

An Application Possibility of Self-Ordered Mesoporous Silicate for Surface Photo Voltage (SPV) Type NO Gas Sensor (II): Self-Ordered Mesoporous Silicate Incorporated SPV Device and Its Sensing Property Dependence on Mesostructure

Takeo YAMADA^{†, ††}, Hao-Shen ZHOU^{† a)}, Hidekazu UCHIDA^{†††}, Masato TOMITA^{††††}, Yuko UENO^{††††}, Keisuke ASAI^{††}, Itaru HONMA[†], *Nonmembers*, and Teruaki KATSUBE^{†††}, *Regular Member*

SUMMARY Self-ordered mesoporous silicate films from organic-inorganic compound materials are successfully fabricated into the surface photo voltage (SPV) type gas sensor device as a gas adsorption insulator layer. These kinds of gas sensors device exhibit NO gas sensing property dependent on their mesoporous film structure. We are succeeded in indication about a possibility of mesoporous silicate film for the SPV type gas sensor application.

Key words: *self-ordered mesoporous silicate film, surface photo voltage, hexagonal mesostructure, cubic mesostructure, NO gas sensor*

1. Introduction

Nitrogen oxides (NO_x) generated by combustion are dangerous and harmful to health and each country limits their alarm level in the environment. Therefore, the development of a highly sensitive, responsive and portable monitoring technique of these gases is an urgent requirement [1]–[8]. However, the conventional NO gas sensing device is inadequate to sense in environmental level, which are using WO₃ or Ti-WO₃ as a gas sensitive material [2]–[8]. There is one way to improve sensing property, in which the device constructions have been refined such as the surface photo voltage (SPV) type [1] and the porous structure type [8].

The SPV construction system which are based on semiconductor characterization technique [1], [9] has a great potential to satisfy sensitive, responsive and portable requirements. The basic principle of this characterization technique is based on the semiconductor surface voltage property of the metal-insulator-semiconductor (MIS) structure [9]. This SPV system detects sensitively the variation of surface voltage, which is induced by the physical adsorption of the target gases and also relies mainly on the interaction between the

target gases and the surface area of the sensitive layer, by the semiconductor photocurrent [1]. Therefore, to improve the sensing performance, the metal and the insulator layer of the MIS structure need to be refined. Especially, the capacitance property of the insulator layer is due to the gas adsorption performance and improvement of the gas adsorption performance directly leads to the progress of SPV gas sensor characteristics.

The large surface area created by the nanosize mesopores of mesoporous materials [10]–[14] gives them the potential to improve the gas adsorption property of SPV devices. Particularly during the past decade, these mesoporous materials have continued to progress through the innovative synthesizing method [10]–[13] which fused the organic surfactant self assemble template system into the inorganic sol-gel synthesis method [10]–[13]. These innovative mesoporous materials, which are produced by organic-inorganic compound material, have uniform pore size, pore channel alignment in two or three dimensions and a high surface area [10]–[13]. Furthermore, another benefit of this innovative synthesis process, this sol-gel synthesis method can be applied to make the film [15]–[20]. The properties of high surface area, bi-continuous mesopore and film form in the mesoporous material film, especially mesoporous silicate film, make it the best candidate for the target gas adsorption insulator layer for the SPV gas sensor. This paper reports a possible application of the self ordered mesoporous silicate film for the NO gas sensor, which is synthesized by nonionic poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) type triblock copolymer surfactant as a structure directing agent by the spin coating method. The NO gas sensor is based on the SPV characterization system. The mesoporous silicate film is assembled as an insulator gas adsorption layer of the MIS structure based on the SPV characterization system. The properties and potential due to the structure of the self-ordered mesoporous silicate film combined SPV NO gas sensor are also examined.

2. Experimental

2.1 Synthesis Mesoporous Silicate Film

The mesoporous silicate film was synthesized by nonionic

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[†] The authors are with National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba-shi, 305-8568 Japan.

^{††} The authors are with the Department of Quantum Engineering and Systems Science, The University of Tokyo, Tokyo, 113-8656 Japan.

^{†††} The authors are with the Department of Information and Computer Science, Saitama University, Saitama-shi, 338-0825 Japan.

