Supporting information

The structure of atomically dispersed Pt in a SnO2 thin film under reaction conditions – Origin of its high performance in MEMS gas sensor catalysis

Naoyoshi Murata1, Takuya Suzuki1, Yunli Lin 2, Hiroaki Nitani3, Yasuhiro Niwa3, Takahiro Wada4, Motohiro Uo4 and Kiyotaka Asakura\*2

1. *Corporate R & D Headquarters, Fuji Electric Co., Ltd., Tokyo 191-8502, Japan*

2. *Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan*

3. *Photon Factory, Institute of Structure Material Science, High Energy Accelerator Research Organization (KEK-PF), Oho 1-1, Tsukuba 305-0811, Japan*

4. *Graduate School of Medical and Dental Sciences, Tokyo Medical and Dental University, Yushima 1-5-45, Bunkyo-ku, Tokyo 113-8549, Japan*

Contents

SI-1. Gas response properties of the sensor

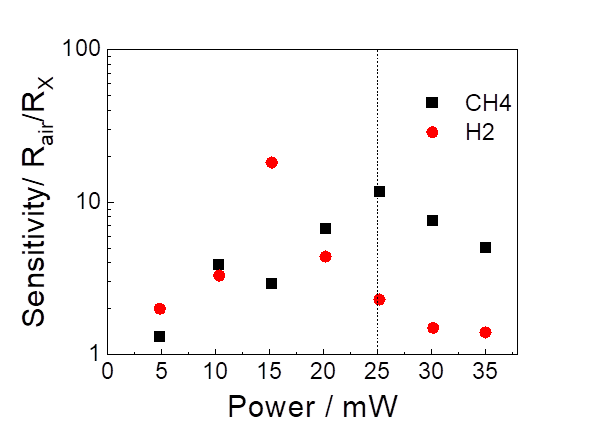
SI-2. Pt L3 and Sn K edge EXAFS oscillations in Pt-SnO2

SI-3. The second and the third shell analysis of Pt-SnO2

SI-1 Gas response properties of the sensor

Figure S1(a) shows the response curve of the conductivity under the 4000 ppm CH4 flow with a 100 cc / min flow rate. At time 0 s, 3 V was suddenly applied to the heater at the bottom of Si substrate and the sample temperature reached the operating temperature of 723 K by the heater within 40 ms. The temperature was measured by the infrared thermography and the heater resistivity.(1) The heater power at 723 K was 30 mW At the same time the conductivity of the sensor reached equilibrium. Thus the sensor is heated with 100 ms pulse with 60 s interval, which guarantees a longer life time than 5 years. Figure S1(b) shows sensitivity (Resistance ratio under air to under the reducing gases.) of the sensor against heater powers (or temperature). At higher temperature, H2 is combusted in the Pd/Al2O3 layer covering the Pt-SnO2 layer. Consequently, high CH4 sensitivity is achieved if the power is applied more than 25 mW (vertical line). Figure S1(c) shows the sensor structure.





(c)

(b)

(a)

ダイアグラム

自動的に生成された説明

Heater

Figure S 1 (a) Conductivity response of Pt-SnO2 empowered SnO2 sensor under the 4000 ppm CH4 flow with 100 cc / min flow rate. (b) The sensitivity of the sensor as a function of applied power (or temperature) reproduced from ref.（[[1]](#endnote-1)）(c)The structure of MEMS sensor.

Table S1 Response time and type of sensor

|  |  |  |  |
| --- | --- | --- | --- |
| Response Time | Type | Literature | Device |
| 60 s | Semiconductive metal oxide (SMO), SnO2 particle | [[2]](#endnote-2) | MEMS |
| 110 s | SMO, SnO2(Pt doped) | [[3]](#endnote-3) | MEMS |
| 20 s | SMO, SnO2(Pd superficially doped | [[4]](#endnote-4) | MEMS |
| 500 ms | Themocatalysis(TC), (NiCo2O4) | [[5]](#endnote-5) | MEMS |
| 500 ms | TC,Pt,Pd/Al2O3 | [[6]](#endnote-6) | MEMS |
| 8s | SMO, Rh2O3/Al2O3 | [[7]](#endnote-7) | MEMS |
| 100 s | SMO , Co3O4 NP | [[8]](#endnote-8) |  |
| 10-20 s | SMO, ZnO +Pd-Ag catalyst | [[9]](#endnote-9) |  |
| 100 ms | SMO, SnO2(Pt-SnO2) | This work, 1 | MEMS |

SI-2 Pt L3 and Sn K edge EXAFS oscillations in Pt-SnO2

Figure S2 shows the Pt L3 edge EXAFS and Sn K-edge EXAFS. Since the L3 and K-edge oscillations are p-radian difference, the phase of the Pt L3 edge EXAFS is added by p radian or multiplied by -1. The good agreement of the oscillation indicates the Pt and Sn have the similar local structure.

