. Hübner, N. Barsan, U. Weimer, M. Sikora, and J. -D. Grunwaldt, *Phys. Chem. Chem. Phys.* **2009**, 11, 8620.
- ¹⁴ M. Hübner, D. Koziej, M. Bauer, N. Barsan, K. Kvashnina, M. D. Rossell, U. Weimar, and J. -D. Grunwaldt, *Angew. Chem., Int. Ed.* **2011**, 50, 2841.
- ¹⁵ M. Hübner, D. Koziej, J.-D. Grunwaldt, U. Weimar, and N. Barsan, *Phys. Chem. Chem. Phys.* **2012**, 14, 13249.
- ¹⁶ A. Gurlo, and R. Riedel, *Angew. Chem., Int. Ed.* **2007**, 46, 3826.
- ¹⁷ A. Gurlo, and R. Riedel, *Chem. Phys. Chem.* **2010**, 11, 79.
- ¹⁸ M. Gaidi, M. Labeau, B. Chenevier, and J. L. Hazemann, *Sens. Actuators B Chem.* **1998**, 48, 277.
- ¹⁹ S. Mukerjee, and R. C. Urian, *Electrochim. Acta* **2002**, 47, 3219.
- ²⁰ R. J. K Wiltshire, C. R. King, A. Rose, P. P. Wells, M. P. Hogarth, D. Thompsett, and A. E. Russell, *Electrochim. Acta* **2005**, 50, 5208.
- ²¹ J. -D. Grunwaldt, and C. G. Schroer, *Chem. Soc. Rev.* **2010**, 39, 4741.
- ²² N. Ishiguro, S. Kityakarn, O. Sekizawa, T. Uruga, T. Sasabe, K. Nagasawa, T. Yokoyama, and M. Tada, *J. Phys. Chem. C* **2014**, 118, 15874.
- ²³ M. R. Antonio, L. Soderholm, and I. Song, *J. Appl. Electrochem.* **1997**, 27, 784.
- ²⁴ M. Balasubramanian, C. A. Melendres, and A. N. Mansour, *Thin Solid Films* **1999**, 347, 178.
- ²⁵ S. Modiano, J. A. V. Carreno, C. S. Fujivara, R. M. Torresi, V. Vivier, A. V. Benedetti, and O. R. Mattos, *Electrochim. Acta* **2008**, 53, 3670.
- ²⁶ J. Monnier, S. Reguer, E. Foy, D. Testemale, F. Mirambet, M. Saheb, P. Dillmann,

and I. Guillot, Corros. Sci. **2014**, 78, 293.

²⁷ M. Nomura, J.Synchrotron Rad. **1998**, 5, 851.

²⁸ M. Nomura, A. Koyama, Design and performance of a new XAFS beamline at the Photon Factory; BL12C, in: KEK Report, Photon Factory, **1996**.

²⁹ M. Nomura, Y. Koike, M. Sato, A. Koyama, Y. Inada, K. Asakura, AIP Conf. Proc. **2007**, 882, 896.

³⁰ K. Asakura, Analysis of EXAFS, in: Y. Iwasawa (Ed.) X-ray Absorption Fine Structure for Catalysts and Surfaces, World Scientific, Singapore, **1996**, pp. 33.

³¹ T. Taguchi, AIP Conf. Proc. **2007**, 882, 162.

³² K. Asakura, Polarization-dependent Total Reflection Fluorescence Extended X-ray Absorption Fine Structure and its Application to Supported Catalysis, in: J.G. Catalano (Ed.) Catalysis Book Series, **2012**, pp. 281.

³³ J. W. Cook, D. E. Sayers, J.Appl.Phys. **1981**, 52, 5024.

³⁴ M. Newville, J. J. Kas, J. J. Rehr, Journal of Physics: Conference Series **2009**, 190, 012023.

³⁵ J. J. Rehr, J. J. Kas, M. P. Prange, A. P. Sorini, Y. Takimoto, F. Vila, Comptes Rendus Physique **2009**, 10, 548.

³⁶ J. J. Rehr, Radiation Phys.Chem. **2006**, 75, 1547.

³⁷ W. C. Hamilton, Acta Cryst. **1965**, 18, 502.

³⁸ J. C. Bart, Adv. Catal. 1986, 34, 203.

³⁹ R. Kiebach, N. Pienack, W. Bensch, J. -D. Grunwaldt, A. Michailovski, A. Baiker, T. Fox, Y. Zhou, and G. R. Patzke, Chem. Mater. **2008**, 20, 3022.

⁴⁰ M. Deepa, P. Singh, S. N. Sharma, and S. A. Agnihotry, Sol. Energy Mater. Sol. Cells **2006**, 91, 1305.

Chapter 3

Characterization of Pt doped SnO₂ Catalyst for a high performance micro gas sensor

1. Introduction

SnO₂ has been widely utilized for gas sensors as its conductivity varies with partial pressures of oxygen and reductive gases.^{1,2} The SnO₂ sensor requires the high operation temperature necessary for the reaction between the SnO₂ and gases and an electric power supply. The external power-driven type SnO₂ sensors have been developed upto now. In order to increase the number of home-use gas sensor, battery-driven type or wireless models are important for their good appearance and their free installation. The battery-driven sensors should have longer life time than 5 years and thus the low power consuming sensors has to be developed with high selectivity for methane, which is a main ingredient in natural gas. The strategy is to enhance the sensor activity by the addition of metal catalyst and to miniaturize the sensor to reduce the energy consumption. Yamazoe et al has studied the effects of additives on SnO₂ gas sensors.³ M.Labeau et al has demonstrated that Pd and Pt additives play important role in the electrical properties of SnO₂-thin film-based sensor.⁴ From this standpoint of view, Suzuki et al. have developed SnO₂ thin film produced by MEMS method.^{5, 6} Recently I found that the Pt doping increases methane sensitivity of SnO₂ thin film sensor device which will provide the new pathway to realize a low power consumption gas sensor. The sensor can detect the 12500 ppm methane which is a 1/4 of the methane explosion limit (53000 ppm) even after the 5 years. The mass production of the high performance sensors requires further clear understanding of the atomic structure of the gas sensors.

Since Pt metallic cluster is a good catalyst for many reactions including the hydrogen and hydrocarbon oxidation reaction. There are several mechanisms to improve the sensor performance by the additives. One is an electronic effect and the other is a spillover effect. Yamazoe and Kocemba et al reported that Pt nanoparticles on the SnO₂ surface improve the performance by the spillover reaction.^{7,8} Thus Pt clusters deposited on the SnO₂ were expected to enhance the sensor sensitivity by the spillover reaction. In the previous papers about the characterizations of Pt-SnO₂ sensor, the oxidized Pt or Pt aggregates are present in SnO₂ substrate depending on the atmosphere and Pt concentration.^{1,9,10,11,12} But details in Pt structures have not been determined. In this paper, I have studied the local structure of Pt in the highly active SnO₂ film base sensor by X-ray

diffraction(XRD), X-ray photoelectron spectroscopy(XPS) and X-ray absorption fine structure(XAFS).

2. Experimental

2.1. Catalyst preparation

Pt doped SnO₂ thin layer with 400 nm thickness (denoted as X% Pt-SnO₂ where X indicates the atomic % of Pt) was prepared by the sputtering method on the p-type Si substrate covered with naïve SiO₂ film (600 nm) followed by annealing at 803 K. Pt and SnO₂ ratio was controlled by the loading ratio in the targets and finally the concentration of Pt in the film was determined by the ICP(Inductively Coupled Plasma) by dissolving the film using hydrochloric acid.

2.2. Characterization of the catalysis

XRD patterns were recorded by using a Cu K α from RIGAKU ATX-G with X-ray tube voltage =50 kV and X-ray tube current =300 mA. XPS spectra were measured in ULVAC Phi Quantum-2000 using monochromated-Al K α X-ray operated at 15 kV-15 mA.

Pt L₃-edge XAFS spectra were measured at BL-12C of KEK-PF using a Si(111) monochromator in a fluorescence mode^{13,14}, and the Sn K edge XAFS spectra were measured at the NW-10A of KEK-PF-AR equipped with a Si(311) monochromator also in a fluorescence mode.¹⁵ XAFS spectra were analyzed with REX2000 (Ver. 2.5, RIGAKU).^{16,17,18} The backgrounds of all XAFS spectra were removed by a spline smoothing method with Cook and Sayers criteria and normalized by the edge height.¹⁹ The k^3 -weighted EXAFS oscillations were Fourier-transformed to k -space over $k = 14 - 148$ nm⁻¹ for Pt L₃-edge spectra, over $k = 23 - 144$ nm⁻¹ for Sn K-edge spectra. The each peak in the Fourier transforms was filtered and inversely Fourier transformed to the k -space for the curve fitting analysis. I carried out the non-linear least square curve fitting using the following equations.

$$k^3 \chi(k) = \sum_j S_0^2 \frac{k^2 N_j F_j(k)}{r_j^2} e^{-2k^2 \sigma_j^2} e^{-\frac{2r_j}{\lambda_j}} \sin(2kr_j + \phi_j)$$

$$k = \sqrt{\frac{2m}{\hbar^2} (h\nu - E_o - \Delta E)}$$
(1)

where S_0^2 , N_j , r_j , and σ_j are amplitude reduction factor, coordination number, bond distance, and Debye Waller factor, of the j -th coordination shell, respectively. λ is a mean free path. $F_j(k)$ and $\phi_j(k)$ are backscattering amplitude and phase-shift functions which were obtained from FEFF (ver. 8.0).^{20,21,22} E_0 is the absorption edge energy tentatively determined as the inflection points and energy shift ΔE is adjusted during the fitting process.

The errors were estimated by Hamilton test on R-factor with a significance level over 90 %.²³

2.3. Catalyst performance

We evaluated the catalyst performance with a flow reactor (Okura Riken Co) with a space velocity of 16800 SV [h⁻¹]. Two catalytic combustion reactions of 5000 ppm CH₄ or 5000 ppm H₂ balanced with O₂ were performed with the products being analyzed by gas chromatography.

3. Results

3.1. Catalytic active of Pt/SnO₂

Figure 1 shows the combustion rates toward methane (reaction temperature = 723 K) and hydrogen (reaction temperature = 473 K). The methane combustion rates gradually rose with the increase of Pt content upto 5 at% and then were saturated at 6 at% followed by drastically dropped at more than 10 at%. On the other hand, the combustion rates to H₂ also rose with the increase of Pt loading, and the gas was burned about 100 % at near 9 at% Pt/SnO₂ and kept at higher H₂ activity at more Pt content.

Figure 2 shows the electric resistance dependence on the CH₄ and H₂ concentrations on the 9 at% Pt doped SnO₂ together with non-doped SnO₂ sample. The electric resistance change was proposed as due to the adsorption and desorption of oxygen.²⁴ The electrical resistance (R) decreased with the gas concentrations(p). It is $R=10^b p^a$ [O₂]^b, where p was a partial pressure of hydrogen or methane and a was -0.92 and -0.36 for hydrogen and methane, respectively, on the 9 at % Pt/SnO₂ while those on the SnO₂ film without Pt were -0.26 and -0.16, respectively. The oxygen dependence on the oxygen pressure was reported to be 0.154.²⁴ The conductivity dependence of Pt/SnO₂ on hydrogen nearly = -1 indicated that

the reaction might be diffusion limited of hydrogen. The Pt enhanced the activity of the surface reaction.

3.2. Crystal structure Analysis of Pt/SnO₂ by XRD

Figure shows XRD patterns of Pt/SnO₂ thin film on Si substrate with different Pt loadings. The SnO₂ thin film has a rutile structure giving the peaks at 26.7, 33.8, 38.3, 52.2°, corresponding to (1,1,0), (1,0,1), (2,0,0) and (2,1,1) of rutile structure. Pt/SnO₂ with the Pt loading less than 10at% had in principle a rutile structure and no platinum particle peak was observed. However, the peak broadening and peak shift were observed in SnO₂ lattice, indicating the modification of SnO₂ lattice and the decreasing crystallinity under the influence of the Pt. Finally, the broad pattern like amorphous was observed at Pt doping of 14 at%. In addition, diffraction peaks were shifted to larger angles with the Pt loading indicating the shrink of the rutile lattice. I calculated the a-axis and the c-axis for rutile structure from XRD peak positions in each platinum-concentration as shown in Figure 4. I found both a and c axes were contracted. The Pt species should have a strong interaction with SnO₂ lattice upto 9 at%. The 1.5 % and 0.5 % contraction along a-axis (4.75 to 4.68 Å) and along c-axis (3.195 to 3.18Å) were observed, respectively as shown in Figure 4. One possible interpretation of the contraction in Figure 4 was the creating of the Pt particle at the boundary of SnO₂ particle that compressed the SnO₂ particles. The other idea was most Pt atoms were solved in the SnO₂ lattice to form a solid solution, being substituted with the Sn. The inclusion of Pt induced the lattice disorder and finally the amorphous state at 11 at% Pt loading. In order to confirm this hypothesis I investigated Pt local structure by XAFS.

3.3. XAFS result of Pt/SnO₂

3.3.1. XANES of Pt/SnO₂

Figure shows XANES spectra of the Pt/SnO₂ samples and references. Compared with the XANES spectra of SnO₂, SnO, Sn-foil, Sn in PtSn alloy, the Pt/SnO₂ had a similar structure to for the SnO₂. The absorption of Sn K-edge was shifted to the lower energy side with the increase of platinum loading as shown in Figure 6. It was quite interesting that a few % Pt modified the electronic structure of Sn. These phenomena were well understood by the second hypothesis that the Pt was highly dispersed

throughout the SnO_2 matrix and affected the Sn electronic state. Comparing electronegativities of Pt (2.2) and Sn(1.8), more electron remained in Sn in the Pt-O-Sn than in Sn-O-Sn.

Figure shows Pt L_3 -edge XANES spectra of the Pt/ SnO_2 samples and the references. The white line heights of 5 at% and 9 at% Pt/ SnO_2 spectra showed a little larger intensity than that of PtO_2 and much larger than those of Pt and PtSn alloy. Figure 6 shows the concentration dependence of the white line intensity. Pt at low loading showed the higher peak height and that of 14 at% Pt/ SnO_2 was a little smaller than PtO_2 . Since the origin of the white line peak was transition from the $2p_{3/2}$ core state to 5d empty state, the stronger intensity suggested the presence of more empty 5d state in the Pt/ SnO_2 samples with the Pt content less than 10 at % than that in the PtO_2 while there is less d vacancy in the 14 at% Pt/ SnO_2 . The d electron in the Pt in the SnO_2 lattice was strongly drawn by the surrounding Sn^{4+} , giving stronger white line height than PtO_2 .

3.3.2. EXAFS spectra of Pt/ SnO_2

Figure 8 shows the k^3 -weighted Sn K-edge EXAFS oscillations ($k^3\chi(k)$) and the Fourier transform (FT) of 9 at% Pt/ SnO_2 together with several reference samples. The FT of Pt/ SnO_2 was close to that of SnO_2 , indicating that the Sn rutile structure was maintained in the sample. The first peak was corresponding to Sn-O while characteristic peaks appeared in 2.5 – 4 Å corresponding to the two Sn-Sn interactions of rutile SnO_2 . Figure 9 shows the Sn K-edge $k^3\chi(k)$ and the FT of Pt/ SnO_2 with various Pt contents. The Pt/ SnO_2 samples with the Pt content less than 9 at% had the similar $k^3\chi(k)$ and the FT to those of SnO_2 . The EXAFS oscillations were gradually reduced with the increase of Pt content. The Sn-Sn interaction disappeared in more than 14 at% samples, indicating the formation of amorphous local structure.

Figure 10 shows Pt L_3 edge $k^3\chi(k)$ and the FT of Pt/ SnO_2 samples together with reference samples. Pt L_3 -edge $k^3\chi(k)$ and FT of PtO_2 showed the different oscillations from those of Pt/ SnO_2 indicating the structure of Pt was not PtO_2 . The peak appeared at 1 – 2 Å was corresponded to the Pt-O. The peaks in the range of 2.5 – 4 Å were different from PtO_2 , which might be assigned to Pt-Sn or Pt-Pt.

Figure 11 shows the Pt L_3 -edge $k^3\chi(k)$ and the FT of Pt/ SnO_2 with different

Pt loadings. The complex structures appeared in high k region for the samples with less than 10 at% Pt loading but the sample more than 11 at % Pt loading showed simpler oscillations. Correspondingly the peak intensities in the range of 2.5 – 4 Å decreased with the increase of the Pt concentration and the peaks disappeared at 11 at %.

The changes in FT and $k^3\chi(k)$ could be rationalized as follows. If the Pt was located in the lattice of SnO₂, Pt L₃ edge should have the similar $k^3\chi(k)$ and FT to those of corresponding Sn K-edge. In fact, FT had the similar structure to that of SnO₂ though the Sn K-edge was located at high energy and the resolution was less because of the life-time broadening. The increase of Pt concentration diminished the peak at the 2.5 – 4 Å because the interference of Pt(Sn)-Pt and Pt(Sn)-Sn interactions appears as a result of the replacement of Sn with Pt. More increase of the Pt loading broke the SnO₂ lattice to form the amorphous structures. I concluded that Pt and Sn were located at octahedral site of rutile oxygen lattice up to 10 at% and the amorphous formation starts at 11 at %.

In order to obtain more detailed information about the structure, I carried out curve fitting analyses as shown in Tables 1-4. First I carried out the curve fitting analyses of the first peak. Table 1 and 2 show the results for the Pt-O and Sn-O bond, respectively. The Pt-O distance in Pt/SnO₂ samples was a little shorter than that of PtO₂ and much shorter than SnO₂. The distance was almost the same within the limit of error, independent of the Pt loading. The coordination number was 6.0 in 5 at% Pt/SnO₂, indicating the octahedral coordination around the Pt, and the Pt was located in the octahedral site of SnO₂ rutile crystal lattice. The Pt-O coordination number remained 6 up to 10 at% and gradually decreased with the increase in the Pt content probably because of the partial formation of amorphous structure around Pt which induced the local disorder that could not be compensated Debye-Waller factor. In the 14 at%, the Pt-O coordination number was further diminished. Sn-O showed 6 as a coordination number and 2.05 Å as a bond distance in 5 at% Pt/SnO₂ with other parameters almost the same as those of SnO₂. However, Sn-O was diminished at 14 at% Pt-SnO₂ probably due to the amorphous phase formation. It is interesting that Sn-O coordination number remained 6 at 11 at % Pt-SnO₂ while that of Pt decreased a little. It might be due to the amorphous structure formation occur at 11 at % only around the Pt site and many Sn

atoms are in the crystal lattice.