^{††††} The authors are with NTT Lifestyle and Environmental Technology Laboratories, NTT Corporation, Atsugi-shi, 243-0198 Japan.

a) E-mail: hs.zhou@aist.go.jp

PEO-PPO-PEO triblock copolymer surfactant as the structure directing agent by the spin coating method [16], [17]. The precursor for the coating sol solution was prepared from two solutions. One is the polymer solution, which is dissolved in an $\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}$ (BASF Corporation: Pluronic P123, $M_{av} = 5750$) type triblock copolymer or an $\text{EO}_{100}\text{-PO}_{65}\text{-EO}_{100}$ (BASF Corporation: Pluronic F127, $M_{av} = 12600$) type triblock copolymer into ethanol (Wako Pure Chemical Industries, Ltd.: EtOH Super Special Grade, $M = 46.07$) solution whilst stirring for about 2 hours at room temperature; the other is the silica solution, which consists of a mixed Tetraethyl Orthosilicate (Wako Pure Chemical Industries, Ltd.: TEOS Special Grade, $M = 208.33$), EtOH, distilled water and Hydrochloric Acid (Wako Pure Chemical Industries, Ltd.: HCl Super Special Grade, $M = 36.46$) whilst stirring for 1–2 hour from room temperature to 60 °C. The mole ratio of the chemicals is 1 TEOS: 0.014 P123: 15 H_2O : 0.16 HCl: 39 EtOH for the self-ordered hexagonal structure film and 1 TEOS: 0.0041 F127: 15 H_2O : 0.16 HCl: 40 EtOH for the self-ordered cubic structure film. After the above treatment, the ethanol solution and the silica solution are mixed. The mixed solution is stirred for a further 2 hours at room temperature and then the coating precursor solution is prepared. Next, the coating solution is used for film deposition on substrates by the spin coating method. This method is performed at a low-speed of 400 rpm for the initial 3 seconds and at a high-speed of 3000 rpm for the final 10 seconds. Finally, calcination is carried out by slowly increasing the temperature from a room temperature to 450 °C in 12 hours and heating at 450 °C for 24 hours and decreasing the temperature from 450 °C to 100 °C in 12 hours and allowing to cool naturally from 100 °C to room temperature. These processes result in homogeneous and transparent mesoporous silicate films.

2.2 Construction of SPV Sensor

The SPV sensor system is constructed by the MIS structure of semiconductors. Therefore, the n-type silicon (n-Si: 30–50 $\Omega\text{-cm}$) with SiO_2 (about 100 nm) and Si_3N_4 (about 100 nm) layer is used as a substrate. Self-ordered hexagonal or cubic mesostructure film is prepared on the Si_3N_4 layer of the substrate as a gas adsorption insulator layer by the above film preparation method. After that, an Au electrode is deposited on the mesoporous film by sputtering for the non-reactive metal layer of the MIS structure and an Al electrode is fabricated on the backside of the n-Si surface in order to achieve a good ohmic constant by the vacuum vapor deposition technique. Consequently, the constitution of the Au/ self-ordered hexagonal or cubic mesoporous silicate film/ Si_3N_4 / SiO_2 / n-Si/ Al as shown in Fig. 1(a) is constructed as the mesoporous silicate combined MIS structure for the SPV sensor.

Hereafter, we call SPV device with self-ordered hexagonal and cubic mesoporous silicate film as SPV-hex and SPV-cub, respectively.

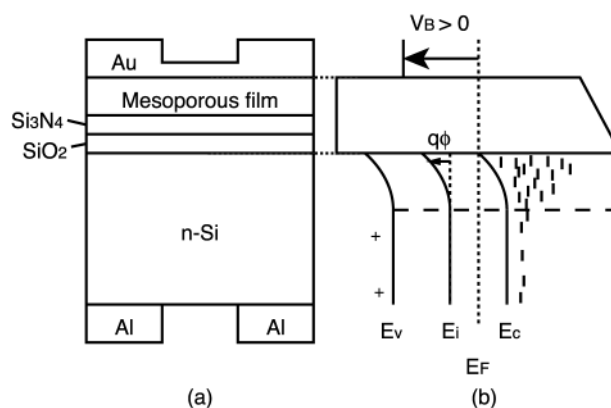


Fig. 1 (a) The structure of the mesoporous silicate film combined SPV gas sensor cell. (b) The scheme of the energy band diagram and the definition for ϕ . Where V_B , E_F , E_i , E_c and E_v are bias voltage, fermi level, intrinsic fermi level, conduction band level and valence band level, respectively.