グラフ, 折れ線グラフ, ヒストグラム

自動的に生成された説明

Figure S2 Pt L3 edge and Sn K-edge of 7.5 wt % Pt-SnO2 sample.

Since the L3 edge EXAFS is p rad different from that of K-edge, the oscillation is multiplied by -1. The Pt L3-edge EXAFS oscillation is shifted by 6 eV. Consequently, the oscillation is in good agreement with each other indicating the Pt and Sn are mostly at the same lattice position.

SI-3 The second and the third shell analysis of Pt-SnO2

SnO2 has a rutile structure where one Sn is at the center and eight Sn atoms are at the corner of the tetragonal unit cell with Sn-Sn distance of 3.76 Å. Two other neighbor Sn atoms at 3.16 Å are located at the center of the neighboring tetragonal unit cells along the c-axis. There are totally two shorter and eight longer Sn-Sn bonds as shown in Table S1. To confirm the random distribution of Pt in the SnO2, curve fitting analyses in the second and the third shells are carried out. However, we need a total of 16 fitting parameters for 4 shells of two Pt–Sn(Sn–Sn) and two Pt–Pt(Sn–Pt). The amount of information, *M,* can be calculated as . Thus, the analyses of 2nd and 3rd shells are impossible for Pt–SnO2. However, if two edges are simultaneously analyzed and the following constraints are applied, it is possible to analyze the data by curve fitting.

1. rPtSn = *r*SnPt and *C*Pt·*CN*PtSn = *C*Sn ·*CN*SnPt should be satisfied. The composition ratio is *C*Pt:*C*Sn = 1:3.5.
2. The *E* for Sn–Sn in Sn K-edge of Pt–SnO2 must be equal to those of SnO2.
3. All Pt atoms are located at the substitution site of Sn in the SnO2 lattice.

The total number of information (*M*) is 30 (=15×2 for Sn K-edge and Pt L3-edge). The number of fitting parameters () is 32 (=4× 4 for Sn K-edge and 4× 4 for Pt L3-edge) with 6 constraints (*C*). Consequently, . Table S1 provides the results. The fitting showed the bond distances around Pt atoms are shorter than those of SnO2 corresponding to the smaller lattice constants in Pt–SnO2 than those of SnO2 as shown in XRD.[[10]](#endnote-10) The total coordination numbers around Pt and Sn (Ntotal) for the second and third nearest neighbors are 1.6 (=1.3+0.3) and 7.2 (=5.6+1.6) for Sn edge and 1.5 (=1.05+0.45) and 7.2 (=5.6+1.6) for Pt L3-edge, respectively. The total coordination numbers around Sn and Pt agree well, indicating that Pt atoms are not on the surface but in the bulk. The ratio of homo bond (Pt–Pt and Sn–Sn) to hetero bond (Pt–Sn) at the corresponding shells is roughly 3.5, indicating the Pt should be randomly distributed in the SnO2 lattice. We have concluded that the Pt is located at the Sn site in the SnO2 lattice and randomly distributed in the thin film layer.

Table S1. Curve fitting results for the higher shell peaks to Sn K-edge and Pt L3-edge FT-EXAFS of SnO2 and Pt–SnO2 using FEFF

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | | *r* / Å | *E* / eV | 2 / Å2 |  | shell |  |
| SnO2 | | 3.16 ± 0.02 | -4.1 | 0.0014 ± 0.0005 | (2) |  | |
| 3.76 ± 0.02 | 4.1 | 0.0019 ± 0.0006 | (8) |  | |
| SnO2 film Sn-Sn | | 3.16 ± 0.02 | (-4.1) | 0.0007 ±0.0005 | 1.6 ± 0.4 |  | |
| 3.72 ± 0.02 | (4.1) | 0.0012 ± 0.0006 | 7.2 ± 0.7 |  | |
| Pt-SnO2  Sn K-edge | Sn-Sn | 3.14 ± 0.03 | (-4.1)\* | 0.0011 ± 0.0010 | 1.3± 0.5 | 2nd | 1.6±  0. 5 |
| 3.73 ± 0.04 | (4.1)\* | 0.003 ± 0.001 | 5.6 ± 1.0 |
| Sn-Pt | 3.06\* ± 0.04 | -15 ± 5 | 0.0009 ± 0.0007 | 0.3\* ± 0.1 | 3rd | 7.2±  1.1 |
| 3.71\* ± 0.04 | 15 ± 5 | 0.0081 ± 0.0015 | 1.6\* ± 0.5 |
| Pt-SnO2  Pt L3-edge | Pt-Sn | 3.06\* ± 0.04 | -15 ± 5 | 0.0008 ± 0.001 | 1.05\* ± 0.3 | 2nd | 1.5±  0.4 |
| 3.71\* ± 0.04 | 15 ± 5 | 0.0051 ± 0.001 | 5.6\* ± 1.5 |
| Pt-Pt | 3.03 ± 0.04 | 10 ± 5 | 0.0006 ± 0.0004 | 0.45 ± 0.2 | 3rd | 7.2±  1.6 |
| 3.61 ± 0.04 | 5 ± 5 | 0.0009 ± 0.0007 | 1.6 ± 0.6 |