Next I tried to carry out the second shell analysis. However, it was quite difficult. There were at least 2 shells in M-Sn (M=Pt or Sn) interaction. As the Pt content increased, two more M-Pt interactions occurred and their XAFS oscillations interfered with those of the original M-Sn interaction. Consequently, I need 4-shell fitting analyses and 16 fitting parameters though the degree of freedom in the analysis which was nearly $17(= 2\Delta k\Delta r/\pi)$ and the 4 shell fittings with full parameters were optimized quite erroneous and less reliable.

Thus I first carried out 2 shell fittings of 5 at% Pt/SnO₂ for both edges where the least M-Pt contributions exist. I obtained the Sn-Sn bond distances in the Sn K-edge of Pt-SnO₂ at 3.16 Å and 3.72 Å which was well corresponding to those in the SnO₂ (3.16 and 3.73 Å), indicating again the SnO₂ rutile structure was maintained. The local structure around Pt was obtained from Pt L₃ edge XAFS. Pt-Sn distances were found at 3.13 and 3.68 Å shorter than those obtained in Sn K-edge SnO₂. The curve fitting analysis clearly suggested that the Pt was located in the SnO₂ lattice and the local structure of Pt was explained by the PtO₂-SnO₂ solid solution model. When I applied 2 shell fitting of M-Sn on other Pt-SnO₂ samples (Pt content less than 11 at %), the bond distances were almost the same as those found in 5at % Pt-SnO₂, though the M-Sn coordination numbers decreased with the content of Pt owing to the neglect of the increasing contribution of M-Pt interaction and the increasing the local disorder in SnO₂ lattice induced by the Pt replacement which had shorter Pt-O and Pt-Sn(Pt) distances than those in SnO₂ lattice.

In these analyses, I could not get evidence for the formation of Pt metal cluster because I could not get good fitting results when I fitted the data assuming Pt-Pt distance at 0.277 nm. However, EXAFS was a bulk technique and nobody knew the surface Pt state. I carried out XPS analyses to see the surface structure and state of Pt species.

3.4. Surface Analysis of Pt/SnO₂ by XPS

Figure 12 shows XPS spectra of O 1s, Sn 3d and Pt 4f in Pt/SnO₂ samples. The binding energy of Sn 3d_{5/2} coincided with that of the tetravalent state. The binding energy was little shifted to lower energy side according to the Pt doping amount well corresponding to the XANES results, *i.e.*, Pt did not

draw so much electron in the Pt-O-Sn as Sn did in the Sn-O-Sn. The binding energy of Pt $f_{7/2}$ appeared at 75.2 eV which corresponds to Pt⁴⁺.²⁵ A small rise was observed at 73.1 eV which appeared remarkably for the sample with Pt content more than 11 at%. I performed the peak deconvolution of Pt4f peak in Pt/SnO₂ as shown in Figure. There were two Pt species on SnO₂, with their binding energies 75.2 eV and 73.1 eV, respectively. The former corresponded to Pt⁴⁺ while the latter was in good agreement with Pt²⁺. I could find a small amount of 73.1 eV peak even in the sample with the Pt content less than 10 at%. I evaluated the ratio of 75.2 eV and 73.1 eV as shown in Table 5. The ratio of peaks of 75.0 eV to 73.1 in the 5 -10 at % Pt/SnO₂ were almost 84 :16. Pt²⁺ content increases at more than 11 at%. This indicated the Pt species were mainly presented in tetravalent even on the surface at less than 10 at%. Pt²⁺ increases at more than 11 at %. Pt⁰ was never observed in XPS. Judging from the white line intensity of Pt L₃ edge, the bulk Pt was tetravalent. The white line intensity decreased with more than 11 at % well corresponding to the XPS observation where Pt²⁺ starts to increases. Thus the surface Pt valence state had not big difference from that in the bulk. Since amorphous phase increases at more than 11 at% as demonstrated by XRD and XAFS, Pt²⁺ may be mainly present in the amorphous phases. Combining XAFS and XPS results I concluded Pt metal was not formed in the Pt/SnO₂

4. Discussion

4.1. Local structure of Pt species

Contrarily to the expectation I could not find any Pt nano particles in the whole range of Pt content and all measurements indicated that the Pt species was located at the Sn site in the SnO₂ lattice. In other word, *Pt and SnO₂ made a solid solution structure*. The replacement of Pt induces the lattice contraction and distortion as demonstrated by XRD. This might be due to the smaller Pt-O distances as found in XAFS. This lattice distortion induced the vitrification of the SnO₂ crystal lattice at more than 11 at % and the Pt/SnO₂ was transformed completely into amorphous state at 14 at %. This is due to the difference in the ionic radius of Pt⁴⁺ and Sn⁴⁺. The ion radius of Pt⁴⁺ is 0.77 Å while those of Sn⁴⁺ is 0.83 Å. This different ionic distance was reflected in the shorter Pt-O and Pt-Sn distances around Pt. I noted that the contraction of the lattice in a-axis was larger than in the

c-axis. The XAFS analyses indicated that the each Sn-Sn or Pt-Sn bond distance had little concentration dependence. I inferred that that more Sn-Pt interaction was present in the ab plane than in the c axis. Considering the rutile lattice structure, Pt-Pt interaction occurs between the center and the corner site rather than that between centers along c axis. Consequently the lattice shrinkage mainly arose in the ab plane. These lattice shrinkages and distortions caused by the Pt replacement may lead to amorphous structure at 14 at% Pt-SnO₂.

In the previous studies, there were some reports that claimed the Pt was oxidized state in the Pt-SnO₂. Gaidi et al. reported that Pt was oxidized states with Pt-O distance =0.196 nm while at higher loading of Pt and under reductive conditions, Pt was found in a metallic form.¹² They did not mention the location of Pt but seemingly most of them were in the amorphous oxide or metal particles. They also found that the Pt was reduced to metallic state in the reducing gas and this redox of Pt was related to sensing property. Lee et al. studied XPS and XRD on the Pt/SnO₂.²⁶ They claimed that Pt metallic particles covered with PtO₂ was present in the sensor. Kappler investigated that the Pt-SnO₂ by TEM, RAMAN and XPS.²⁷ They suggested that Pt was mostly in oxidized state on the Pt particle or in its near-surface region. They denied the Pt promotion effect was due to spill-over effects or Fermi energy control of Pt nanoparticles. In this study, I clearly demonstrated that the high performance sensor with long lifetime should have the Pt located at the lattice point of SnO₂. The amorphous phase PtO_x(Pt²⁺ or Pt⁴⁺) was not active. As pointed out by the Gaidi, *in situ* characterization must be necessary to confirm the real active structure and reaction mechanism yet our preliminary *in situ* EXAFS study indicated the substituted Pt in the lattice was stable under the sensing conditions.

Noble metals such as Pt and Pd are easily reduced and aggregated to metal particles, However, they could sometimes be atomically dispersed and/or placed in the lattice position of oxide matrix in the oxidized form. Pt-Ce_xTi_{1-x}O₂ prepared by solution combustion method gave the Pt located at the oxide lattice which showed high activity for CO oxidation reaction.²⁸ The Pt was atomically dispersed on Na-promoted TiO₂ surface to show high activity for HCHO oxidation reaction.²⁹ Thus the Pt in the oxide lattice can oxidize CO and the organic compounds.

4.2. The structure and activity

9 at % Pt/SnO₂ showed the highest activity towards CH₄ oxidation reaction. The XRD, XAFS and XPS have demonstrated that the Pt was located in the SnO₂ lattice and no evidence was found for the formation of Pt nanoparticles. More than that concentration, the lattice structure started to be destroyed and in the 14 at % sample, the structure was changed to the amorphous phase where there was a little activity for CH₄ oxidation as shown in Figure 2. In this amorphous structure, Pt⁴⁺ and Pt²⁺ were observed but no evidence was obtained for Pt metal cluster formation. Consequently, Pt⁴⁺ in the Sn position in the lattice was necessary conditions for high activity for CH₄ combustion. The oxidation of CH₄ may proceed with the Mars-van Krevelen mechanism. Pt may oxidized the CH₄ using the lattice oxygen which produces conduction electron. The lattice Pt might be stable and reoxidized to Pt⁴⁺ that must be necessary for the long life time. Thus the Pt/SnO₂ prepared by cosputtering method effectively replaces the Sn with Pt in SnO₂ lattice which caused the high-performance and long-life time gas sensor.

5. Conclusions

I investigated the crystal structure and the combustion property for CH₄ and H₂ gas of Pt/SnO₂ catalyst to evaluate advantage of the methane gas sensor. The structural property of the Pt/SnO₂ prepared by sputter technique was characterized by XRD, XPS, XAFS and the catalyst activity was examined by combustion property of methane and hydrogen gas. Pt/SnO₂ took a solid solution structure in rutile crystal with Pt loading up to 10 at%. The catalyst activity to methane was the highest at 9at%. The CH₄ combustion property was lost at more than 11 at% of Pt loading accompanied by the structure distortion and the change to amorphous structure. On the other hand, the combustion property of H₂ steadily increased with the Pt loading. It is our next challenge to clarify the mechanism of the reaction of the Pt/SnO₂ catalyst.

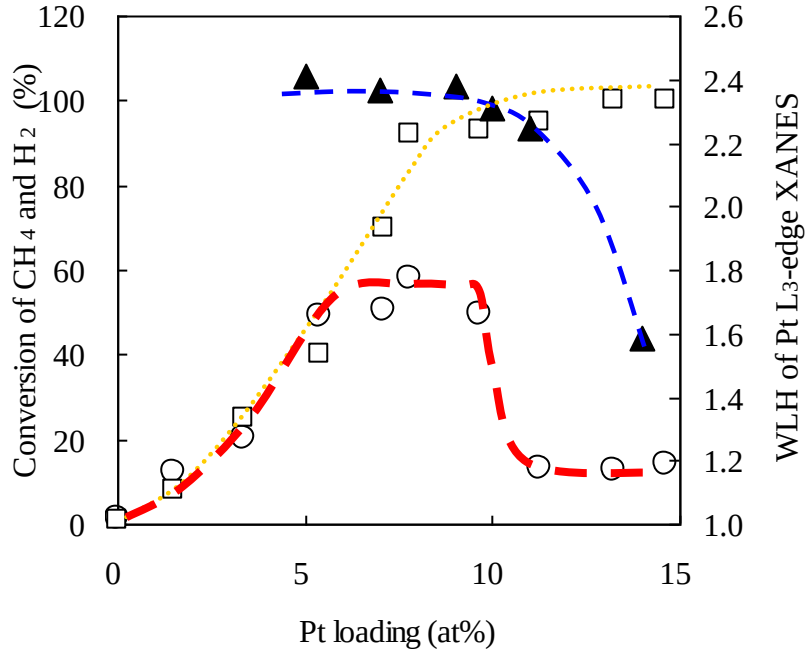


Figure 1. Conversion property for CH₄ at 450 °C (Circle) and H₂ at 200 gas (Square). Compared with White Line Peak Intensity of Pt L₃-edge XANES (Triangle). WLH of Pt L₃-edge XANES were defined as Δ WLH from White Line peak Height on figure 7. Δ WLH of PtO₂ is 2.1 .

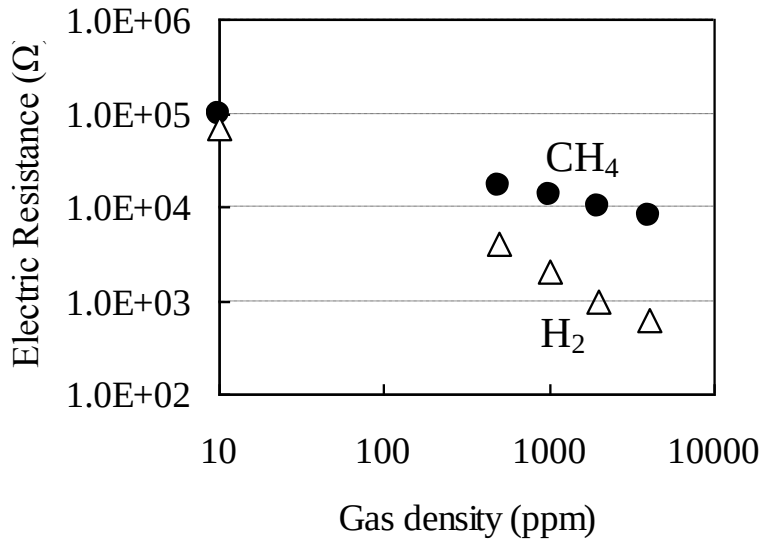


Figure 2. Dependency of gas density to electric resistance for 9 at% Pt doped SnO₂/Non doped SnO₂.

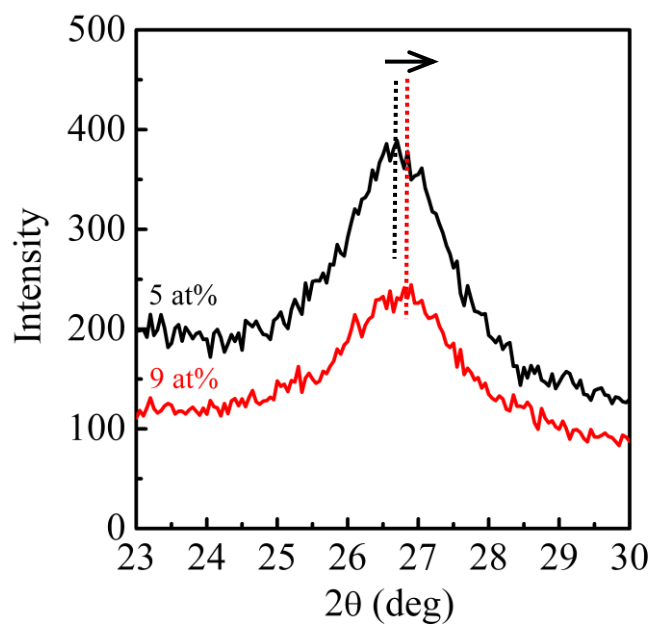
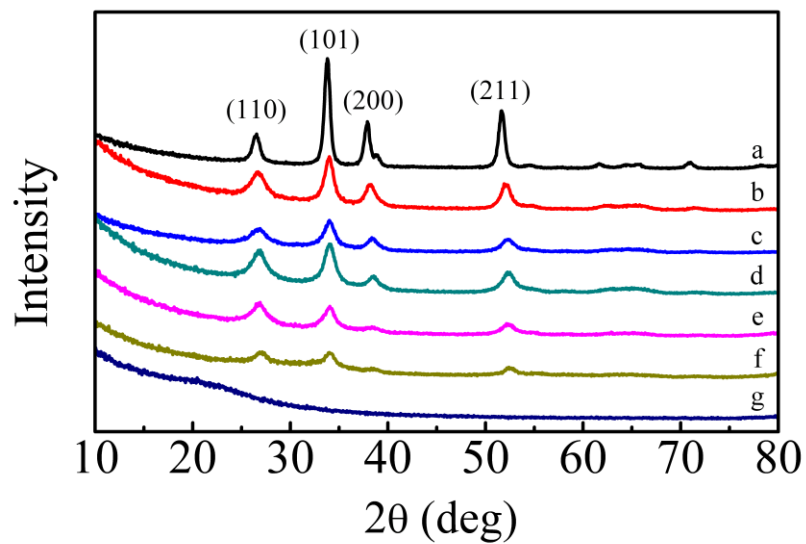


Figure 3. XRD patterns of different Pt loadings and SnO₂. Compare with the a: SnO₂ b: 5at% c: 7 at% d: 9 at% e: 10 at% f: 11 at% g: 14 at%. Plane indices peak of (1,0,1) ($2\theta=33.800^\circ$) at 5 at% and 9 at%.