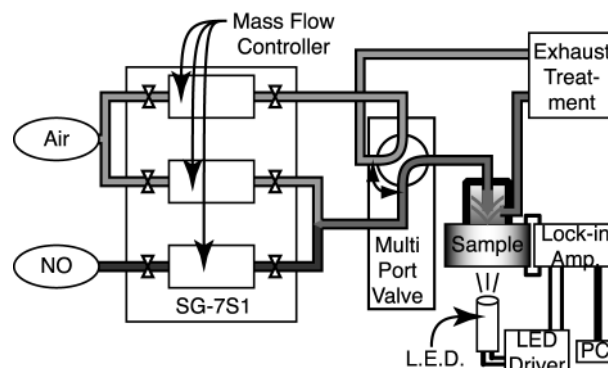


Fig. 2 The gas flow diagram and the SPV gas sensor detection system.

2.3 Measurement System of SPV

The measurement system of the SPV method is assembled as shown in Fig. 2. The basic sensing principle is based on the detection of the potential change of the semiconductor surface. It induced a variety of insulator capacitors due to gas adsorption and trapped charges in the insulator. The electric response of the sensor to NO gas is measured under the cyclic gas flow between the NO gas (100 ppm) and the standard air. These gases are controlled by a mass flow controller (Aera Japan Limited: SG7S1) and a multi-port valve. The 100 ppm NO gas is prepared by this mass flow control system with source NO gas and standard air. Both the NO gas and the standard air are supplied to the sensor at a constant flow rate of 100 sccm.

In this measurement system, the bias voltage, which is controlled by a Lock-in amplifier (Stanford Research Systems: SR830) is applied between the Au and Al electrodes. An alternating modulated LED beam ($\lambda = 930$ nm, $\nu = 1$ kHz), which is also controlled by a Lock-in amplifier, is irradiated on the backside of the semiconductor to induce an AC photocurrent. The supplied NO gas sensitivity is estimated

by the induced photocurrent through the MIS structure.

2.4 Principle of SPV Method

The SPV gas-sensing system is based on according with the semiconductor property of the MIS structure, especially the semiconductor surface charge density and surface voltage.

Figure 1(b) shows the band diagram of the MIS structure. In this figure, the surface charge density Q_s has three pictures according to the applied bias voltage (V_B). One is the accumulation of electrons ($\phi_s > 0$), another is the depletion ($\phi_B < \phi_s < 0$) and the last one is inversion ($\phi_s < \phi_B$). Where ϕ_s and ϕ_B are the surface potential ($\phi_s = \phi$ at the semiconductor surface) and the potential difference between the fermi level and the intrinsic fermi level. In the accumulation picture, a positive voltage ($V_B > 0$) is applied to the metal electrode of the MIS structure in an n-type semiconductor. The conduction band, valence band and intrinsic Fermi level bends downward and the electron conduction band is closer to the Fermi level E_F , the electrons density depends exponentially on the $q\phi_s$. In the case of depletion, each level is upward with an applied small negative bias voltage ($V_B < 0$). Then the majority carrier electrons are depleted in the surface layer of the semiconductor. In the final inversion case, the bands also bend even more upward with a large negative bias voltage ($V_B < 0$) and the intrinsic level E_i crosses over the Fermi level E_F . In this region, the property of the n-type semiconductor changes to that of p-type in the surface range of the semiconductor, which depend on the Fermi level position. And therefore, the number of minority carrier, holes, in the n-type semiconductor is larger than that of the majority carrier, electrons, in the surface range of the semiconductor. From these pictures, the SPV device exhibits the bias voltage dependent characters. Therefore, the gas sensitivity was observed as the shift in them. The basic relation between bias voltage V_B , surface voltage and surface charge are described in Eqs. (1)–(4).

$$V_B = \phi_s - \frac{Q_s + Q_0}{C_i} \quad (1)$$

$$\frac{1}{C_i} = \frac{1}{C_{meso}} + \frac{1}{C_{Si_3N_4}} + \frac{1}{C_{SiO_2}} \quad (2)$$

$$C_i = \frac{\epsilon_i}{d} \quad (3)$$

$$Q_0 = Q_f + Q_m + Q_{ox} \quad (4)$$

where C_i is the insulator capacitance including the capacitance of the mesoporous silicate film (C_{meso}), substrate Si_3N_4 layer ($C_{Si_3N_4}$) and substrate SiO_2 layer (C_{SiO_2}). ϵ_i and d exhibit the dielectric constant and the thickness of the insulator layer, respectively. Q_f , Q_m and Q_{ox} are the oxide fixed charge, net mobile ions and the oxide-trapped charges, respectively. From these equations, the surface voltage depends on the insulator capacitance. The dielectric constant of the insulator is varied by gas adsorption for this layer and the capacitance C_i is change. Therefore, the surface voltage is influenced by gas adsorption for the insulator layer. This surface voltage change

can be measured by photocurrent.

