Particle Size Distribution of SnO₂ Nano-Particles Synthesized by Pulsed Wire Discharge

Yoshiaki KINEMUCHI, Kimiyasu SATO, Koji WATARI, Chuhyun CHO,* Keiichi MURAI,*
Hisayuki SUEMATSU,* Weihua JIANG* and Kiyoshi YATSUI*

*Ceramics Research Institute, National Institute of Advanced Industrial Science and Technology,
2266-98, Anagahora, Shimo-shidami, Moriyama-ku, Nagoya-shi 463-8560*

**Extreme Energy-Density Research Institute, Nagaoka University of Technology,
1603-1, Kamitomioka-machi, Nagaoka-shi, Niigata 940-2188*

パルス細線放電法による SnO₂ ナノ粒子の粒径分布

杵鞭義明・佐藤公泰・渡利広司・曹 柱鉉*・村井啓一*・末松久幸*・江 偉華*・八井 浄*

産業技術総合研究所セラミックス部門, 463-8560 名古屋市守山区下志段味穴ヶ洞 2266-98

*長岡技術科学大学極限エネルギー密度工学研究センター, 940-2188 長岡市上富岡町 1603-1

The variation in particle size distribution of SnO₂ nano-particles by the pulsed wire discharge (PWD) process has been clarified. Special attention has been paid for the influence of both synthesis conditions of ambient pressure and charging voltage on the distribution. The geometric standard deviation (σ_g) and the count mean diameter (d) were clearly influenced by these conditions. This can be summarized by means of a parameter being proportional to the plasma expansion volume. It was found that σ_g and d monotonically decreased with increasing this parameter. This tendency can be explained by the reported results of numerical simulations in which both coagulation and chemical reaction in the free molecule regime are taken into account, indicating that a relatively slow reaction rate compared to the coagulation rate broadens the particle size distribution during PWD process.

[Received November 12, 2003; Accepted April 27, 2004]

Key-words : Nano particles, Wire discharge, Tin oxide, Particle size distribution

1. Introduction

The synthesis of nano-particles with controlled particle size attracts interests of not only scientists but also engineers. Reduction of energy consumption and production rate in the process is also important from the industrial standpoint.

So far, solid nano-particles have been prepared in gas phase¹⁾ or liquid phase.²⁾ Most synthesis methods for nano-particles in the gas phase are based on homogeneous nucleation in the gas phase and subsequent condensation and coagulation. In liquid-based methods, precipitation reactions can yield nano-particles, and matrices such as micelles, gels or polymers have often been used to limit the particle size to which crystallites can grow.

It has been pointed out that gas-phase processes may in some cases be better than liquid-phase methods due to their following inherent advantages: pure process, a potential to create complex chemical structures, easy process control for adjusting material properties, and mostly continuous processes, giving better quality control of products.¹⁾ Meanwhile, lowering energy consumption, increasing production rate and reducing equipment cost are challenging issues in gas-phase processes.

Most of the energy used in gas-phase synthesis is consumed in raising the energy state of atoms, i.e. high temperature. The energy conversion efficiency can be increased by decreasing heat dissipation from the materials. One method for achieving this condition is to heat materials instantaneously, that is, to supply an intense pulsed current directly to the materials.

When the energy supplied by the pulsed current is sufficient, vaporization of the materials occurs, as seen in the exploding wire phenomenon.³⁾ The exploding wire phenomenon was adapted to produce nano-particles of a

variety of materials: oxides,⁴⁾⁻¹⁰⁾ nitrides,^{7),11)-14)} arsenide,¹⁵⁾ and metals.^{4),5),7)} This process is called pulsed wire-discharge (PWD)^{7)-10),12)-14)} or electrical explosion of wire (EEW).^{5),6),11)} For synthesis of AlN nano particles, by PWD, high energy efficiencies of 40–200 g/kWh,^{7),14)} and high production rates of the order of 1 kg/h have been demonstrated.⁵⁾

Control of particle size of the particles synthesized by PWD was also attempted by adjusting input energy,⁶⁾ wire diameter⁶⁾ or ambient gas pressure.^{7),8)} As a result, the average particle size could be controlled within the range of 20 to 100 nm. Not only the control of average particle size but also the elimination of sub-micrometer sized particles, which were frequently observed in the present process, became possible by the optimization of processing conditions.^{13),14)} The particle size distribution has been found to obey a log-normal distribution with a geometric standard deviation of 1.2–1.6.^{5),10),14)}

These results indicate that PWD process is advantageous for the synthesis of nano-particles with a narrow size distribution when a homogeneous vapor is formed as a result of the uniform heating of a wire, proceeding to quenching of the vapor by the ambient gas. However, the relation between the processing conditions and the particle size distribution has not been clarified. Previous work has indicated that charging voltage was the most influential factor in eliminating submicron particles,^{13),14)} indicating that the heating process is strongly influenced by this factor. Another experimental fact, revealed by high-speed photography, was that plasma expansion volume was increased with decreasing the ambient gas pressure.⁸⁾ After the expansion, the plasma was cooled by the ambient gas and coagulated in solid particles. Thus, the pressure of ambient gas can influence the coagulation process, which eventually affects the particle size distribution. The

Fig. 1. Experimental setup for pulsed wire discharge.

purpose of the present paper was, therefore, to elucidate the dependence of particle size distribution on charging voltage and ambient gas pressure.

2. Experiment

The experimental setup for PWD is shown in **Fig. 1**. The basic discharge system consists of a high voltage power supply, a capacitor and a gap switch. A wire is placed in a chamber filled with ambient gas. The capacitor is discharged through a wire by closing the gap switch, generating a pulsed high current in the wire. The wire is melted, evaporated and ionized by the energy deposition by Joule's heating. The vaporized wire material collides and reacts with the gas molecules, forming compounds that will cool and condense into nano-particles through clusters.