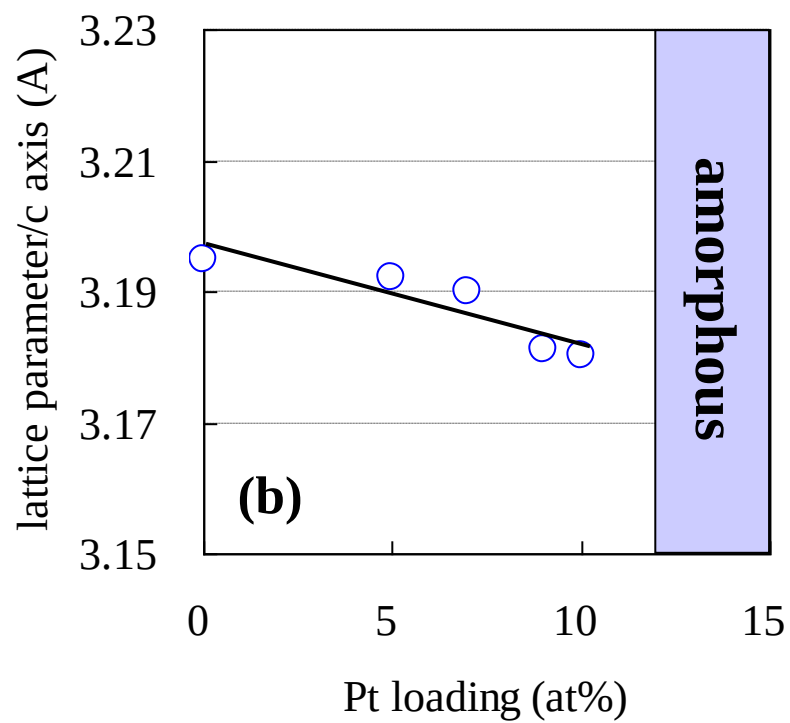
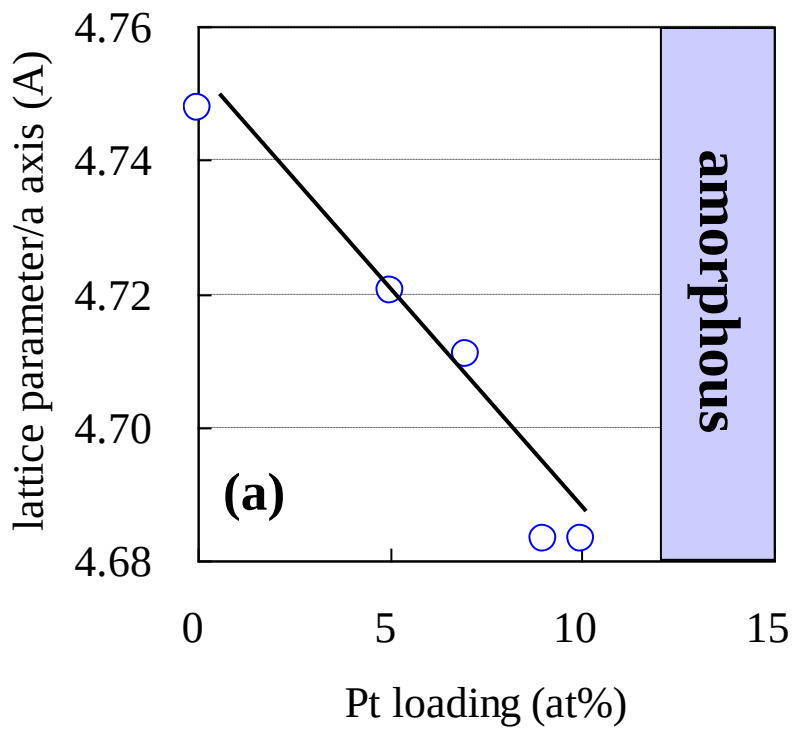


Figure 4. Change of lattice parameter for rutile crystal. (a) a axis (b) c axis

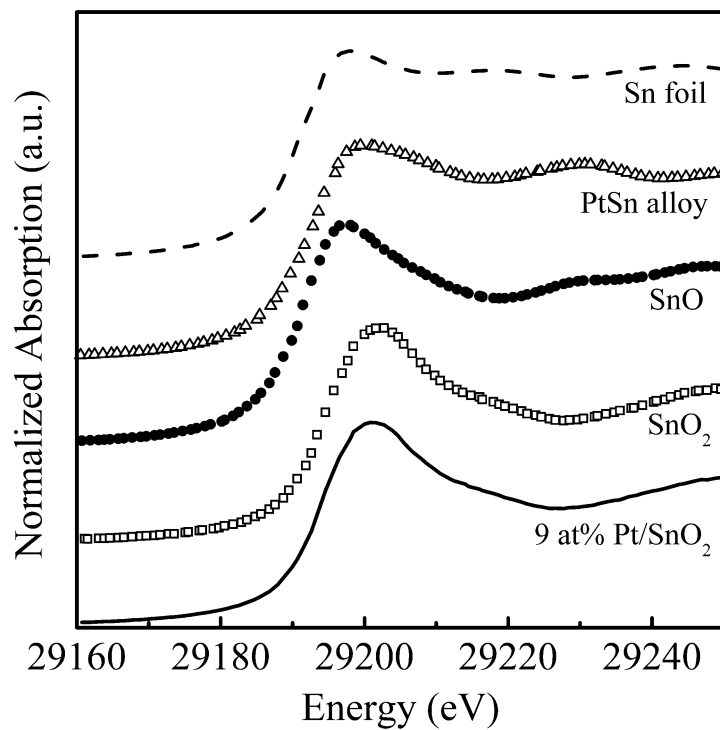


Figure 5. Sn K-edge XANES spectra of Pt/SnO₂
 Compared with the White Line peak Height of SnO₂, SnO, Sn-foil, Sn in
 PtSn alloy (Loading of Pt in alloy is 37 wt%).

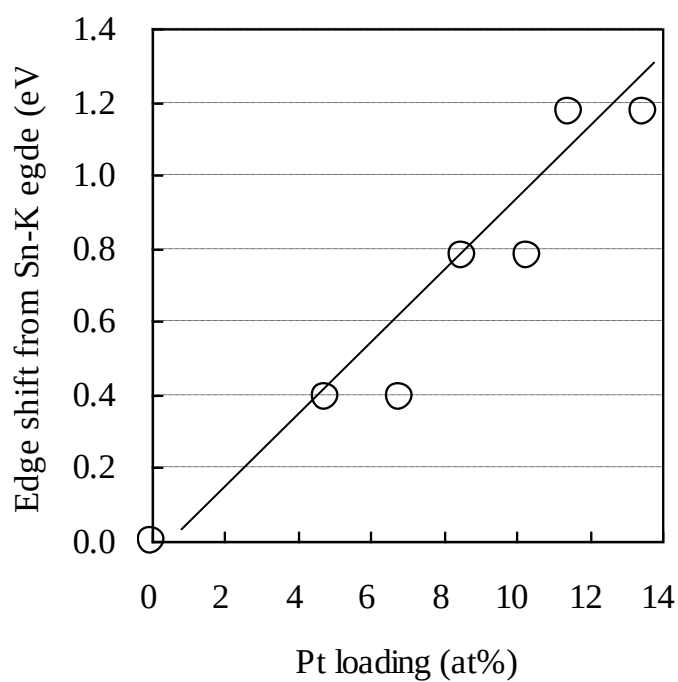
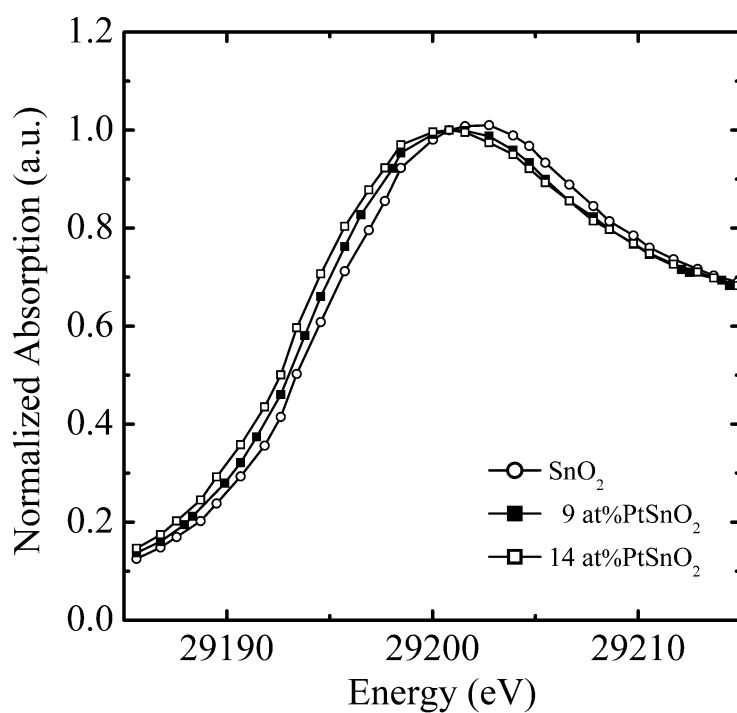


Figure 6. Compared with SnO_2 , platinum-concentration is 9 at% and 14 at%. The edge shift to Sn-K edge
It is plotted max value of liner differential spectra to XANES

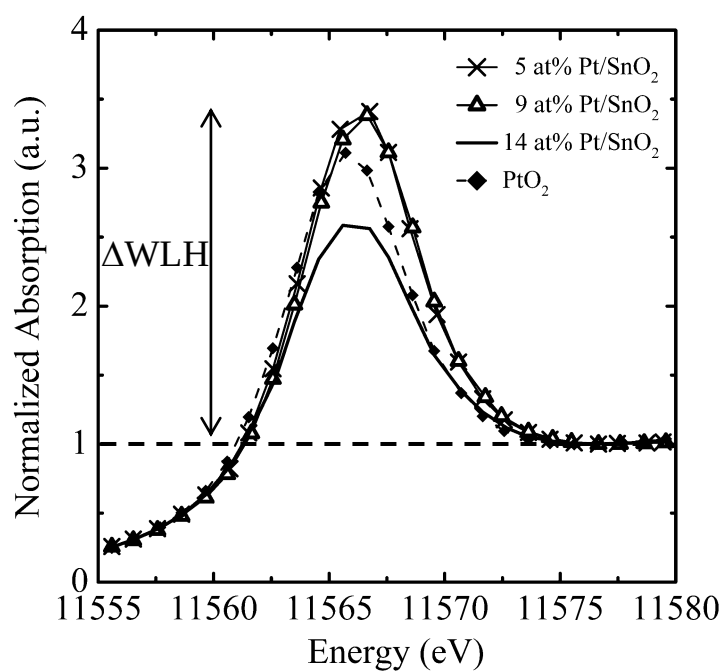
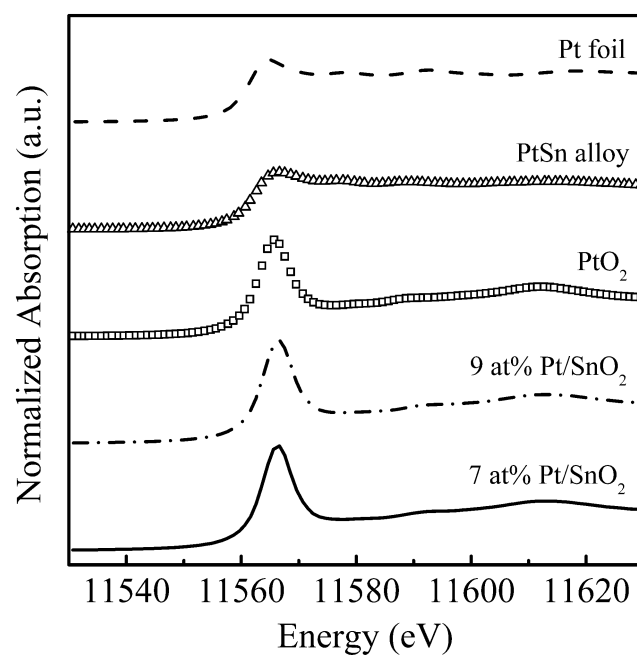


Figure 7. Pt L_3 -edge XANES spectra of Pt-SnO₂ Compared with the WLH of 7 at% and 9 at% Pt-SnO₂, PtO₂, Pt-foil, Pt in PtSn alloy. Compared with PtO₂, platinum-concentration is 5 at%, 9 at% and 14 at%

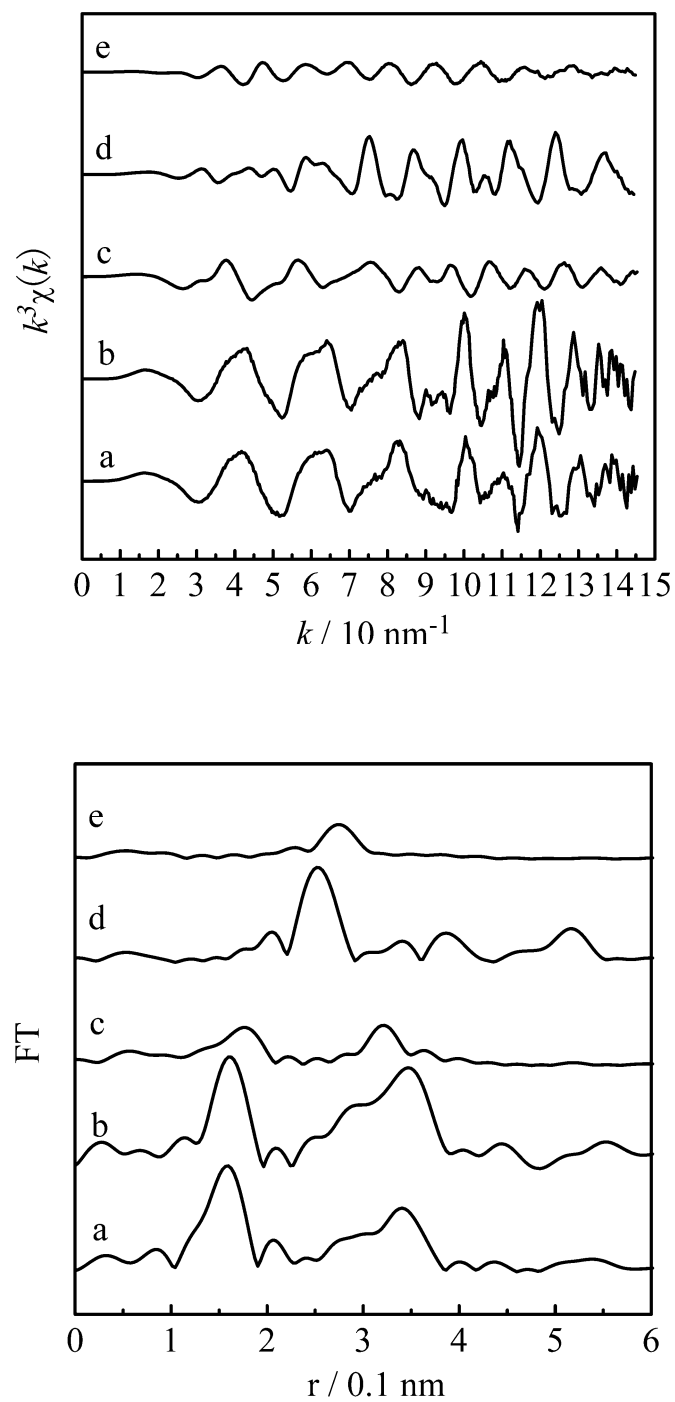


Figure 8. EXAFS oscillation by Sn K-edge and FOURIER Transform of Pt-SnO₂. Compared with a:9 at % Pt/SnO₂ b:SnO₂ c:SnO d:PtSn alloy e:Sn-foil

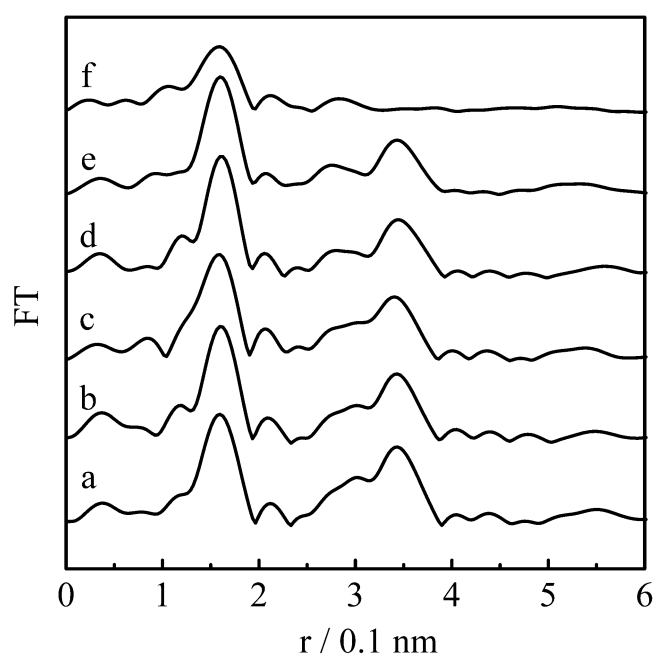
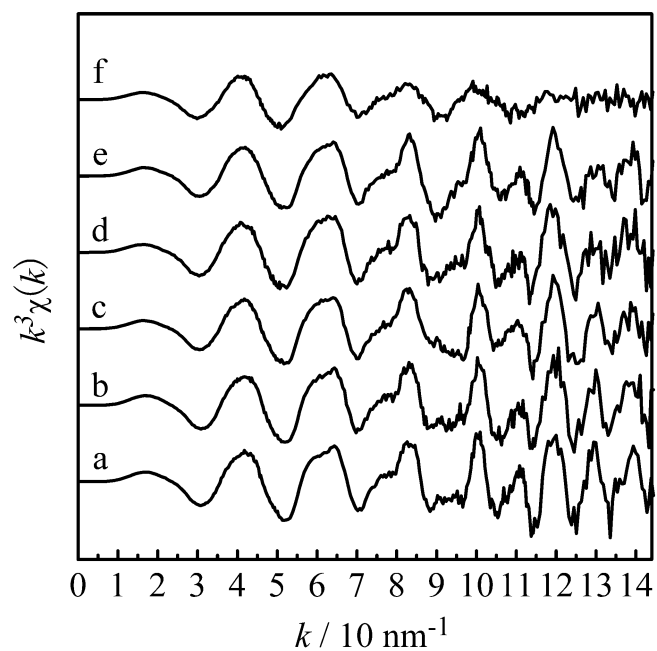


Figure 9. Dependency on the amount of platinum to EXAFS spectra by Sn K-edge. It is EXAFS oscillation and Fourier Transform. Compared with a: 5at% b: 7 at% c: 9 at% d: 10 at% e: 11 at% f: 14 at%

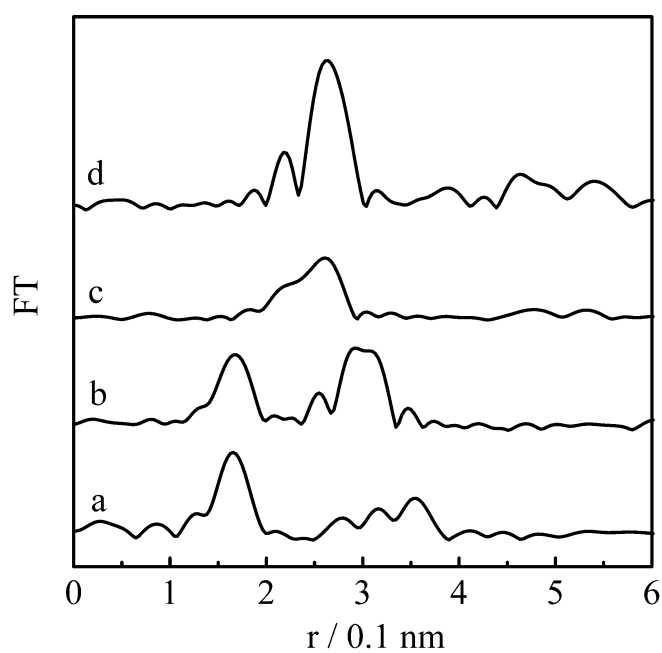
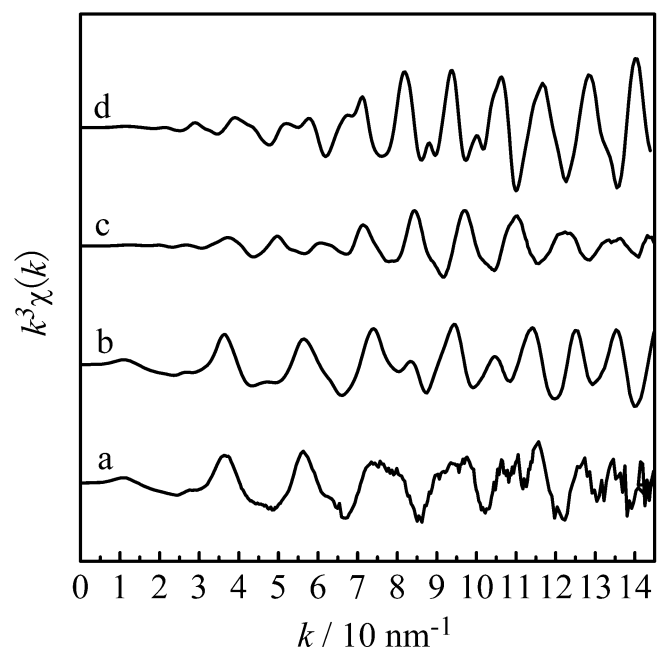