3. Results and Discussions

3.1 Film Structure

Figure 3 and Fig. 4 show the X-ray diffraction (Material Analysis and Characterization Science Co., Ltd.: XRD, M03XHF22) pattern and the transmission electron micrograph (HITACHI, Ltd.: TEM, HF-2000) image of self ordered hexagonal and cubic structure film after calcination, respectively. In Fig. 3, The XRD patterns and TEM images indicate the ordered hexagonal pore structure in the self-ordered hexagonal structure film. The film has a highly oriented hexagonal structure and the pore channels are parallel to the substrate surface [17], [18]. Therefore, the self-ordered hexagonal structure film is estimated as a one-dimensional hexagonal (1DH) structure. In Fig. 4, although it is difficult to infer exactly the structure in the self-ordered cubic film structure, the pores are in a three-dimensional cubic structure according to the TEM image. Also, from the powder

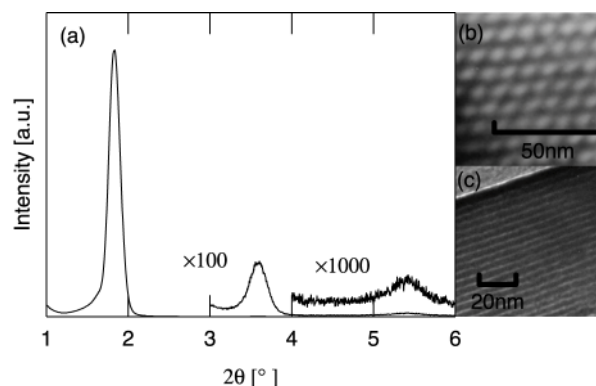


Fig. 3 (a) The XRD pattern of self-ordered hexagonal film. (b) The TEM image of SBA-15 powder, which is synthesized by P123 as the structure directing agent. The image exhibits a hexagonal honeycomb structure. (c) The TEM image of self-ordered hexagonal film.

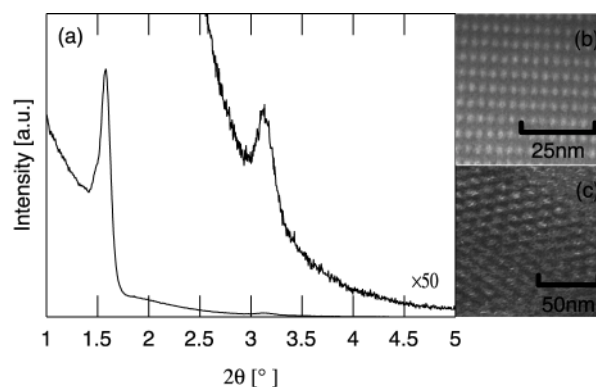


Fig. 4 (a) The XRD pattern of self-ordered cubic film. (b) The TEM image of SBA-16 powder, which is synthesized by F127 as the structure directing agent. The image exhibits the (110) surface of the cubic structure. (c) The TEM image of self-ordered cubic film.

results, the SBA-16 powder has a cubic mesostructure as shown in Fig. 4(b). This SBA-16 powder and film use the same triblock copolymer F127 ($\text{EO}_{100}\text{EO}_{65}\text{EO}_{100}$) as the structure directing agent. Therefore, the self-ordered cubic structure film has a cubic structure with bi-continuous mesopore.

3.2 SPV Character

Figure 5 and Fig. 6 show the photocurrent and the phase property dependence on the bias voltage in SPV-hex and SPV-cub, respectively. These properties are due to the change of band structure and capacitor in the semiconductor/MIS interface layer from the inversion picture to the depletion picture described the above explanation. In addition, the bias

shifts of these properties are belong to standard air exposure condition (O_2 : 20%, N_2 : 80%; 100 sccm) and NO exposure condition (100 ppm; 100 sccm) at room temperature.

The bias shift of the photocurrent and the phase property were observed in each SPV device from air exposure to the 100 ppm NO gas exposure condition. They were estimated as 28 mV and 99 mV shift at 400 nA in the photocurrent property of SPV-hex and SPV-cub, respectively. So, the Bias voltage shift of SPV-cub is about 4 times more than that of SPV-hex.