**\*** means the values are corresponding to the 6 constraints shown in text.

Parentheses mean the fixed parameters.

for each shell.

1. Suzuki, T.; Kunihara, K.; Kobayashi, M.; Tabata, S.; Higaki, K.; Ohnishi, H., A Micromachined Gas Sensor Based on a Catalytic Thick Film/SnO2 Thin Film Bilayer and Thin Film Heater: Part 1, CH4 Sensing, *Sens. Actuator B Chem:* **2005**, 109, 185-189. [↑](#endnote-ref-1)
2. Chen, Y.; Xu, P.; Zhang, P.; Li, X. In Long-Term Stability Improvement of Micro-Hotplate Methane Sensor Product, *2020 IEEE 33rd International Conference on Micro Electro Mechanical Systems (MEMS), IEEE*: **2020**; pp 1300-1303. [↑](#endnote-ref-2)
3. Das, I.; Bhattacharyya, R.; Saha, H.; Ghosh, S., Enhanced Response of Co-Planar Mems Microheater-Based Methane Gas Sensor. *IEEE Sens., J.* **2020**, 20, 14132-14140. [↑](#endnote-ref-3)
4. 4 Pisliakov, A. V.; Sokolov, A. V.; Polovko, O. V.; Guarnieri, V.; Lorenzelli, L.; Samotaev, N. N.; Kujawski, W.; Kujawska, A.; Vasiliev, A. A.; Legin, A. V., Pervaporation Unit with Mems Gas Sensor for the Measurement of Methane Concentration in Water. *2015 IEEE Workshop on Environmental, Energy, and Structural Monitoring Systems (EESMS) Proceedings,* **2015**; pp 136-140. [↑](#endnote-ref-4)
5. Das, I.; Bhattacharyya, R.; Saha, H.; Ghosh, S., Enhanced Response of Co-Planar Mems Microheater-Based Methane Gas Sensor. *IEEE Sens., J.* **2020**, 20, 14132-14140. [↑](#endnote-ref-5)
6. Pisliakov, A. V.; Sokolov, A. V.; Polovko, Samotaev, N.; Dzhumaev, P.; Oblov, K.; Pisliakov, A.; Obraztsov, I.; Ducso, C.; Biro, F., Silicon Mems Thermocatalytic Gas Sensor in Miniature Surface Mounted Device Form. *Chemosensors* **2021**, 9. 340(1)-(10) [↑](#endnote-ref-6)
7. Su, J.; Cao, L.; Li, L.; Wei, J.; Li, G.; Yuan, Y., Highly Sensitive Methane Catalytic Comb Bierer, B.; Grgić, D.; Yurchenko, O.; Engel, L.; Pernau, H.-F.; Jägle, M.; Reindl, L.; Wöllens [↑](#endnote-ref-7)
8. tein, J., Low-Power Sensor Node for the Detection of Methane and Propane. *J. Sens. Sens. Sys.* **2021**, 10, 185-191.

   8 Shaalan, N. M.; Rashad, M.; Moharram, A. H.; Abdel-Rahim, M. A., Promising Methane Gas Sensor Synthesized by Microwave-Assisted Co3o4 Nanoparticles. *Mater. Sci. Semicond. Proces.* **2016**, *46*, 1-5. [↑](#endnote-ref-8)
9. Bhattacharyya, P.; Basu, P. K.; Saha, H.; Basu, S., Fast Response Methane Sensor Using Nanocrystalline Zinc Oxide Thin Films Derived by Sol–Gel Method. *Sens. Actuator B: Chemical* **2007**, 124, 62-67. [↑](#endnote-ref-9)
10. Murata, N.; Suzuki, T.; Kobayashi, M.; Togoh, F.; Asakura, K., Characterization of Pt-Doped SnO2 Catalyst for a High-Performance Micro Gas Sensor. *Phys. Chem. Chem. Phys* **2013**, *15*, 17938-17946. [↑](#endnote-ref-10)