Figure 10. EXAFS oscillation by Pt L₃-edge and Fourier Transform of Pt-SnO₂. Compared with a:9at % Pt-SnO₂ b:PtO₂ c:PtSn alloy d:Pt-foil

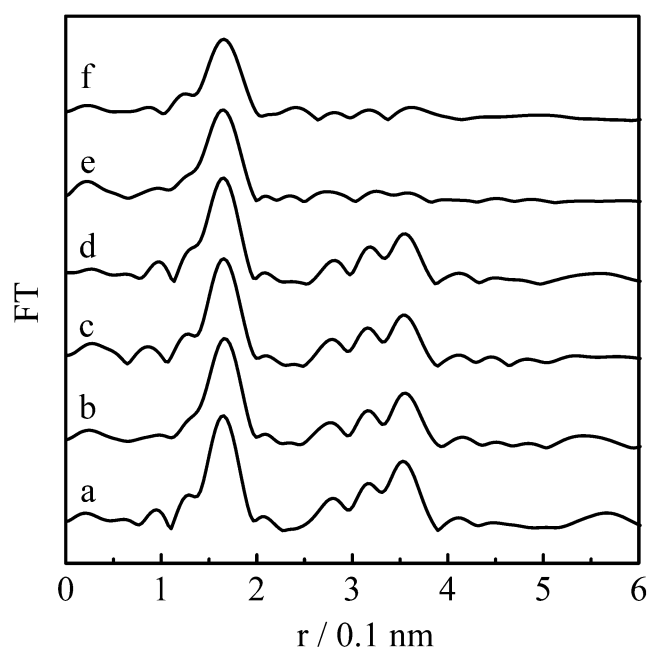
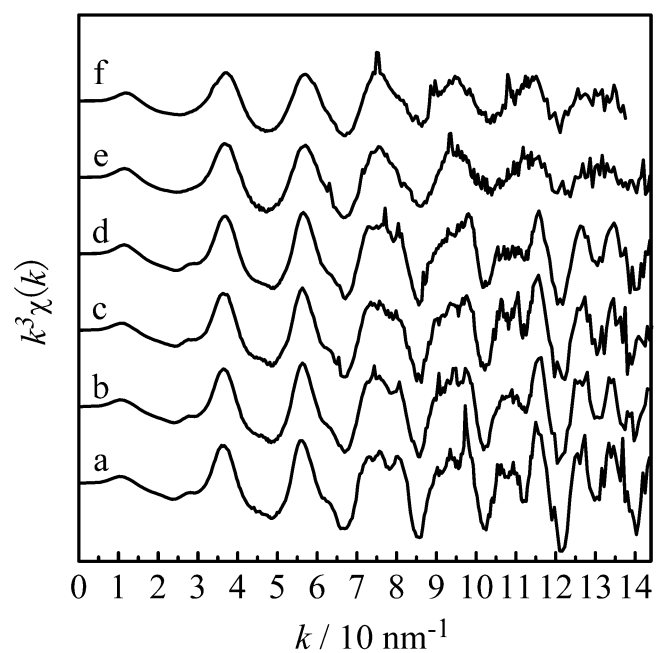


Figure 11. Dependency on the amount of platinum to EXAFS spectra by Pt L₃-edge. It is EXAFS oscillation and Fourier Transform. Compared with a: 5at% b: 7 at% c: 9 at% d: 10 at% e: 11 at% f: 14 at%

Table1. Curve fitting result by FEFF for Pt-O bond to Pt L₃-edge FT-EXAFS.

Pt L ₃ -edge EXAFS spectra		Curve fitting result by FEFF for Pt-O bond coordination number (CN) bond distance (r), Debye-Waller factor (σ)				
Concentration of Pt / at%		CN	R / nm ⁻¹	ΔE / eV	σ ² / 10 ⁻² nm ²	R factor / %
Pt/SnO ₂	5	6.0 (±1)	2.005 (±0.005)	25 (0)	0.0018 (0)	1.5
	7	6.0 (±1)	2.005 (±0.005)	25 (0)	0.0018 (0)	2.6
	9	5.8 (±1)	2.005 (±0.005)	25 (0)	0.0018 (0)	3.9
	10	5.8 (±1)	2.005 (±0.005)	25 (0)	0.0018 (0)	2.6
	11	5.2 (±1)	2.005 (±0.005)	25 (0)	0.0018 (0)	5.1
	14	4.7 (±1)	2.005 (±0.005)	25 (0)	0.0018 (0)	3.9
PtO ₂		6.0 (0)	2.023 (0)	25 (0)	0.0018 (0)	6.0

k range/ 10 nm⁻¹ is $1.4 \leq k \leq 14.8$, r range/ 10 nm⁻¹ is $1.3 \leq r \leq 1.9$
Fitting space is back k space.

Table2. Curve fitting result by FEFF for Sn-O bond to Sn K-edge FT-EXAFS.

Sn K-edge EXAFS spectra		Curve fitting result by FEFF for Sn-O bond coordination number (CN) bond distance (r), Debye-Waller factor (σ)				
Concentration of Pt / at%		CN	R / nm ⁻¹	ΔE / eV	σ ² / 10 ⁻² nm ²	R factor / %
Pt/SnO ₂	5	6.0 (±0.3)	2.045 (±0.005)	28 (0)	0.0018 (0)	5.0
	7	6.0 (±0.3)	2.045 (±0.005)	28 (0)	0.0018 (0)	2.5
	9	6.0 (±0.3)	2.045 (±0.005)	28 (0)	0.0018 (0)	3.6
	10	6.0 (±0.3)	2.045 (±0.005)	28 (0)	0.0018 (0)	1.1
	11	6.0 (±0.3)	2.045 (±0.005)	28 (0)	0.0018 (0)	1.2
	14	3.8 (±0.3)	2.045 (±0.005)	28 (0)	0.0018 (0)	8.7
SnO ₂		6.0 (0)	2.045 (±0.005)	28 (0)	0.0018 (0)	1.0

k range/ 10 nm⁻¹ is $2.3 \leq k \leq 14.4$, r range/ 10 nm⁻¹ is $1.3 \leq r \leq 1.9$
Fitting space is back k space.

Table3. Curve fitting result by FEFF for Pt-Sn bond to Pt L₃-edge FT-EXAFS.

Pt L ₃ -edge EXAFS spectra		Curve fitting result by FEFF for Pt-Sn bond coordination number (CN) bond distance (r), Debye-Waller factor (σ)				
Concentration of Pt / at%		CN	R / nm ⁻¹	ΔE / eV	σ ² / 10 ⁻² nm ²	R factor / %
Pt/SnO ₂	5	1.3 (0)	3.13 (±0.01)	-3 (0)	0.0014 (0)	6.6
		7.0 (±0.2)	3.68 (±0.02)	5 (0)	0.0023 (0)	
	7	1.1 (±0.1)	3.12 (±0.01)	-3 (0)	0.0014 (0)	12.0
		5.1 (±0.1)	3.68 (±0.01)	5 (0)	0.0023 (0)	
	9	1.1 (±0.1)	3.12 (±0.01)	-3 (0)	0.0014 (0)	9.0
		4.8 (±0.4)	3.68 (±0.02)	5 (0)	0.0023 (0)	
	10	0.7 (±0.1)	3.14 (±0.01)	-3 (0)	0.0014 (0)	10.0
		4.7 (±0.4)	3.67 (0)	5 (0)	0.0023 (0)	
	11					
	14					

k range/ 10 nm⁻¹ is $2.3 \leq k \leq 14.8$, r range/ 10 nm⁻¹ is $2.2 \leq r \leq 4.0$

Fitting space is back k space.

Table4. Curve fitting result by FEFF for Sn-Sn bond to Sn K-edge FT-EXAFS.

Sn K-edge EXAFS spectra	Curve fitting result by FEFF for Sn-Sn bond				
	coordination number (CN) bond distance (r), Debye-Waller factor (σ)				
Concentration of Pt / at%	CN	R / nm ⁻¹	ΔE / eV	$\sigma^2 / 10^{-2}$ nm ²	R factor / %
Pt/SnO ₂	5	1.3 (± 0.1)	3.16 (± 0.01)	-3 (0)	0.0014 (0)
		5.6 (± 0.5)	3.72 (± 0.01)	5 (0)	0.0023 (0)
	7	1.0 (± 0.2)	3.16 (± 0.01)	-3 (0)	0.0014 (0)
		4.8 (± 0.3)	3.72 (± 0.01)	5 (0)	0.0023 (0)
	9	0.9 (± 0.1)	3.15 (± 0.01)	-3 (0)	0.0014 (0)
		4.6 (± 0.1)	3.72 (± 0.01)	5 (0)	0.0023 (0)
	10	0.9 (± 0.1)	3.17 (± 0.01)	-3 (0)	0.0014 (0)
		4.2 (± 0.2)	3.72 (± 0.01)	5 (0)	0.0023 (0)
	11	0.9 (± 0.2)	3.16 (± 0.01)	-3 (0)	0.0014 (0)
		3.8 (± 0.3)	3.71 (± 0.01)	5 (0)	0.0023 (0)
	14				
SnO ₂		2.0 (0)	3.16 (0)	-3 (0)	0.0014 (0)
		8.0 (0)	3.73 (± 0.01)	5 (0)	0.0023 (0)

k range/ 10 nm⁻¹ is $2.3 \leq k \leq 14.4$, r range/ 10 nm⁻¹ is $2.2 \leq r \leq 4.0$
Fitting space is back k space.

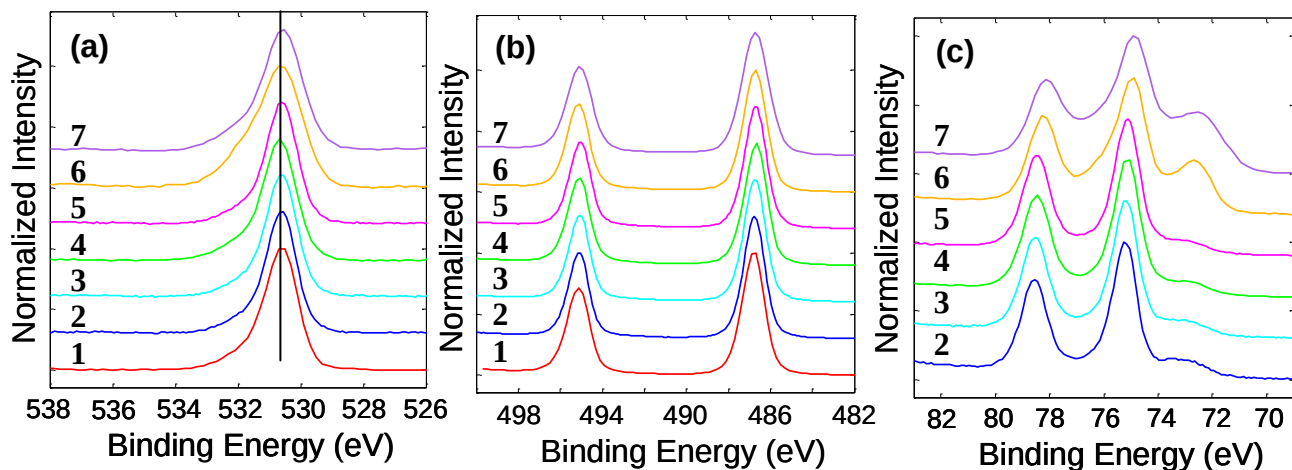


Figure 12. XPS spectra of Pt/SnO₂. (a) O 1s (b) Sn 3d (c) Pt 4f
 Compared with 1: SnO₂, 2: 5at%, 3: 7 at%, 4:9 at%, 5: 10 at%, 6: 11 at%, 7: 14 at%

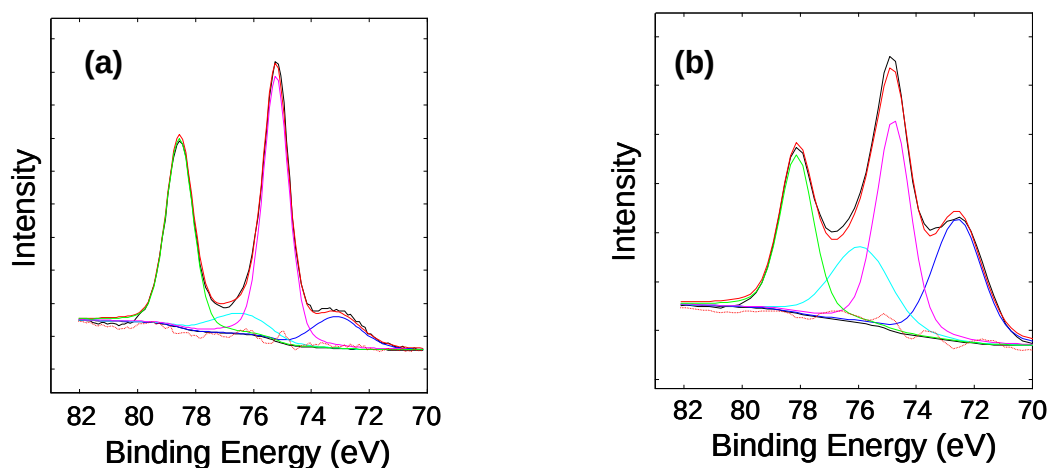


Figure 13. Curve fitting result for Pt 4f for by XPS.

a) 5 at% Pt-SnO₂, b) 14 at % Pt-SnO₂

The f levels become split upon ionization, leading to vacancies in the $f_{5/2}$, $f_{7/2}$ to Pt. The spin-orbit splitting ratio is 3:4 for f levels. The spin-orbit splitting energy gap is 3.33 eV for f levels of Pt.

Table 5. Binding energy of Pt 4f and Sn 3d photoelectron spectra of Pt/SnO₂ and SnO₂. It shows the ratio of each energy about Pt 4f_{7/2}

Concentration of Pt / at%		Binding energy (eV)					
		Pt 4f _{7/2}			Sn 3d _{5/2}		O 1s
Pt/SnO ₂	5	75.2	85%	73.0	15%	486.8	530.6
	7	75.2	83%	73.0	17%	486.8	530.6
	9	75.2	87%	73.0	13%	486.7	530.6
	10	75.1	82%	73.0	18%	486.7	530.6
	11	75.0	69%	72.8	31%	486.7	530.6
	14	74.9	65%	72.9	35%	486.7	530.6
SnO ₂		—	—	—	—	486.8	530.6

-
- ¹ G. Heiland, *Sens. Actuators* **1982**, 2, 343.
 - ² N. Barsan, D. Koziej, U. Weimar, *Sens. Actuators B: Chem.* **2007**, 121, 18.
 - ³ N. Yamazoe, Y. Kurokawa, T. Seiyama, *Sensors and Actuators* **1983**, 4, 283.
 - ⁴ A.V. Tadeev, G. Delabouglise, M. Labeau, *Materials Science and Engineering*. **1998**, B57,76.
 - ⁵ T. Suzuki, K. Kuniyama, M. Kobayashi, S. Tabata, K. Higaki, H. Ohnishi, *Sens. Actuators B: Chem.* **2005**, 109, 185.
 - ⁶ S. Tabata, K. Higaki, H. Ohnishi, T. Suzuki, K. Kuniyama, M. Kobayashi, *Sens. Actuators B: Chem.* **2005**, 109, 190.
 - ⁷ N. Yamazoe, *Sens. Actuators B* **1991**, 5, 7.
 - ⁸ I. Kocemba, J. Rynkowski, *Sens. Actuators B: Chem.* **2011**, 155, 659.
 - ⁹ M. Gaidi, M. Labeau, B. Chenevier, J.L. Hazemann, *Sens. Actuators B: Chem.* **1998**, 48, 277.
 - ¹⁰ L. Mädler, T. Sahm, A. Gurlo, J.-D. Grunwaldt, N. Barsan, U. Weimar, S.E. Pratsinis, *Journal of Nanoparticle Research* **2006**, 8, 783.
 - ¹¹ A. Kowal, M. Li, M. Shao, K. Sasaki, M.B. Vukmirovic, J. Zhang N.S. Marinkovic, P. Liu, A.I. Frenkel, R.R. Adzic, *Nat. Mater.* **2009**, 8, 325.
 - ¹² M. Gaidi, J.L. Hazemann, I. Matko, B. Chenevier, M. Rumyantseva, A. Gaskov, M. Labeau, *J. Electrochem. Soc.* **2000**, 147, 3131.
 - ¹³ M. Nomura, *J.Synchrotron Rad.* **1998**, 5, 851.
 - ¹⁴ M. Nomura, A. Koyama, Design and performance of a new XAFS beamline at the Photon Factory; BL12C, in: KEK Report, Photon Factory, **1996**.
 - ¹⁵ M. Nomura, Y. Koike, M. Sato, A. Koyama, Y. Inada, K. Asakura, *AIP Conf. Proc.* **2007**, 882, 896.
 - ¹⁶ K. Asakura, Analysis of EXAFS, in: Y. Iwasawa (Ed.) *X-ray Absorption Fine Structure for Catalysts and Surfaces*, World Scientific, Singapore, **1996**, pp. 33.
 - ¹⁷ T. Taguchi, *AIP Conf. Proc.* **2007**, 882, 162.
 - ¹⁸ K. Asakura, Polarization-dependent Total Reflection Fluorescence Extended X-ray Absorption Fine Structure and its Application to Supported Catalysis, in: J.G. Catalano (Ed.) *Catalysis Book Series*, **2012**, pp. 281.
 - ¹⁹ J.W. Cook, D.E. Sayers, *J.Appl.Phys.* **1981**, 52, 5024.
 - ²⁰ M. Newville, J.J. Kas, J.J. Rehr, *Journal of Physics: Conference Series* **2009**, 190, 012023.
 - ²¹ J.J. Rehr, J.J. Kas, M.P. Prange, A.P. Sorini, Y. Takimoto, F. Vila, *Comptes Rendus Physique* **2009**, 10, 548.
 - ²² J.J. Rehr, *Radiation Phys.Chem.* **2006**, 75, 1547.
 - ²³ W.C. Hamilton, *Acta Cryst.* **1965**, 18, 502.
 - ²⁴ S. Samson, C.G. Fonsted, *J.Appl. Phys.* **1973**, 44, 4618.
 - ²⁵ D. Briggs, M.P. Seah, *Practical surface analysis*. John WILEY & SONS. Vol. 1, second edition, **1993**.