The bias shift resulted from the change of the dielectric constant and the charge in the insulator layer by physical adsorption and chemical interaction between the detected gases and the gas sensitive film. The bias shift at the flat

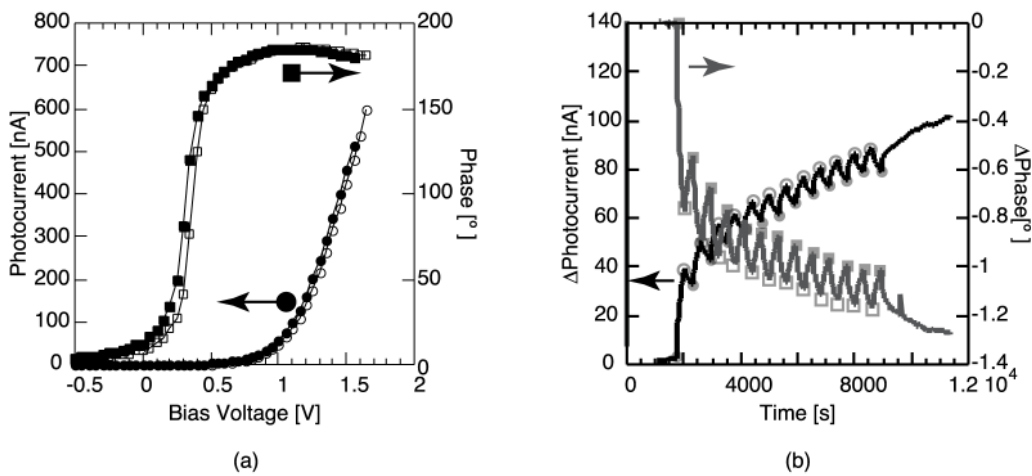


Fig. 5 (a) Bias voltage – photocurrent curve (circle) and bias voltage – phase curve (square) characteristics of SPV-hex. Closed and open points mean the NO gas exposure and the standard air exposure, respectively. (b) The photocurrent (solid line) and the phase (dotted line) response of SPV-hex, where bias voltage is fixed at 1.25 V. Closed and open points mean turning on the NO gas exposure and the standard air exposure, respectively.

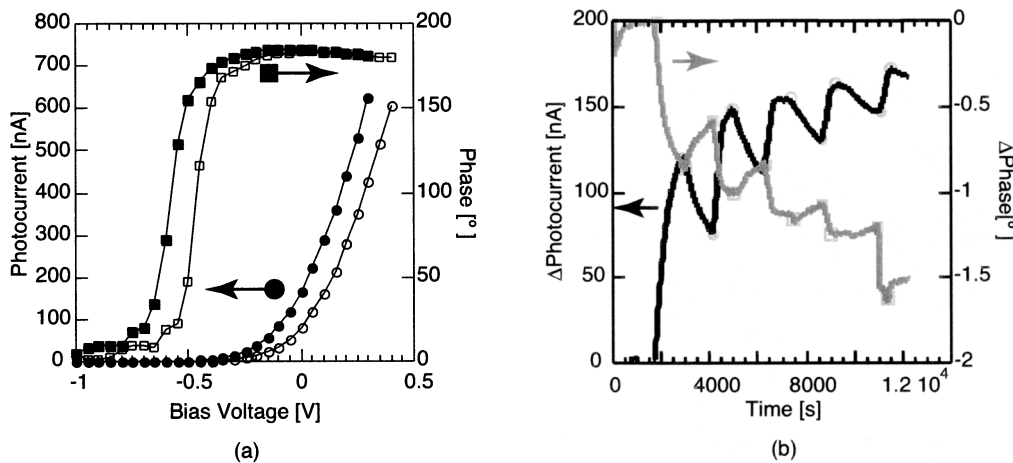


Fig. 6 (a) Bias voltage – photocurrent curve (circle) and bias voltage – phase curve (square) characteristics of SPV-cub. Closed and open points mean the NO gas exposure and the standard air exposure, respectively. (b) The photocurrent (solid line) and the phase (dotted line) response of SPV-cub, where bias voltage is fixed at 0.25 V. Closed and open points mean turning on the NO gas exposure and the standard air exposure, respectively.

band, which is defined as $\phi_s = 0$, is described below equation.

$$\begin{aligned} \Delta V_B &= \frac{Q_{0AD}}{C_{iAD}} - \frac{Q_0}{C_i} = \frac{Q_0 + \Delta Q_0}{\epsilon_i + \Delta \epsilon_i} d - \frac{Q_0}{\epsilon_i} d \\ &= \frac{\epsilon_i \Delta Q_0 - \Delta \epsilon_i Q_0}{(\epsilon_i + \Delta \epsilon_i)} \cdot \frac{d}{\epsilon_i} \end{aligned} \quad (5)$$

where ΔQ_0 , C_{iAD} and $\Delta \epsilon_i$ are the charge density variation, the variation in capacitance and dielectric constant, respectively. In the case of physical adsorption, $\Delta Q_0 = 0$.

The bias shift difference between SPV-hex and SPV-cub depends on the change of dielectric constant $\Delta \epsilon_i$, which directly belongs to the amount of gas adsorption in mesoporous film. Therefore, the difference exhibits the structure dependent gas accessibility to the mesopore. In the case of SPV-hex, which has a 1DH mesostructure, the pore channels align and parallel onto the substrate surface as shown in Fig. 7(a). The gas should gain access from the side and not at the top of the mesoporous film, as it is difficult for the gas to gain access and be adsorbed inside the mesopore. Therefore, SPV-hex exhibits a slightly bias shift. On the other hand, in the case of SPV-cub, the pore channels connect with each other in three dimensions as shown in Fig. 7(b). The gas could

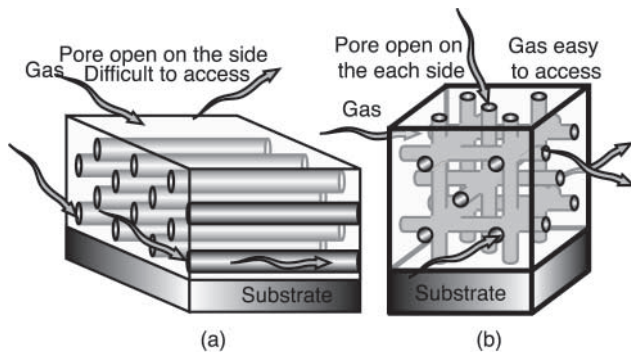


Fig. 7 The image of gas accessibility between one-dimensional hexagonal mesoporous material (a) and cubic mesoporous material (b).

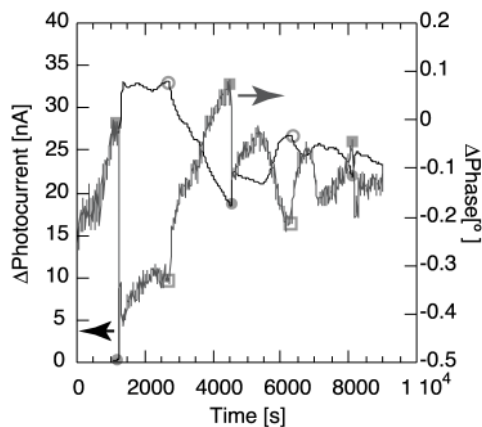


Fig. 8 The photocurrent (solid line) and the phase (dotted line) response of SPV-non, where bias voltage is fixed at 1.20 V. Closed and open points mean turning on the NO gas exposure and the standard air exposure, respectively.

gain access to the film from both the top and the side of the mesoporous insulator layer. Consequently, SPV-cub is better than SPV-hex for gas accessibility. These sensing results are in respect of the mesostructure differences.

Figure 5(b), Fig. 6(b) and Fig. 8 show the response property in cyclic air exposure and the 100 ppm NO exposure condition in SPV-hex, SPV-cub and simple SPV system without self-ordered mesoporous silicate film (SPV-non) respectively.

The results of recoverable response are accomplished at the bias voltage of 1.25 V, 0.25 V and 1.20 V for SPV-hex, SPV-cub and SPV-non, respectively. In the SPV-non sample, the NO gas is adsorbed immediately and the current is changed for the first NO gas turning on step. However, after the first gas adsorption step, the current exhibits a lack of recoverability property.

On the other hand, in the SPV-hex and SPV-cub sample, the currents are increased and decreased by the 100 ppm NO gas exposure and the standard air exposure cycle. The results of the gas exposure cycle for SPV-hex and SPV-cub are different from that for SPV-non. The difference between these sample structures was only the introduction of the self-ordered mesoporous film as an insulator layer. Therefore, these results are caused by the self-ordered mesoporous silicate insulator layer. Consequently, considering above bias shift properties, SPV-cub exhibits good sensitivity for NO gas exposure according to the adsorption capacity of the mesoporous silicate insulator layer. From these results, SPV-cub material exhibits a good potential as an NO gas sensor, which is reflected in the property of the mesoporous silicate.