-
- ²⁶ D.-D. Lee, W.-Y. Chung, *Sens. Actuators* **1989**, 20, 301.
- ²⁷ J. Kappler, N. Bârsan, U. Weimar, A. Diègue, J.L. Alay, A. Romano-Rodriguez, J.R. Morante, W. Göpel, *Fresenius. J. Anal. Chem.* **1998**, 361, 110.
- ²⁸ T. Baidya, K.R. Priolkar, P.R. Sarode, M.S. Hegde, K. Asakura, G. Tatenno, Y.J. Koike, *Chem. Phys.* **2008**, 128, 124711.
- ²⁹ C. Zhang, F. Liu, Y. Zhai, H. Ariga, N. Yi, Y. Liu, K. Asakura, M. Flytzani-Stephanopoulos, H. He, *Angew. Chem. Int. Ed.* **2012**, 51, 9628.

Chapter 4

A Pd-local Structure of the Pd/Al₂O₃ – Pt/SnO₂ Model Thin Film for High – Performance Micro Gas Sensor

1. Introduction

The demand for natural gas is increasing because of the easy supply and of its eco-friendliness as an energy source.¹ However, there is a safety problem and the means to detect gas leakage have to be developed. SnO₂ gas sensor is the most widely used gas sensor but it requires high temperature and AC power supply. I have developed battery-driven gas sensor by improving the sensor sensitivity and miniaturization.^{2,3} Battery-driven type is necessary for the household use. The system is produced by the Micro Electro Mechanical Systems (MEMS) technique on a silicon tip composed of laminated structures with electrode, Sb-doped SnO₂ thin film layer, Pt-doped SnO₂ thin film layer and Pd/Al₂O₃ co-catalyst layer in order to enhance selectivity for the methane (main component of the natural gas) to other gas and long life time.^{2,3} Pd/Al₂O₃ increases the selectivity of the methane.⁴ I characterized the structure using X-ray absorption fine structure (XAFS), X-ray photoelectron spectroscopy (XPS) etc. and have revealed the origin of the high sensitivity.^{5,6,7} However in the real sensor device, the life time was not stable enough in the selectivity for methane though the sensitivity of SnO₂ thin layer was maintained. The structure of Pd active species and its stability under the sensor-driven condition is not clear. The real sensor system is a micro device with a size of about 300 μm². In order to characterize the system i prepared a model system with the same laminated structure in the same way with a large area. In this paper I characterized the Pd local structure in the Pd/Al₂O₃ by the fluorescence XAFS. I also studied the structure of Pd under the sensor-driven environment.

2. Experimental

2.1. Sensor performance

Since various gases (hydrogen, alcohol, carbon monoxide and etc.) exist at ordinary homes, it is necessary to enhance the selectivity of methane to other gases. Figure 1 shows gas selectivity (RH₂/RCH₄) on a sensor system. Pd in mix structure of Pd/Al₂O₃ enhanced the selectivity for methane to other gas.

2.2. Catalyst preparation

7 wt % Pd catalysts were supported on γ-Al₂O₃ (confirmed using XRD) by impregnation. It was followed by the calcination at approximately 803 K in

air. The Pd/Al₂O₃ catalyst was deposited on Pt-SnO₂ film on the Si wafer by a screen printing method.

2.3. Characterization of the catalyst

XRD patterns were recorded using a diffractometer(Rigaku, ATX-G) with Cu K α radiation operated at 50 kV-300 mA. Pd K-edge XAFS spectra were measured at the NW-10A of Photon Factory Advanced Ring, Institute for Materials Structure Science, High Energy Accelerator Organization, (KEK-IMSS=PF-AR) equipped with a Si(311) monochromator in a fluorescence mode⁸. *In situ* XAFS was measured using a reaction and fluorescence XAFS measurement cell described in chapter 2. The dry air was flowed with a flow speed of 200 L/min. 1 % Hydrogen was mixed with dry air or wet air(water content was 17 vol%). Temperature was set at 583 K and 703 K using a micro heater (HTR1001, Adcap Vacuum Technology, Japan) controlled by PID controller (SCR-SHQ-A, Sakaguchi Electric Heating, Japan)

XAFS spectra were analyzed with a XAFS analysis program, REX2000 (Ver. 2.5, RIGAKU)^{9,10,11} using the theoretical backscattering and phase shift parameters derived from FEFF.¹² XAFS spectra were divided into two regions: the X-ray absorption near edge structure(XANES) region and Extended x-ray absorption fine structure(EXAFS) region. The errors were estimated by Hamilton test on R-factor with a significance level over 90 %.¹³

3. Results

3.1. The structure of Pd in Pd/Al₂O₃ of the fresh sample

Figure 2 showed XRD patterns of fresh samples. It giving at the peaks of 33.8, 42.3, 54.9, 71.4° corresponding to (101) and (002), (110), (112) and (202) of tetragonal PdO species. The size of the PdO from Debye method was estimated at 3.2 nm. No Pd metal was observed. In addition to the PdO peaks I found the peaks at 37.4, 39.5, 45.6, 60.4, 67.2 °, corresponding to γ -Al₂O₃. There was still possibility that XRD patterns of Pd metal nanoparticle were not observed because the Pd nanoparticles were too small. I carried out XAFS observations of the sample.

Figure 3 shows the Pd K-edge XANES spectra of the gas sensor together with those of reference compounds such as Pd foil, Pd(OH)₂ and PdO. Pd K-edge XANES spectra of the sample was identical to those of Pd(OH)₂ and

PdO, indicating that most Pd was in the oxidized state but not metallic state.

Figure 4 shows k^3 -weighted EXAFS and its Fourier transforms of the Pd in the fresh sample. The Fourier transforms give two peaks at 0.1-0.2 nm and around 0.3 nm with a small shoulder at 0.28 nm. The former peak corresponds to Pd-O and the latter to the Pd-Pd. Compared to the EXAFS oscillation and the Fourier transform of the sample with those of reference compounds, I found the sample gave the EXAFS oscillation and Fourier transform similar to those of PdO. Therefore the PdO nanoparticles were present on the sample. No oscillation for metallic Pd-Pd bond was observed, indicating Pd metallic species was less possible.

Table 1 shows results of the coordination numbers and bond distances around the Pd atom derived from Pd K-edge EXAFS oscillations under dry air at R.T. Curve fitting data coincide with those of reference PdO.

3.2. The stable structure of Pd catalyst under sensor driven condition

The sample structure may change under the working conditions. I carried out in situ XAFS measurements under several conditions (dry air, H_2 -containing air and $H_2 + H_2O$ containing air at several temperatures). H_2 represents the reductive atmosphere in the dining room where alcohols and volatile organic compounds are present. Although I did not find any change in the EXAFS region, subtle changes occur in the XANES regions according to the atmosphere. Figure 5 shows the Pd K-edge XANES results under dry air at room temperature, 583K and 703 K. In the dry air the Pd K-edge XANES rarely changed so that the PdO in the sample was stable under the dry air conditions.

When the sample was exposed to H_2 in dry and wet air, the XANES structure was changed in figure 6. The peak intensities decreased at 583 K under the H_2 in dry and wet air. The peak height under the H_2 in wet air is a little larger than that under the H_2 in the dry air.

Interesting, the PdO was recovered at 703 K (Operating conditions) even in the H_2 atmosphere.

4. Discussion

In the Pd/Al₂O₃ - Pt/SnO₂ model thin film for high-performance micro gas sensor, it was demonstrated by XAFS, XRD and the fresh sample contains PdO. The PdO structure was modified below temperature of 673 K under

the H_2 -contained air, was re-oxidized to PdO at 703 K. In previous paper showed that Pd and PdO have different activation behavior for hydrogen and other gases.¹⁴ Methane gas is inertness compared to other gases(hydrogen, alcohol, carbon monoxide and etc.). The PdO in Pd/ Al_2O_3 burns completely other gases except CH_4 , which reach at sensing layer(SnO_2). In this sensor system, it is necessary to keep state of PdO to maintain high selectivity even under sensor driven.

Gas sensor was driven for long time under the exposure to reductive gas and water vapor. Especially reductive gas or moisture can modify structure of catalyst. Maione et al, suggested that the PdO became inactive by the reduction and sintering over 1073 K.¹⁵ Water also inhibited the reaction by the formation of inactive $Pd(OH)_2$.¹⁶ The structural change of PdO may cause the degradation of sensor performance which requires the structure analysis of real sensor tip after the degradation. Note that the sample was reduced at intermediate temperature in the presence of H_2 . The presence of water inhibits the reactivity of PdO towards the H_2 and thus the degree of reaction is diminished.

The modified PdO in moisture and reduction gas at 583 K was re-oxidized over 700 K. I concluded that a driven temperature over 700 K to keep high-performance gas sensor for long time is necessary.

5. Conclusions

The local structure of Pd nanoparticles on Al_2O_3 used as a cocatalyst in SnO_2 MEMS methane leakage sensor to enhance the sensitivity for methane gas detection was investigated. I prepared a model system on the Si substrate and found PdO was present in the fresh SnO_2 sensor by X-ray absorption fine structure(XAFS). The PdO was observed at 703 K, under sensor working conditions even if the presence of reductive gas. I concluded that PdO was active species in high-performance gas sensor and a driven temperature over 700 K to keep the performance for a long time is necessary.

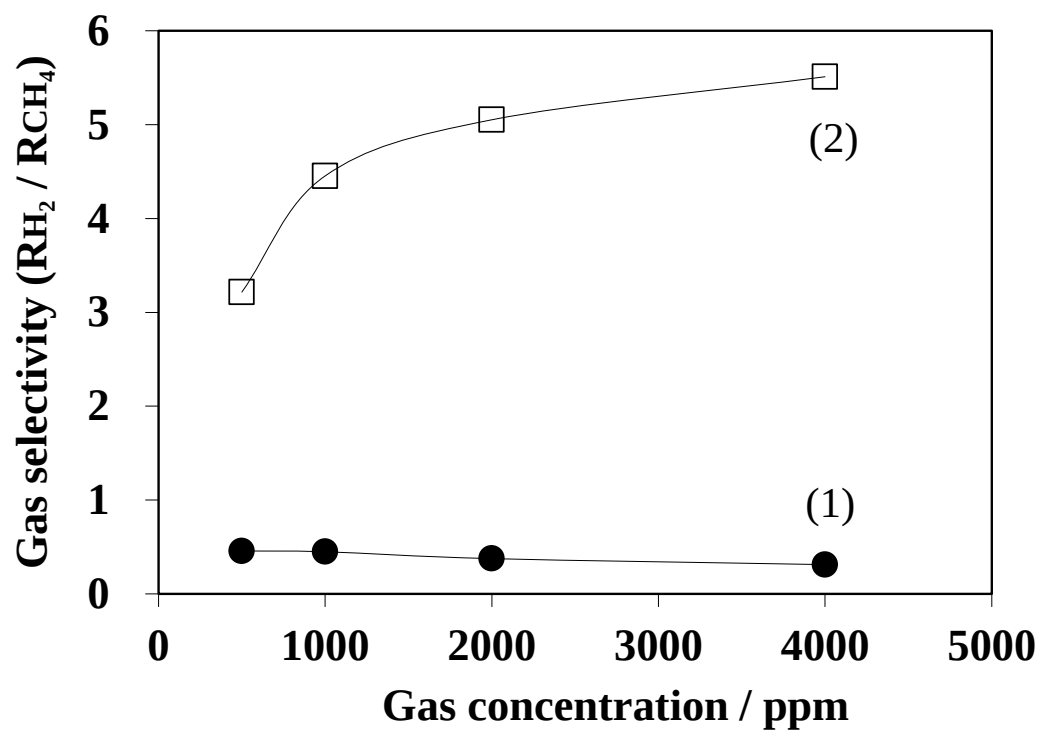


Figure 1. The selectivity of methane to hydrogen of gas sensor. (1) only SnO_2 (2) laminated structure of $\text{Pd}/\text{Al}_2\text{O}_3$ and SnO_2 . It was defined as R_{H_2}/R_{CH_4} .

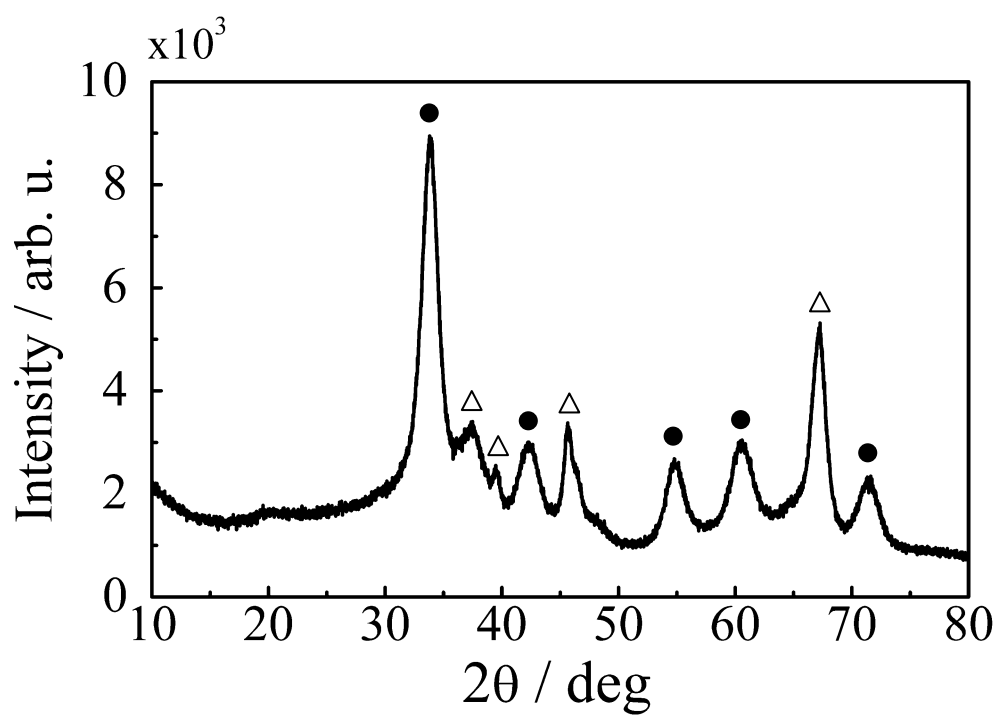


Figure 2. XRD pattern of Pd supported on Al_2O_3 catalyst for micro gas-sensor
Close circle is PdO of tetragonal pattern, open triangle is $\gamma\text{-Al}_2\text{O}_3$ pattern

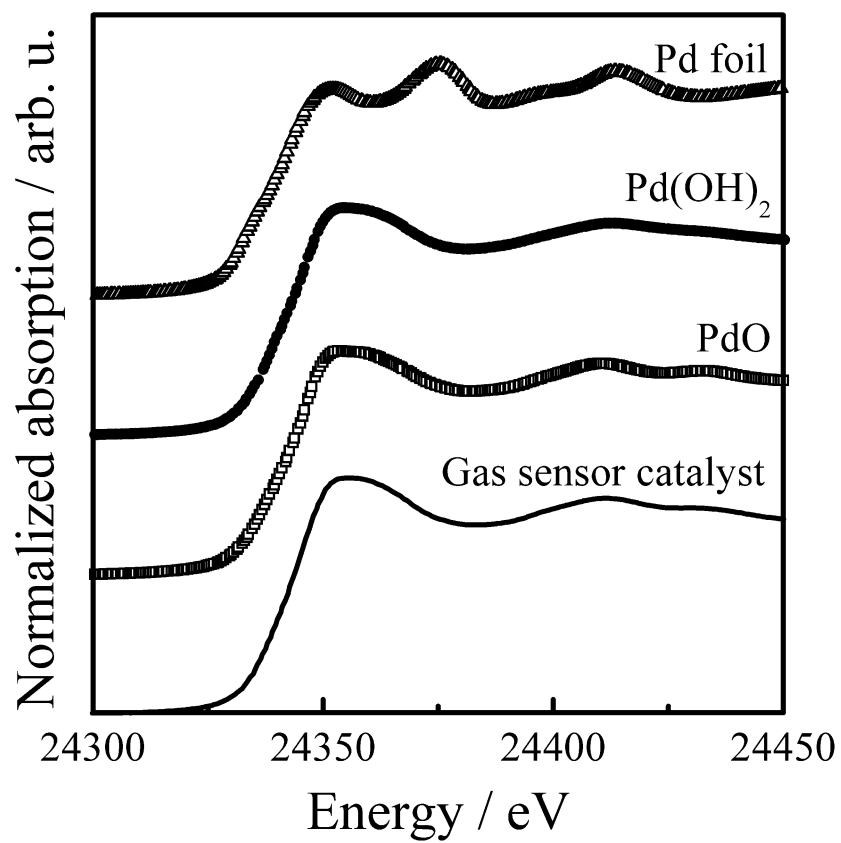


Figure 3. Pd K-edge XANES spectra of Pd supported on Al₂O₃ catalyst for micro gas-sensor with reference of Pd foil, Pd(OH)₂ and PdO