4. Conclusions

Self-ordered hexagonal and cubic structure mesoporous silicate film combined SPV type gas sensors (SPV-hex and SPV-cub) have been successfully fabricated. These sensors have sensitivity for NO gas (100 ppm and 100 sccm) and also exhibit different sensing performance dependence on the gas accessibility of the mesostructure. In the case of SPV-hex with self-ordered 1DH mesostructure film, there is poor gas accessibility to the mesopore, because the pore is only opened on the side of film due to its highly ordered structure. In the case of SPV-cub, which has a self-ordered cubic mesostructure film, the gas could be accessed on both the side and top of the film due to its bi-continuous three-dimensional pore structure. Consequently, self-ordered cubic structure mesoporous silicate film is more suitable for the SPV type gas sensors. Furthermore, comparing simple SPV-device SPV-non, both SPV-hex and SPV-cub exhibit good gas exposure response properties. Therefore, the self-ordered mesoporous silicate films especially cubic mesoporous silicate film improves the sensing property of the SPV gas sensor and are effective material for the SPV gas sensor application. Here, we could exhibit great possibilities of the SPV device with mesoporous materials. However, these kinds of SPV device is not so good in response and recovery time, which might be due to the device structure and high surface porous structure of sensing

films. The high sensitivity and selectivity of SPV-cub is progressing by improving the pore size, structure and modifying the inner surface of the self-ordered mesoporous film.

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References

- [1] W. Zhang, H. Uchida, T. Katsube, T. Nakatsubo, and Y. Nishioka, "A novel semiconductor NO gas sensor operating at room temperature," *Sensors and Actuators B*, vol.49, pp.58-62, 1998.
- [2] N. Miura, S. Yao, Y. Shimizu, and N. Yamazoe, "Development of high-performance solid-electrolyte sensors for NO and NO₂," *Sensors and Actuators B*, vol.13-14, pp.387-390, 1993.
- [3] M.J. Tierney, H.O.L. Kim, M. Madou, and T. Otagawa, "Microelectrochemical sensor for nitrogen oxides," *Sensors and Actuators B*, vol.13-14, pp.408-411, 1993.
- [4] M. Akiyama, Z. Zhang, J. Tamaki, N. Miura, N. Yamazoe, and T. Harada, "Tungsten oxide-based semiconductor sensor for detection of nitrogen oxides in combustion exhaust," *Sensors and Actuators B*, vol.13-14, pp.619-620, 1993.
- [5] G. Sberveglieri, L. Depero, S. Groppelli, and P. Nelli, "WO₃ sputtered thin films for NO_x monitoring," *Sensors and Actuators B*, vol.26-27, pp.89-92, 1995.
- [6] C. Cantalini, M. Pelino, H.T. Sun, M. Faccio, S. Santucci, L. Lozzi, and M. Passacantando, "Cross sensitivity and stability of NO₂ sensors from WO₃ thin film," *Sensors and Actuators B*, vol.35-36, pp.112-118, 1996.
- [7] L.E. Depero, M. Ferroni, V. Guidi, G. Marca, G. Martinelli, P. Nelli, L. Sangaletti, and G. Sberveglieri, "Preparation and micro-structural characterization of nanosized thin film of TiO₂-WO₃ as a novel material with high sensitivity towards NO₂," *Sensors and Actuators B*, vol.35-36, pp.381-383, 1996.
- [8] L. Boarino, C. Baratto, F. Geobaldo, G. Amato, E. Comini, A.M. Rossi, G. Faglia, G. Lérondel, and G. Sberveglieri, "NO₂ monitoring at room temperature by a porous silicon gas," *Sensors and Actuators B*, vol.69-70, pp.210-214, 2000.
- [9] D.K. Schroder, "Surface voltage and surface photovoltage: History, theory and applications," *Meas. Sci. Technol.*, vol.12, pp.R16-R31, 2001.
- [10] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J.L. Schlenker, "A new family of mesoporous molecular sieves prepared with liquid crystal templates," *J. Am. Chem. Soc.*, vol.114, no.27, pp.10834-10843, 1992.
- [11] X.S. Zhao, G.Q. (Max) Lu, and G.J. Millar, "Advances in mesoporous molecular sieve MCM-41," *Ind. Eng. Chem. Res.*, vol.35, pp.2075-2090, 1996.
- [12] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, and G.D. Stucky, "Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores," *Science*, vol.279, pp.548-552, 1998.
- [13] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, and G.D. Stucky, "Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures," *J. Am. Chem. Soc.*, vol.120, no.24, pp.6024-6036, 1998.
- [14] K.S.W. Sing, "The use of gas adsorption for the characterization of porous solids," *Colloids and Surfaces*, vol.38, pp.113-124, 1989.