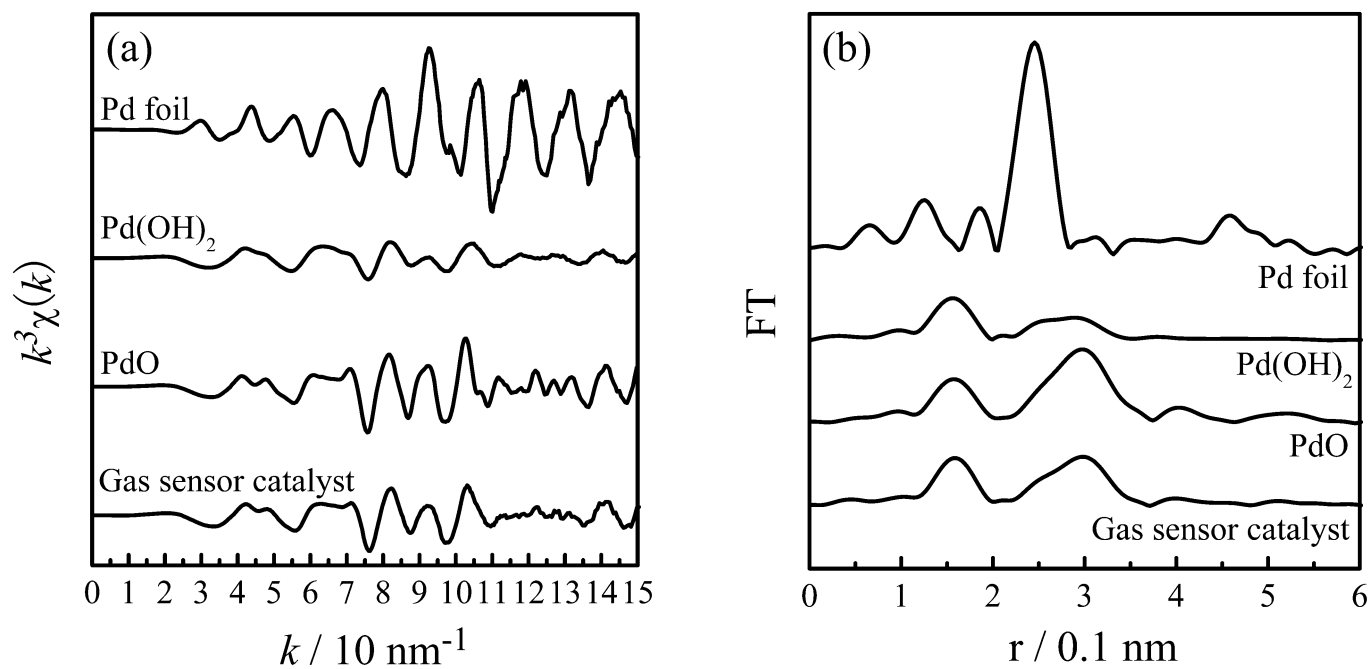


Figure 4. Pd K-edge EXAFS spectra of Pd supported on Al_2O_3 catalyst for micro gas-sensor with reference of Pd foil, Pd(OH)_2 and PdO

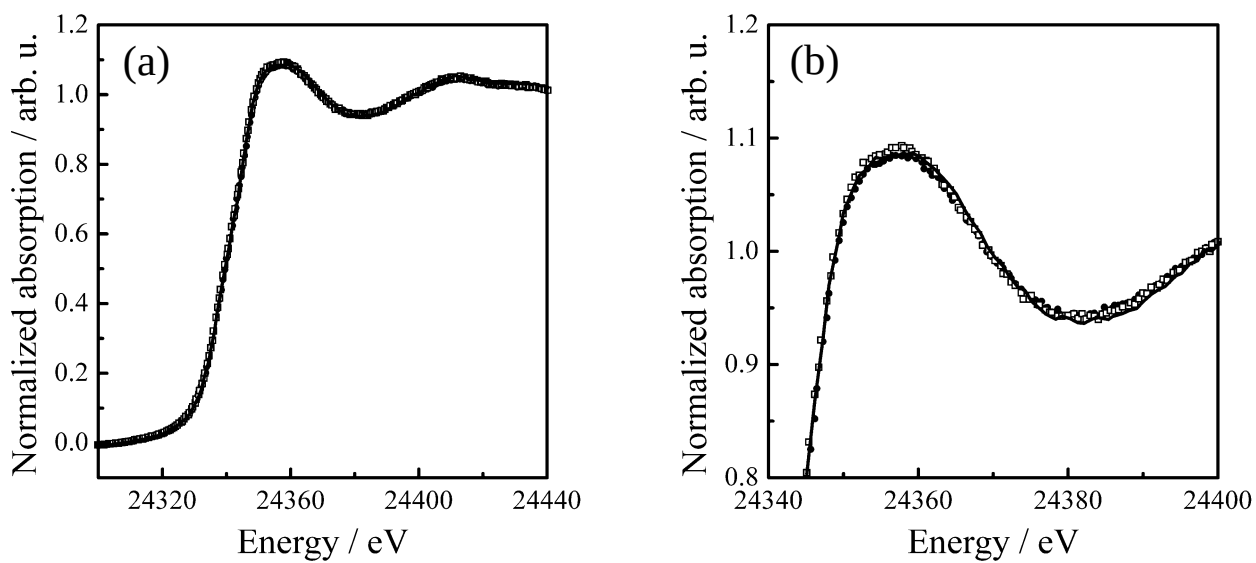


Figure 5. *in situ* XANES spectra under dry air(a) and magnified in the edge peak region.

Line is in R.T., open square is in 583 K, close circle is in 703 K.

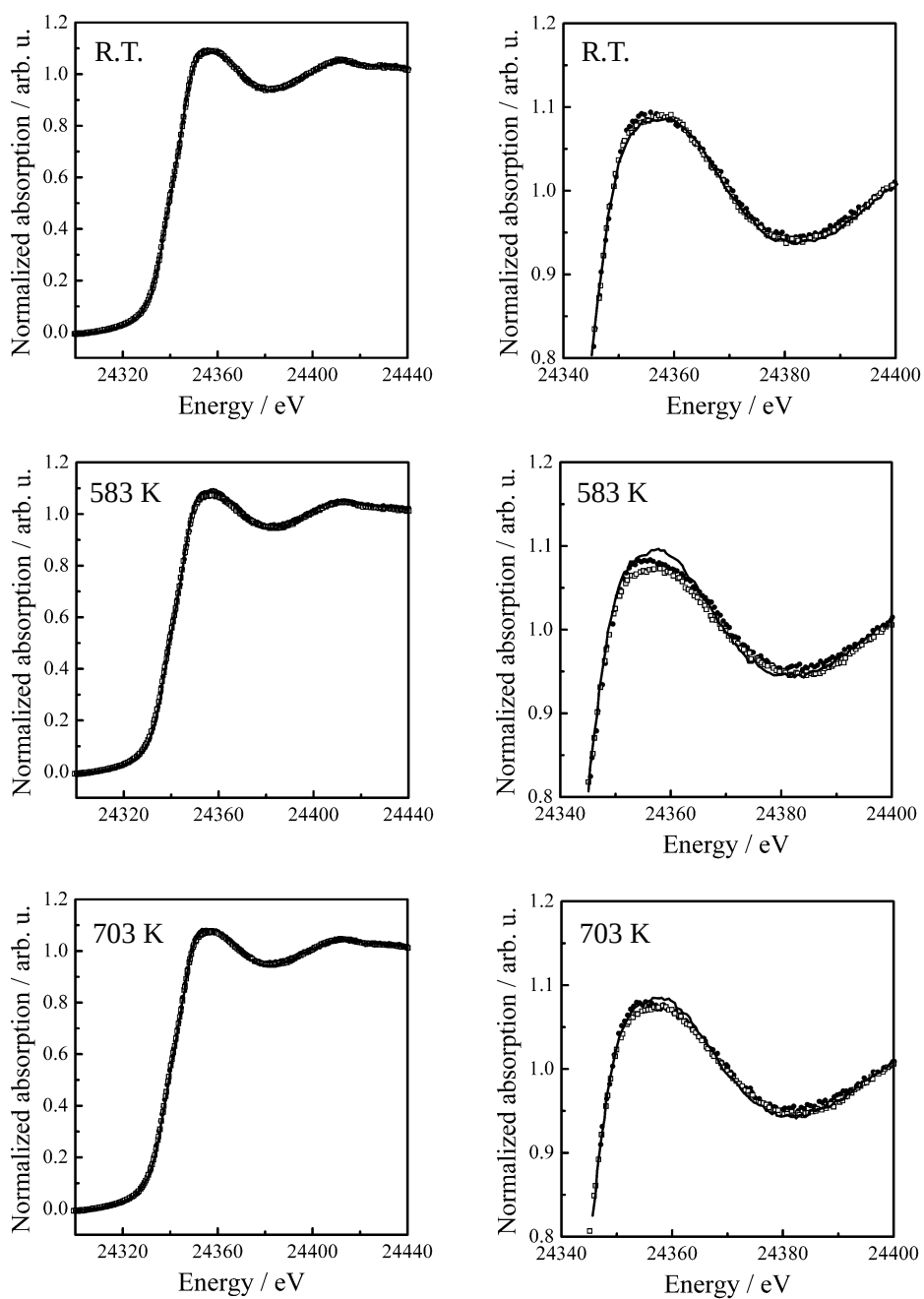


Figure 6. It was showed in-situ XANES spectra in left (which is expansion in right) under sensor deactivation condition at R.T., 583 K, 703 K and R.T. after 703 K. Line is in dry air, open square is in dry H_2 , close circle is in wet H_2 .

Table 1 Curve fitting results for the Pd-O bond to Pd K-edge FT-EXAFS using FEFF

Pd K-edge EXAFS spectra		Curve fitting results by FEFF for Pd-O bond coordination number (CN), bond distance (r) and Debye-Waller factor (σ)				
Atmosphere/Temperature		CN	$r/\text{\AA}$	$\Delta E/\text{eV}$	$\sigma^2/\text{\AA}^2$	R factor/%
Dry air	R.T.	3.3 (± 0.5)	2.049 (± 0.004)	25 (0)	0.0027 (0)	5.6
	583 K	3.3 (± 0.5)	2.047 (± 0.005)	25 (0)	0.0042 (0)	0.8
	703 K	3.3 (± 0.5)	2.040 (± 0.003)	25 (0)	0.0061 (0)	1.8
	R.T. after 703 K	3.2 (± 0.5)	2.056 (± 0.004)	25 (0)	0.0027 (0)	0.4
reference / PdO		3.7 (± 0.5)	2.049 (± 0.004)	25 (0)	0.0027 (0)	0.3
reference / Pd(OH) ₂		3.5 (± 0.5)	2.042 (± 0.004)	25 (0)	0.0027 (0)	0.1
k range is $1.1 \leq k \leq 12.0$; r range is $1.1 \leq r \leq 2.1$; fitting space is back k space.						

-
- ¹ United Nations (UN), *2010 Energy Statistics Yearbook* United Nations, New York, 2014.
- ² T. Suzuki, K. Kuniyara, M. Kobayashi, S. Tabata, K. Higaki, H. Ohnishi, *Sens Actuators B* **2005**, 109, 185.
- ³ S. Tabata, K. Higaki, H. Ohnishi, T. Suzuki, K. Kuniyara, M. Kobayashi *Sens Actuators B* **2005**, 109, 190.
- ⁴ J. C. Kim, H. K. Jun, J.-S. Huh, and D. D. Lee, *Sens. Actuators B Chem.* **1997**, 45, 271.
- ⁵ N. Murata, T. Suzuki, M. Kobayashi, F. Togoh, and K. Asakura, *Phys. Chem. Chem. Phys.* **2013**, 15, 17938.
- ⁶ F. Mauriello, H. Ariga, N. Murata, and K. Asakura, *JPS Conf. Proc.* **2013**, 2, 010307.
- ⁷ N. Murata, M. Kobayashi, Y. Okada, T. Suzuki, H. Nitani, Y. Niwa, H. Abe, T. Wada, S. Mukai, H. Uehara, H. Ariga, S. Takakusagi and K. Asakura, *Rev. Sci. Instrum.* **2015**, 86, 034102.
- ⁸ Nomura M, Koike Y, Sato M, Koyama A, Inada Y, Asakura K (2007) *AIP Conf Proc* 882:896
- ⁹ K. Asakura, in: *Analysis of EXAFS in X-ray Absorption Fine Structure for Catalysts and Surfaces*, eds. Y. Iwasawa (World Scientific, Singapore, 1996) p. 33.
- ¹⁰ Taguchi T (2007) *AIP Conf Proc* 882:162
- ¹¹ K. Asakura, in: *Catalysis*, Vol. 24, eds. J. G. Catalano, 2012, p. 281.
- ¹² Rehr, J.J.; Kas, J.J.; Prange, M.P.; Sorini, A.P.; Takimoto, Y.; Vila, F. *Comptes Rendus Physique* **2009**, 10, 548-559.
- ¹³ Hamilton, W.C. *Acta Cryst.* **1965**, 18, 502-510.
- ¹⁴ M. G. Jones, T. G. Nevell, R. J. Ewen, and C. L. Honeybourne, *Applied Catalysis* **1991**, 70, 277.
- ¹⁵ A. Maione and Ruiz P. André F, *Appl Catal B: Environmental* **2007**, 75, 59.
- ¹⁶ R. Burch, P. K. Loader and F. J. Urbano, *Catalysis Today* **1996**, 27, 243.

Chapter 5

in situ XAFS investigation of Pt doped SnO₂ Catalyst for
a high performance micro gas sensor

1. Introduction

The demand for natural gas is increasing because of the easy supply and of its eco-friendliness as an energy source.¹ However, the safety problem prevents the further utilization of the natural gas, because of explosion by methane gas leakage is 665 cases in Japan in 2010 which is 60 % of which took place in residential use.² Semiconductor type gas sensor was studied by Seiyama et al. in 1960's.^{3,4} The SnO₂ of n-type semiconductor has been widely used for gas sensor as its conductivity varies with partial pressures of oxygen and reductive gases.^{5,6} The SnO₂ sensor requires the high operation temperature necessary for the reaction between the SnO₂ and gases and an electric power supply. Taguchi et al. proposed the gas leak alarm used this type.⁷ This Taguchi type's sensor has been become widespread since in practical use as TGS 109 from Figaro Co. Ltd. in 1970's with external power supply. In order to increase the number of home-use gas sensor, battery-driven type or wireless models are important for their good appearance and their free installation. The battery-driven sensors should have longer life time than 5 years and thus the low power consuming sensors has to be developed with high selectivity for methane, which is a main ingredient in natural gas. In order to increase the number of home-use gas sensor, battery-driven type or wireless models are important for their good appearance and their free installation. The battery-driven sensors should have longer life time than 5 years and thus the low power consuming sensors has to be developed with high selectivity for methane, which is a main ingredient in natural gas.

From this standpoint of view, Suzuki et al. have developed the gas sensor by MEMS (Micro Electro Mechanical Systems) method.^{8,9} This sensor has the layer structure of Pd-Al₂O₃ catalytic thick film/SnO₂ thin film/Pt electrode/Thin film heater. Pd-Al₂O₃ is to enhance selectivity to gas other than methane. Recently I found that the Pt doping increases methane sensitivity of SnO₂ thin film sensor device which will provide the new pathway to realize a low power consumption gas sensor with long life time.^{10,11} The sensor can detect the 12 500 ppm methane which is a 1/4 of the methane explosion limit (53 000 ppm) even after the 5 years.

Since Pt metallic cluster is a good catalyst for many reactions including the hydrogen and hydrocarbon oxidation reaction. There are several mechanisms to improve the sensor performance by the additives. One is an

electronic effect and the other is a spillover effect. Yamazoe and Kocemba et al reported that Pt nanoparticles on the SnO₂ surface improve the performance by the spillover reaction.^{12,13} Thus Pt clusters deposited on the SnO₂ were expected to enhance the sensor sensitivity by the spillover reaction. In the previous papers about the characterizations of Pt-SnO₂ sensor, the oxidized Pt or Pt aggregates are present in SnO₂ substrate depending on the atmosphere and Pt concentration.^{5,14,15,16,17} On the other hand EXAFS techniques on the real gas sensor have suggested a quite different model where the Pt ion is located at the Sn position in the rutile structure on Pt-SnO₂.^{18,19} However the information derived from the EXAFS was limited to the concentration as low as 0.2 wt% which is lower than the Pt content in our highest performance sample. I have demonstrated this model on Pt-SnO₂ thin film in a wide concentration range using the EXAFS in addition to structure analyses such as X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).²⁰

However *in situ* characterization must be necessary to confirm the real active structure as pointed out by the Gaidi. I will demonstrate the stability during reduction gas reaction of Pt-SnO₂ as rutile structure, and reaction mechanism in this paper structure.

2. Experimental

2.1. Sample preparation

The work for *in situ* XAFS used 400 nm thick Pt-SnO₂ thin layers were prepared on Si substrates covered with native SiO₂ film (600 nm) using a sputter-deposition method. Sample of layer of Pt-SnO₂ (~400 nm)/SnO₂ (~400 nm) which was annealed for 4 hours under air (20 % oxygen) at about 703 K was prepared for TDS measurement. Pt concentration was deposited at 8 at% (and 4 at% as only TDS measurement) which take solid solution.

2.2. *in situ* XAFS characterization of the catalyst

Pt L₃-edge XAFS spectra were measured at BL-12C of KEK-PF using a Si(111) monochromator in a fluorescence mode^{21,22}, and the Sn K edge XAFS spectra were measured at the NW-10A of KEK-PF-AR equipped with a Si(311) monochromator also in a fluorescence mode.²³ *In situ* XAFS was measured using a reaction and fluorescence XAFS measurement cell described elsewhere.²⁴ XAFS spectra were analyzed with REX2000 (Ver. 2.5,

RIGAKU).^{25,26,27} The backgrounds of all XAFS spectra were removed by a spline smoothing method with Cook and Sayers criteria and normalized by the edge height.²⁸ The k^3 -weighted EXAFS oscillations were Fourier-transformed to k -space over $k = 14 - 148 \text{ nm}^{-1}$ for Pd K-edge spectra, over $k = 11 - 120 \text{ nm}^{-1}$ in the *in situ* measurement. Each peak in the Fourier transform was filtered and inversely Fourier-transformed to the k -space for the curve fitting analysis. I carried out the non-linear least square curve fitting using the following equations.

$$k^3 \chi(k) = \sum_j S_0^2 \frac{k^2 N_j F_j(k)}{r_j^2} e^{-2k^2 \sigma_j^2} e^{-\frac{2r_j}{\lambda_j}} \sin(2kr_j + \phi_j) \quad (1)$$

$$k = \sqrt{\frac{2m}{\hbar^2} (h\nu - E_o - \Delta E)}$$

where S_0^2 , N_j , r_j , and σ_j are amplitude reduction factor, coordination number, bond distance, and Debye Waller factor, of the j -th coordination shell, respectively. λ is a mean free path. $F_j(k)$ and $\phi_j(k)$ are backscattering amplitude and phase-shift functions which were obtained from FEFF (ver. 8.0).^{29,30,31} E_o is the absorption edge energy tentatively determined as the inflection points and energy shift ΔE is adjusted during the fitting process. The errors were estimated by Hamilton test on R-factor with a significance level over 90 %.³²

For the *in situ* XAFS measurement, a 1 cm^2 sample was loaded in the cell and heated to 703 K at 100 K/min. Experiments were carried out in two steps. In the first step, sample was heated to 703 K under 200 ml/min of a dry air gas flow. In the second step the cell was refilled with the 1% H_2 and CH_4 gas (dry air base) in the same flow rate.