- [15] M. Ogawa, "Formation of novel oriented transparent films of layered silica-surfactant nanocomposites," *J. Am. Chem. Soc.*, vol.116, no.17, pp.7941-7942, 1994.
- [16] D. Zhao, P. Yang, N. Melosh, J. Feng, B.F. Chmelka, and G.D. Stucky, "Continuous mesoporous silica films with highly ordered large pore structures," *Adv. Mater.*, vol.10, no.16, pp.1380-1385, 1998.
- [17] T. Yamada, K. Asai, A. Endo, H.S. Zhou, and I. Honma, "Size control of oriented hexagonal mesoporous silicate thin film prepared by triblock copolymer templates," *J. Mater. Sci. Lett.*, vol.19, pp.2167-2169, 2000.
- [18] Y. Lu, R. Ganguli, C.A. Drewien, M.T. Anderson, C.J. Brinker, W. Gong, Y. Guo, H. Soyez, B. Dunn, M.H. Huang, and J.I. Zink, "Continuous formation of supported cubic and hexagonal mesoporous films by sol-gel dip-coating," *Nature*, vol.389, pp.364-368, 1997.



Takeo Yamada received B.Sc. and M.E. degrees in 1995 and 1997 from Chuo University and The University of Tokyo, respectively. In 1997, he joined ASAHI GLASS company. He has been studying at National Institute of Advanced Industrial Science and Technology (AIST) as a Ph. D. candidate of the Department of Quantum Engineering and Systems Science, Graduate School of Engineering, The University of Tokyo since 1998. His research interests are the self-assembled mesoporous materials and their applications.



Hao-shen Zhou received his B.Sc. in Semiconductor Physics in 1985 from Nanjing University, M.S. degree in 1988 from Nanjing Institute of Electronics, China, and Ph.D. degree in 1994 in Chemical Engineering from University of Tokyo. From 1994-1997 he hold a Post Doctor Fellowship of Basic Science Researcher in RIKEN. Now, he is a senior researcher in National Institute of Advanced Industrial Science and Technology (AIST).



Hidekazu Uchida was born on 19 May 1965. He received the B.E., M.E., and Dr.E. degrees from Saitama University, Japan, in 1988, 1990, and 1997, respectively. He is an associate professor at the university. His current research interests are in bio-affinity sensors, gas sensors and a signal processing of chemical sensors. He is a member of The Institute of Electrical Engineers of Japan and The Japan Society of Applied Physics.



Masato Tomita received B.E., M.E. and Dr. E. degrees from Osaka University, Osaka, Japan in 1979, 1981, and 1985, respectively. He joined Nippon Telegraph and Telephone Corporation (NTT) labs, Tokyo, Japan, in 1987 and moved to Corning Technical Center, Shizuoka, Japan in 2001. His research interests have been micro-analysis using TEM and the applications to nano-structured materials.



Yuko Ueno received B.Sc. and M.Sc. degrees from The University of Tokyo in 1995 and 1997, respectively. In 1997, she joined NTT Integrated Information & Energy Systems Labs, and joined NTT Lifestyle and Environmental Technology Labs in 1999. She involved in development of a microfluidic device for environmental monitoring and spectroscopic analysis on materials that are applied to the device.



Keisuke Asai is an associate professor of Quantum Engineering and Systems Science at The University of Tokyo (UT). He graduated from UT in 1986 with a B. Eng. in Applied Physics. He worked as a research engineer at Sony Research Center from 1986 through 1987. In 1991, he earned a M. Eng. from UT and joined the UT faculty in the Department of Quantum Engineering and Systems Science. His Ph. D. degree in Nuclear Engineering was awarded in 1996 by UT under

the direction of Professor Kenkichi Ishigure. Since joining the faculty, he has conducted research in the areas of applied radiation physics with a particular objective of developing new functional materials. His main interests lie currently in fabrication and characterization of quantum confinement structures.



Itaru Honma received B.E. degree in 1984 from department of materials science, University of Tokyo. In 1985, He became Research Assistant of Faculty of Engineering, University of Tokyo, and 1991, Assistant professor at University of Tokyo. In 1995, He joint Electrotechnical Laboratory, AIST and now he is a group leader of energy materials group at enegy electronics institute, National Institute of Advanced Industrial Science and Technology (AIST). His research area is nanomaterials for next generation energy devices.



Teruaki Katsube received his B.S. degree in electrical engineering in 1965 from Nagoya Institute of Technology, and his M.S.(electronic engineering) and Ph.D. degrees in 1971 and 1974, respectively, from University of Tokyo. From 1980 to 1981 he held a Post-Doctoral Fellowship at the University of Pennsylvania. He is currently a professor at the Department of Information and Computer Sciences, Saitama University. His

research activities cover semiconductor surface physics, microelectronic process technology, semiconductor chemical sensors and environmental and medical sensing systems.