2.3. TDS characterization of the catalyst

A TDS (Thermal Desorption Spectroscopy) was measured as $M/z = 32$ to evaluate oxygen desorption from Pt-SnO₂ or SnO₂ using the equipment manufactured by Electron Science Co., Ltd.. Detector used mass spectrometer. Sample was measured up to temperature of 1000 K by the infrared heat lamp into vacuum chamber of $\sim 10^{-9} \text{ Pa}$. Temperature of sample surface was monitored directly by the K type thermocouple.

3. Results

3.1. *in situ* XANES analysis

Figure 1 shows the Sn K and Pt L₃-edge XANES spectra under dry air and reduction gases (CH₄ and H₂). No change in Sn K-edge XANES spectra is even 703 K under reduction gases in Figure 1-a. On the other hands, the Pt L₃-edge XANES intensity under dry air and CH₄ in reduction gases on Figure 1-b-1 and Figure 1-b-2 is not changed to 703 K. However, the intensity under H₂ is decreased with increasing temperature from 303 K (Figure 1-b-3). Peak top of these Pt L₃-edge XANES spectra were plotted on each temperature to evaluate these detailed changes in Figure 2. The change in dry air and CH₄ is same or small. The alteration in H₂ occurs drastically. The XANES intensity is decreased between R.T. and 403 K, and is saturated to 603 K. However, the intensity tends to be increased over 603 K, but the change is very small at about 0.1. Since the origin of the white line peak for Pt L₃-edge XANES was transition from the 2p_{3/2} core state to 5d empty state, the change of intensity under H₂ gas suggested the variance of empty 5d state in the Pt/SnO₂ samples. This means that structure surroundings Pt atoms varies.

3.2. *in situ* EXAFS analysis

Figure 3 shows the k^3 -weighted Sn K-edge and Pt L₃-edge EXAFS oscillations($k^3\chi(k)$) and the Fourier transform(FT) under dry air and reduction gases on 703 K. The Sn K-edge EXAFS oscillation in reduction gases overlaps oscillation in dry air in Figure 3-a-1. I performed FT for confirmation, as shown Figure 3-a-2, where one peak appeared at 0.18 nm, corresponding with Sn-O bond. However, I can't find change of structure. This will mean that no change is in surroundings structure of Sn atoms into Pt-SnO₂ in reduction gases. The other hands, there is change in the Pt L₃-edge EXAFS oscillations under H₂, but no change under CH₄ in Figure 3-b-1. A minor decrease of the oscillation amplitude is founded under H₂. I performed a similar FT to define this difference, as shown Figure 3-b-2, where one peak appeared at 0.18 nm, corresponding with Pt-O. The decrease of the peak amplitude corresponding with Pt-O is founded under H₂, but the oscillation of Pt metal is not found. I already have reported in chapter 2 about this change that the phase of the Pt-SnO₂ peak compared with the imaginary parts in Fourier transform of $k^3\Delta\chi(k)$ was π rad different

from the Pt-SnO₂ before the H₂-containing air flow, indicating a decrease in the main oscillation arising from Pt-O.²⁴ Curve fitting by FEFF is conducted to evaluate this structure in detail as shown table 1. I have confirmed that the Pt-O bond distance (r) and coordination number (CN) of Pt-SnO₂ as solid state is about 2.005 Å and 6.0.²⁰ Firstly, the Debye Waller factor (σ) of 303 K and 703 K under dry air in fixed r (= 2.005) and CN(= 6.0) based on this report is calculated. Curve fitting under CH₄ and H₂ is conducted on the fixed σ . The Pt-O bond distance under these gases is calculated at 2.000 (± 0.005) Å, which is no change for range of error. The CN under hydrogen was decreased about 1.0 compared with variance under methane. This may mean that lattice oxygen (or adsorbed oxygen) in Pt-SnO₂ by H₂ gas varies. Gas reaction at lattice oxygen (or adsorbed oxygen) with maintenance of solid state in Pt-SnO₂ may progress, where the no variance to Pt metal present.

3.3. Stability of Pt-SnO₂ structure as solid state

A series of variance in dry air and reduction gases by Pt L₃-edge XANES to evaluate stability of Pt-SnO₂ structure as solid state is measured. The plot of Pt L₃-edge XANES intensity on the series of variance was showed in Figure 4-a. Temperature is increased in step of 100 K from 303 K to 703 K under the dry air, and 1 % CH₄-containing air is flowed for 1 hour at 703 K. Dry air after exposure of CH₄ is again flowed for 1 hour, and 1 % H₂-containing air is flowed. Dry air after exposure of H₂ is flowed in progress of decreasing of temperature to 303 K. The intensity of XANES in elevated temperature process and the CH₄ exposure process is no change, where intensity in elevated temperature process may decrease but very small. The decreasing of the intensity corresponding with desorption of oxygen in H₂ exposure is founded. However, the intensity was recovered in process of decreasing of temperature to 303 K under dry air after H₂ exposure. This may be for oxygen adsorbed in defect which generated by H₂ reaction with oxygen into Pt-SnO₂. Figure 4-b and c shows Pt L₃-edge EXAFS oscillation and Fourier transform at 303 K on before and after of this series. The EXAFS oscillation pattern in before and after of this series is same, where oscillation after the series compared with it before decreases corresponding with decreasing of Pt-O. The coordination number of Pt-O is calculated 5.5 from result of Curve fitting by FEFF, which is small than 6.0

of before. However, this CN value is high by 0.5 than CN during H₂ reaction. This phenomenon might mean that the oxygen is re-adsorbed in the lattice of Pt-SnO₂.

4. Discussion

As result of *in situ* XAFS measurement for Pt-SnO₂ with solid state under reduction gases of CH₄ and H₂, the decreasing of white line intensity of Pt L₃-edge XANES spectra is found under H₂, where intensity of Sn K-edge XANES under this gas and XANES at both edge under CH₄ is no variance. This change of XANES means the decreasing of Pt-O coordination number from Pt L₃-edge EXAFS measurement, where no Pt metal was observed during reaction. This will means that rutile structure in Pt-SnO₂ is maintained even 703 K during H₂ reaction. Reaction mechanism may be absorption/desorption of a surrounding oxygen atoms of Pt atom, where I can find that the CN of Pt-O is recovered during dry air flow after H₂ reaction by oxygen in Figure 4-a. Pt may oxidized the H₂ using the lattice oxygen which produces conduction electron. In previous paper, I have showed that the oxidative activity for CH₄ is high on this Pt-SnO₂ with solid state.²⁰ However, the change of structure during CH₄ reaction made no appearance by XAFS measurement. Oxygen volume in reduction gases is about 20%, because of the concentration of CH₄ and H₂ is 1%. Oxygen adsorption to surface of Pt-SnO₂ arises very quickly during reaction. Pt also may oxidized the CH₄ using the lattice oxygen, however the no change of XANES was found for quickly oxygen adsorption. The TDS of Pt-SnO₂/SnO₂ layer and only SnO₂ were measured to evaluate the performance of oxygen absorption of Pt-SnO₂. Result of TDS measurement as M/z = 32 was shown in Figure 5. Two peaks of β in 700-900 K and γ over 950 K was found from both of layer and SnO₂ sample. The O²⁻ as β and lattice oxygen as γ was identified in previous paper by study of Yamazoe et al.³³ The O²⁻ may be the absorbed oxygen species on surface of Pt-SnO₂ or SnO₂. The γ may be lattice oxygen by thermal decomposition from sample. The O²⁻ species increases with Pt concentration in Pt-SnO₂ as compared to SnO₂. This means that oxygen absorption as O²⁻ increases by effect of Pt atoms in same rutile structure. This high oxygen storage by Pt atoms in Pt-SnO₂ may arise during reaction with H₂ or CH₄, and change in XAFS measurement looks small in CH₄ in particular. Our sensor is composed by layer of Pt-SnO₂ and SnO₂.

Adsorbed oxygen in Pt-SnO₂ may be supplied to SnO₂ of the lower layer as spillover effect, or it may also occur in CH₄. This spillover effect by Pt-SnO₂ will realize high performance and long life time sensor.

5. Conclusions

The 8at% Pt-SnO₂ with solid state as rutile structure was maintained the structure during reaction from result of *in situ* XAFS measurement under reduction gases of 1% CH₄ and 1% H₂, where no Pt metal was observed during reaction. Moreover the high oxygen storage effect by Pt atoms in Pt-SnO₂ was shown from TDS measurement, will leads to the spillover effect in the sensor driven. This metal oxide solid solution type catalyst will realize high performance and long life time as gas sensor, since with high activity and high thermal stability as compared with metal thin film catalyst of metal supported catalyst.

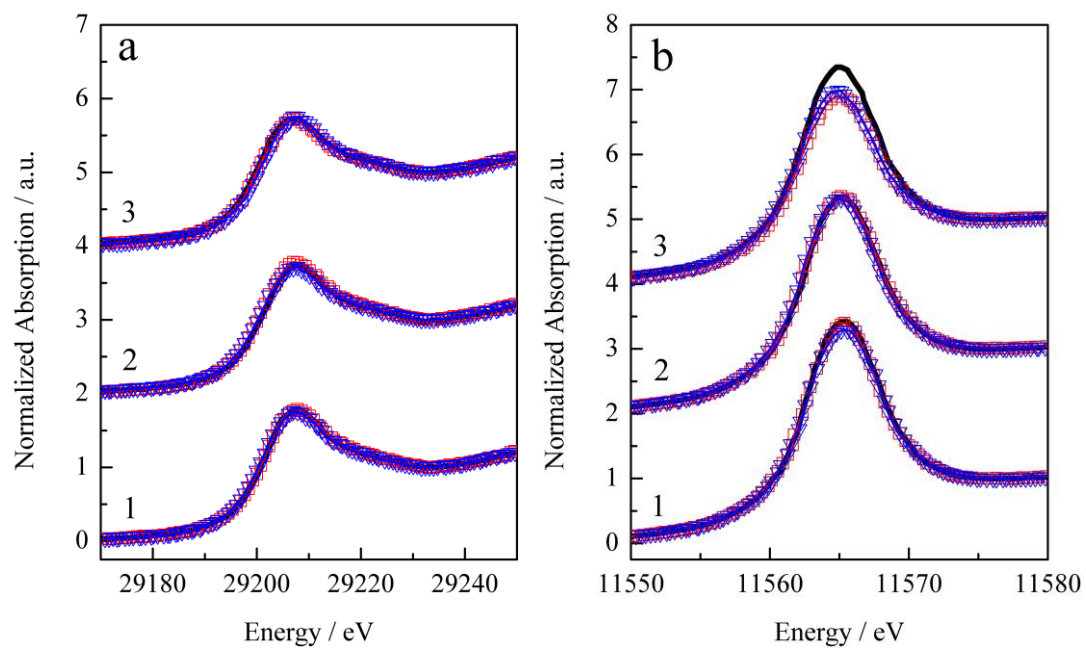


Figure 1. The Sn K (in a) and Pt L₃-edge (in b) XANES spectra under dry air and reduction gases (CH₄ and H₂). 1: under dry air 2: under methane 3: under hydrogen and Black line is in 303 K, Red open square is in 503 K, Blue open revers triangle is in 703 K.

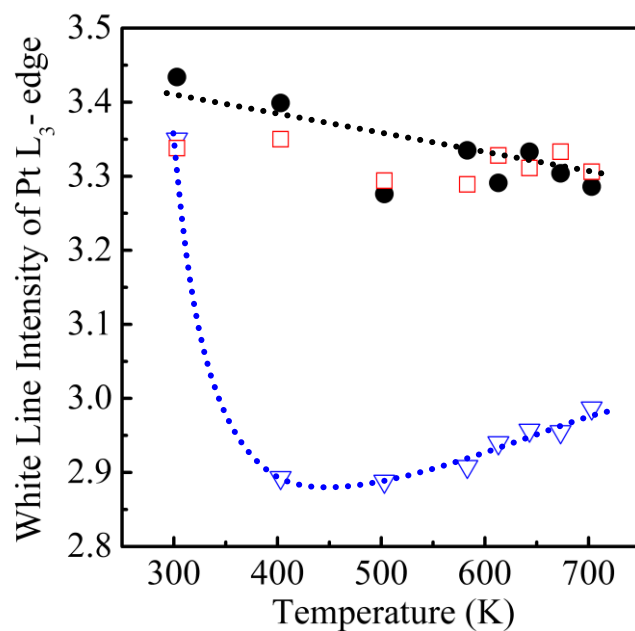


Figure 2. Peak top of these Pt L_3 -edge XANES spectra were plotted on each temperature to evaluate these detailed changes. Black circle is in dry air, red open square is in methane, blue open revers triangle is in hydrogen.

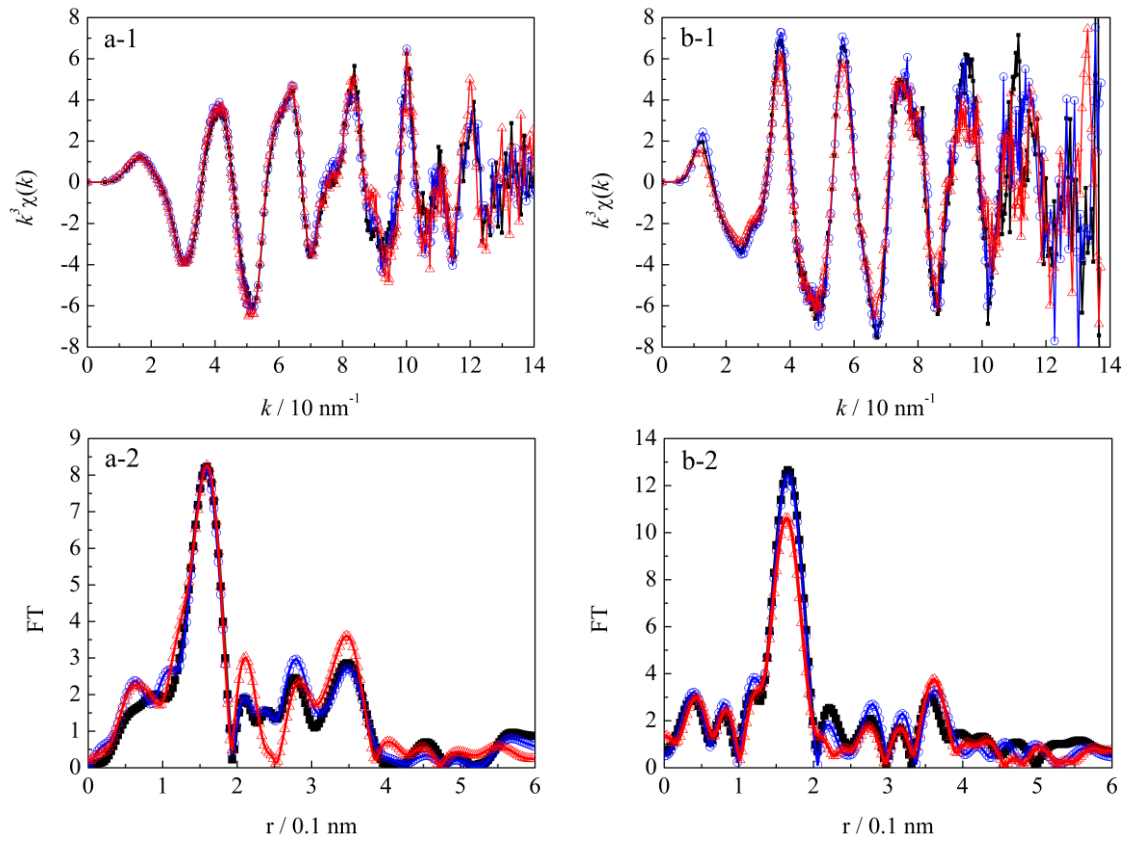


Figure 3. The k^3 -weighted Sn K-edge and Pt L_3 -edge EXAFS oscillations($k^3\chi(k)$) and the Fourier transform(FT) under dry air and reduction gases on 703 K. It is Sn K-edge EXAFS oscillations in a-1 and the FT in a-1, Pt L_3 -edge EXAFS oscillations in b-1 and the FT in b-1. Square is during dry air, open circle is during CH_4 , open triangle is during H_2 .

Table 1. Curve fitting result by FEFF

Pt L ₃ -edge EXAFS spectra		Curve fitting result by FEFF for Pt-O bond coordination number (CN), bond distance (r) and Debye-Waller factor (σ)				
gas	Temperature / K	CN	r / Å	ΔE / eV	σ^2 / Å ²	R factor/%
Dry Air	303	6.0(0)	2.005(0)	25(0)	0.0014	3.0
	703	6.0(0)	2.005(0)	25(0)	0.0035	2.8
Methane	703	5.9($\pm$ 0.5)	2.000($\pm$ 0.005)	25(0)	0.0035	3.7
Hydrogen	703	5.0($\pm$ 0.5)	2.000($\pm$ 0.005)	25(0)	0.0035	2.4
Dry Air*	303	5.5($\pm$ 0.5)	2.005(0)	25(0)	0.0014	3.5

k range is $1.4 \leq k \leq 13.8$; r range is $1.3 \leq r \leq 1.9$; fitting space is back k space.

Dry Air* is result of EXAFS spectra on last 800 min in Figure 4.

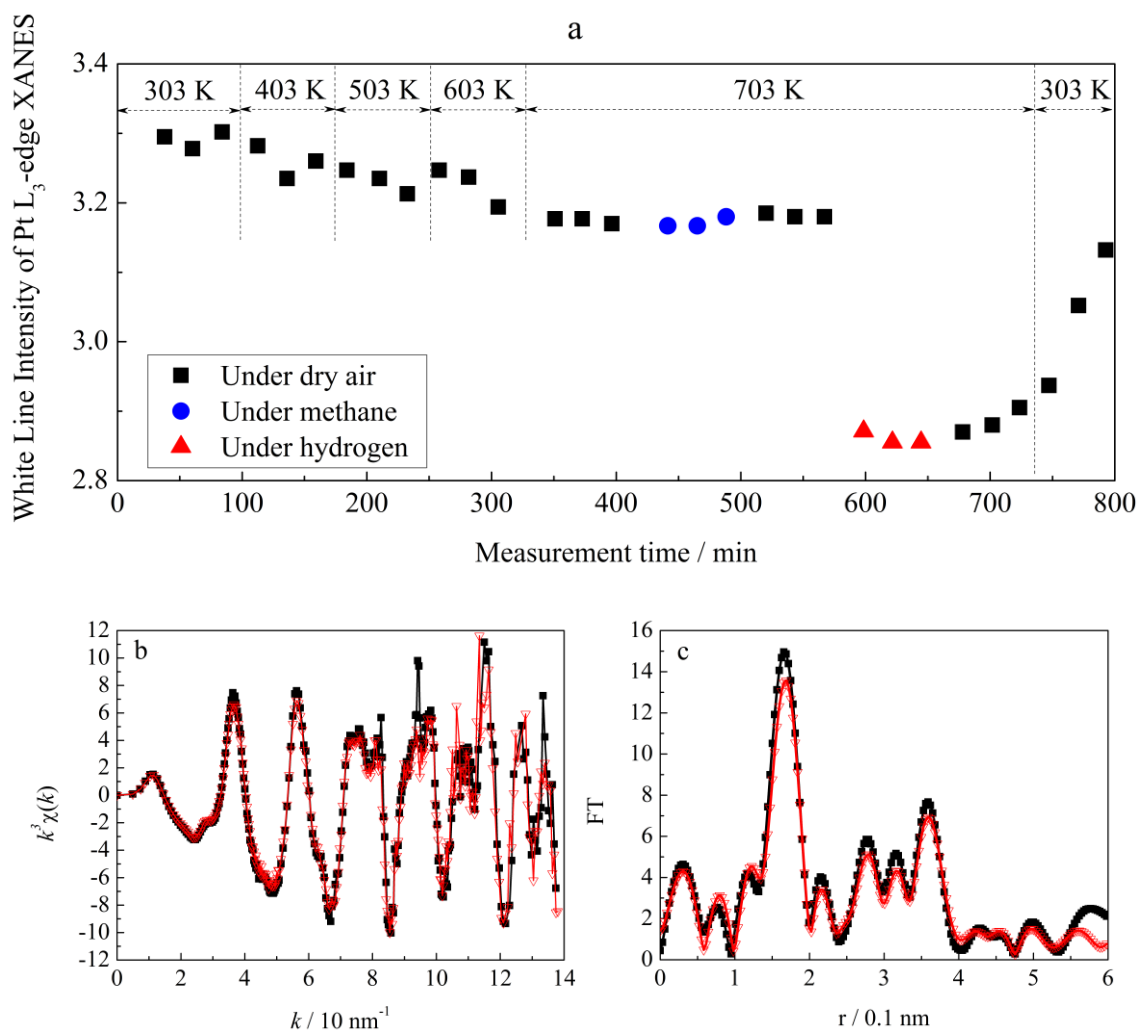


Figure 4. The series of variance in dry air and reduction gases by Pt L₃-edge XANES.

The plot of Pt L₃-edge XANES intensity on the series of variance on a.

Pt L₃-edge EXAFS oscillation in b and Fourier transform in c at 303 K on before and after of this series. Close square is on before, open reverse triangle is on after. Curve fitting result by FEFF was shown on table 1.

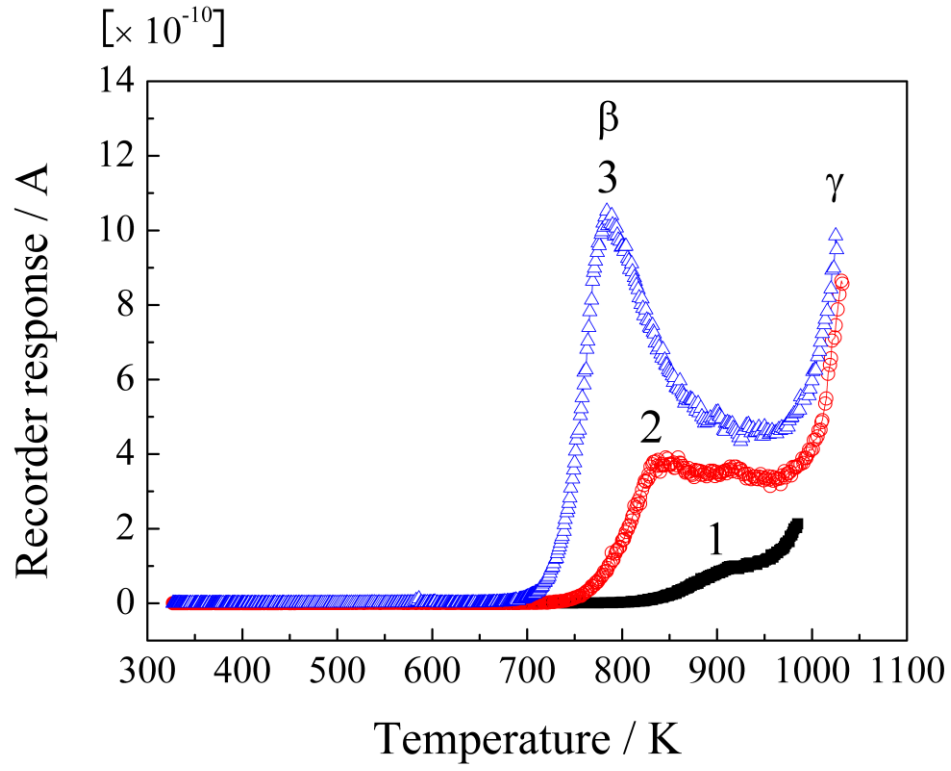


Figure 5. The TDS measurement. 1 : only SnO₂ substrate 2: 4at % Pt-SnO₂/SnO₂ layer 3: 8at % Pt-SnO₂/SnO₂ layer. The β position and γ position was identified as O²⁻ and lattice oxygen in previous study of ref 33.

-
- ¹ United Nations (UN), *2010 Energy Statistics Yearbook* United Nations, New York, 2014.
- ² Fire and Disaster Management Agency of Japan, “Statistical Table for explosion and leakage cases by gases and hazardous chemicals in 2011”
- ³ T. Seiyama, A. Kato, K. Fujiishi and M. Nagatani, *Anal. Chem.* **1962**, 34, 1502.
- ⁴ T. Seiyama and S. Kagawa, *Anal. Chem.* **1966**, 38, 1069.
- ⁵ G. Heiland, *Sens. Actuators* **1982**, 2, 343.
- ⁶ N. Barsan, D. Koziej, and U. Weimar, *Sens. Actuators B: Chem.* **2007**, 121, 18.
- ⁷ N. Taguchi, United States Patent 3,631, 436, July 4th, **1970**.
- ⁸ T. Suzuki, K. Kuniyama, M. Kobayashi, S. Tabata, K. Higaki, and H. Ohnishi, *Sens. Actuators B: Chem.* **2005**, 109, 185.
- ⁹ S. Tabata, K. Higaki, H. Ohnishi, T. Suzuki, K. Kuniyama, and M. Kobayashi, *Sens. Actuators B: Chem.* **2005**, 109, 190.
- ¹⁰ A. Nonaka, T. Nakajima, H. Ohnishi, M. Okamura, N. Murata, T. Suzuki, *Proc. the 57th Chem. Sensor Sym.*, **30** Sup. B (2014).
- ¹¹ T. Suzuki, M. Okamura, N. Murata, A. Nonaka, T. Nakajima and H. Ohnishi, *Proc. The 57th Chem. Sensor Sym.* **2014**, 30 Sup. B
- ¹² N. Yamazoe, *Sens. Actuators B* **1991**, 5, 7.
- ¹³ I. Kocemba, J. Rynkowski, *Sens. Actuators B: Chem.* **2011**, 155, 659.
- ¹⁴ M. Gaidi, M. Labeau, B. Chenevier, and J. L. Hazemann, *Sens. Actuators B: Chem.* **1998**, 48, 277.
- ¹⁵ L. Mädler, T. Sahm, A. Gurlo, J. -D. Grunwaldt, N. Barsan, U. Weimar, S. E. Pratsinis, *Journal of Nanoparticle Research* **2006**, 8, 783.
- ¹⁶ A. Kowal, M. Li, M. Shao, K. Sasaki, M. B. Vukmirovic, J. Zhang, N. S. Marinkovic, P. Liu, A. I. Frenkel, and R. R. Adzic, *Nat. Mater.* **2009**, 8, 325.
- ¹⁷ M. Gaidi, J. L. Hazemann, I. Matko, B. Chenevier, M. Rumyantseva, A. Gaskov, and M. Labeau, *J. Electrochem. Soc.* **2000**, 147, 3131.
- ¹⁸ M. Hübner, D. Koziej, M. Bauer, N. Barsan, K. Kvashnina, M. D. Rossell, U. Weimar, and J. -D. Grunwaldt, *Angew. Chem. Int. Ed.* **2011**, 50, 2841.
- ¹⁹ M. Hübner, N. Bârsan, and U. Weimar, *Sens. Actuators B* **2012**, 171-172, 172.
- ²⁰ N. Murata, T. Suzuki, M. Kobayashi, F. Togoh, and K. Asakura, *Phys. Chem. Chem. Phys.* **2013**, 15, 17938.
- ²¹ Nomura, M. *J. Synchrotron Rad.* **1998**, 5, 851.
- ²² Nomura, M.; Koyama, A. Design and performance of a new XAFS beamline at the Photon Factory; BL12C, in: KEK Report, Photon Factory, **1996**.
- ²³ Nomura, M.; Koike, Y.; Sato, M.; Koyama, A.; Inada, Y.; Asakura, K. *AIP Conf. Proc.* **2007**, 882, 896.
- ²⁴ N. Murata, M. Kobayashi, Y. Okada, T. Suzuki, H. Nitani, Y. Niwa, H. Abe, T. Wada, S. Mukai, H. Uehara, H. Ariga, S. Takakusagi and K. Asakura, *Rev. Sci. Instrum.* **2015**, 86, 034102.
- ²⁵ K. Asakura, in: *Analysis of EXAFS in X-ray Absorption Fine Structure for Catalysts and Surfaces*, eds. Y. Iwasawa (World Scientific, Singapore, 1996) p. 33.
- ²⁶ Taguchi T (2007) *AIP Conf Proc* 882:162
- ²⁷ K. Asakura, in: *Catalysis*, Vol. 24, eds. J. G. Catalano, 2012, p. 281.
- ²⁸ J. W. Cook and D. E. Sayers, *J. Appl. Phys.* 1981, **52**, 5024.

-
- ²⁹ M. Newville, J. J. Kas, J. J. Rehr, Journal of Physics: Conference Series **2009**, 190, 012023.
- ³⁰ J. J. Rehr, J. J. Kas, M. P. Prange, A. P. Sorini, Y. Takimoto and F. Vila, Comptes Rendus Physique **2009**, 10, 548.
- ³¹ J. J. Rehr, Radiation Phys.Chem. **2006**, 75, 1547.
- ³² W. C. Hamilton, Acta Cryst. **1965**, 18, 502.
- ³³ N. Yamazoe, J. Fuchigami, M. Kishikawa and T. Seiyama, Surf. Sci. **1979**, 86, 335.

Chapter 6

General conclusion

The commercialization of cordless city-gas leakage alarm has been desired in the industry segments. The development of MEMS gas sensor is a shortcut to realize of cordless type alarm though the fundamental knowledge (including degradation factor and stability) of Pt-SnO₂ and PdO/Al₂O₃ catalyst which are used as key material for the sensor has been required. In my thesis I have clarified their structures and chemical state applying XAFS technique to model samples which are prepared on the same way with the practical sensor. Firstly I discussed structure and mechanism of Pt-SnO₂ with stability under reaction conditions. Moreover I discussed about origin of high selectivity of sensor by *in-situ* XAFS analysis.

I have found that Pt-SnO₂ has the solid solution structure where the Pt species is located at the Sn site in the SnO₂ lattice on high Pt concentration of 10 at%. Here, this catalyst has high activity when the whole material has the SnO₂ rutile structure while it loses activity in amorphous phase with Pt 11 at%. Pt on SnO₂ has been considered to exist as fine particles. But we have shown as the first example that Pt – solid solution is stable at such high concentration and still have high activity. Moreover I have found that this catalyst is maintained as solid state during the reaction with reduction gases of 1% CH₄ and 1% H₂. This result means that the structure of SnO₂ and Pt atoms highly dispersed in SnO₂ is important for high activity. I think that this metal oxide solid solution type catalyst is good on the following three points as compared with metal thin film catalyst of metal supported catalyst, when this catalyst is applied to the gas sensor.

- 1) The Pt particle growth is unlikely to occur, because of Pt atoms are present in SnO₂ even in the reaction with reduction gases.
- 2) The activity and thermal stability are high.
- 3) The cost is low, because of platinum amount is small highly thanks to the atomic disperse

Consequently I think that gas sensor can have high sensitivity and a long life time from the view point of 1) and 2). The result is reflected to the sensor development, and five years long life sensors are realized.

However I have three questions. What are the active sites? What is the structure of the outermost surface under the gas reaction conditions? What is mechanism of verification process? I think the active sites will be defect of outermost surface, but I still have not confirmed to its presence. I have been paying attention to the muon study on a defect in the Pt-SnO₂. The

origin of the effect of the defect will be clarified and if the control of defect is possible, it will lead to further development of the sensor.

In the sensor development process, it has been found that methane selectivity of sensor is reduced in the long-term running under the reduction gas with moisture. A degraded sensor before improvement is measured by XAFS we have found the PdO in PdO/Al₂O₃ is reduced. PdO is more active than Pd metal for other gases (such as hydrogen, alcohol, and carbon monoxide) than methane, because methane is the most inert gas. Thus, PdO in the Pd/Al₂O₃ overlayer can burn out other gases than methane so that methane reaches the SnO₂ sensor layer through the Pd/Al₂O₃, and this oxide state of PdO is a key factor for high selectivity of the sensor. The heat distribution in the PdO/Al₂O₃ overlayer from the heater where running temperature is ~700 K is inhomogeneous in the sensor before the improvement. In other words, the temperature in the far region from the heater will be reduced with distance from heater. The correlation between Pd metal amount and heat distribution has been found. In the thesis I found that PdO is reduced at temperature below 673 K during reaction of reduction gas with moisture, and is re-oxidized over 673 K. From this result I think that the PdO is strongly influenced of other gases than methane in low temperature region, will be inhibited re-oxidation. Thus the region of this low temperature will lead to the decrease of the selectivity. Based on this knowledge, the sensor with homogeneous heating distribution in PdO/Al₂O₃ overlayer has been improved for a further long life time more than 5 years.

Through this thesis, I demonstrate that the XAFS analysis is effective on the process of obtaining the guidelines for the performance improvement in development of gas sensor. The XAFS is measured with a model sample with a mm size in this thesis. The core-region (sensing parts) of the real gas sensor is ~a few micro meter. Although described above, the partial layers of the gas sensor is adapted to be XAFS analysis. Furthermore the XAFS measurement with a nano-beam size and three-dimensional analysis will be required to further understand the phenomenon occurring in gas sensor. If this technique is established, I think that XAFS further can contribute to the industry where many products such as semiconductor and sensor with MEMS have μm or nm size.

Finally, the world's first cordless city gas alarm has been commercialized

in 2015 utilizing the knowledge of the thesis.

Acknowledgement

I wish to express my sincerest thanks to Professor Kiyotaka Asakura for his invaluable comments, discussions and suggestions and for his constant encouragement during the period of his research project.

Hearty thanks are due to Associate Professor Satoru Takakusagi, Assistant Professor Hiroko Ariga and Assistant Professor Hiromitsu Uehara who acted as examiner of the dissertation, for helpful and useful suggestion.

I grateful acknowledge Shingo Mukai, Hokkaido university, for invaluable suggestion and discussion on artifice of in-situ cell. I grateful acknowledge Assistant Professor Takahiro Wada, Tokyo Medical and Dental University, for invaluable suggestion and discussion on establishment of μ -XAFS system.

I am deeply grateful to the staffs of the Photon Factory of High Energy Accelerator Research Organization (KEK-PF), Professor Masaharu Nomura, Professor Masao Kimura, Associate Professor Hitoshi Abe, Assistant Professor Hiroaki Nitani and Engineer Yasuhiro Niwa for many valuable discussion and advices for XAFS measurement.

I wish to express my appreciation to Takuya Suzuki and Makoto Kobayashi, Fuji electric Co., Ltd. for invaluable suggestion and discussion. I grateful acknowledge Fumiaki Togoh, Yukari Okada and Toshitaka Furuta, Fuji electric Co., Ltd. for the measurement of the XAFS. I am grateful to Yohei Uemura, Institute for Molecular Science, for his helpful suggestion and encouragement.

Finally, I wish to thank General Manager Kiyoaki Sasagawa, General Manager Takashi Yoshida, General Manager Yoshihiko Nagayasu, General Manager Shinichi Souma, Senior Manager Masahiko Takei, Senior Manager Tetsuya Saito and Senior Manager Akira Saito, Chief Expert Takuya Suzuki, Tokumi Nagase, Makoto Okamura, Shunichi Arakawa, Yousuke Ueda and Toshie Nagayama, Fuji electric Co., Ltd., for their constant supports and encouragement, and understanding throughout my Ph. D. Course. I wish to

thank my parents and my brother and sister and Shoko Ringe for their encouragement.

Naoyoshi Murata

Tokyo

March, 2016