Tin oxide, a well known semiconductive material used in gas sensors, was synthesized in the present study. Metallic tin wire (diameter 0.25 mm, length 22 mm; purity 99.9%) was subjected to discharge in an oxygen atmosphere. To vaporize the wire, energy of at least 371 kJ/mol^[6] was required, i.e., 24.6 J in the present experiment. A capacitance of 20 μ F was charged to 2.2, 4.2 and 6 kV, resulting in charging energies of 48.4, 176.4 and 360 J, respectively. It should be noted that some of the charging energy was dissipated during discharge, due to the resistance of circuit components such as the gap switch. The energy contributing to the wire discharge was monitored by measuring the current and the voltage between both ends of the wire.

The circuit parameters of the PWD system were evaluated from the current waveform in the short circuit, in which electrodes were connected by a thick Cu bar. From this result, it was found that the circuit inductance and resistance were 0.7 μ H and 30 m Ω , respectively.

Prior to the discharge, the chamber was evacuated by an oil rotary pump to a vacuum of less than 10 Pa. Oxygen gas was then fed into the chamber to a pressure of 6.7, 26.7 or 100 kPa.

After 8 or 9 discharge shots, the aerosol nano-particles was filtered using a membrane (pore size 0.1 μ m, Millipore) by pumping out the gas from the chamber. The collected particles were used for subsequent analysis.

The compounds were analyzed by X-ray diffraction (XRD; Rigaku RINT 2000, rotating anode, 50 kV, 200 mA, Cu target, parallel beam method using graded d-spacing parabolic multilayer). Based on the diffraction data, average crystallite size was estimated from full width at half maximum of XRD peaks using Scheller's equation. Further lattice constants were estimated from clear SnO₂ peaks using the least squares method.

The morphology of the synthesized nano-particles was observed with a transmission electron microscope (TEM; JEOL JEM 2010, accelerating voltage 200 kV) and the particle size distribution was analyzed based on their bright field images. Particle size was evaluated from the area of primary particles. Based on the area, projected area equivalent diameter, i.e. Heywood diameter, was calculated and adopted to the analysis of particle size distribution. The number of analyzed particles for each synthesized condition was 400–800 particles.

3. Results and discussion

3.1 Wire discharge

A typical wire discharge phenomenon is shown in **Fig. 2**. On triggering the gap switch ($t = 0 \mu$ s in **Fig. 2**), an intense current (I) flows through the wire, which leads to an increase in potential difference (V) between the ends of the wire (i.e., the voltage dropped in the wire) due to the wire's intrinsic resistance. Several microseconds after the trigger, the voltage rapidly increases due to the back electromotive force caused by wire vaporization. Afterwards, the current waveform becomes damped oscillation. During this period, current passed through the plasma. Finally, most of the charging energy is consumed by the resistant components of the circuit, resulting in the current attenuation. The energy consumed by wire discharge can be calculated based on the current and voltage measured during the discharge. The time evolution of energy consumption is also plotted in **Fig. 2**. Although PWD process is very high energy-efficient, as mentioned in the introduction, some energy is dissipated via other resistive components in the circuit. Since the discharge condition is affected by gas pressure, the total energy consumed by the wire discharge (E_t) varies as shown in **Fig. 3**. At $V_{ch} = 2$ kV,

Fig. 2. Typical discharge progress of pulsed wire discharge. Ordinates indicate electric potential difference between the ends of the wire (V), discharge current (I) and energy consumed by wire discharge (E).

Fig. 3. Total energy consumed by wire discharge (E_t) as a function of charging voltage (V_{ch}) under different O_2 pressures.

E_t is almost unchanged with increasing O_2 pressure. On the other hand, at $V_{ch}=4$ kV, E_t increases with increasing O_2 pressure. This O_2 pressure dependence of E_t is more evident at higher charging voltage ($V_{ch}=6$ kV).

3.2 Crystal properties

Patterns of XRD are summarized in **Figs. 4** and **5**, and correspond to that of SnO_2 with a tetragonal rutile structure. In addition, peaks originating in Sn were observed for powders synthesized at 6.7 kPa ($2\theta=30.6, 32.0, 43.8$ and 44.9°). The lattice constant and the crystallite size of the SnO_2 powders are listed in **Table 1**. Most of the powders show smaller lattice constants than that of standard material (PDF #41-1445). Hydrothermally-derived nano- SnO_2 powder also shows a large shift towards smaller size from the standard peaks, which is explained by the presence of vacancies.¹⁷⁾ Taking in consideration of oxygen pressure during synthesis, inclusion of oxygen vacancy is a plausible reason for the decrease in lattice constant.

Crystallite size of the particles ranged from 12 to 36 nm. A relationship between the size and synthesis conditions is seen: lower O_2 pressure and higher charging voltage result in smaller size. Similar relationship had been obtained in synthesis of Al_2O_3 particles by PWD.⁸⁾ This result can be explained in

Fig. 4. XRD patterns of nano-particles synthesized under different O_2 pressures. Arrows indicate peaks originated from metal tin.

Fig. 5. XRD patterns of nano-particles synthesized under different charging voltages.

terms of plasma expansion. Just after wire evaporation, plasma begins a rapid expansion towards the ambient gas due to the enormous difference in temperature and pressure between the plasma and the ambient gas. The expanded plasma particles are gradually cooled during the process of collision with ambient gas molecules. Finally, the plasma loses its expansive driving force. Hence, a low ambient pressure allows a large expansion volume. This leads to low number concentration of the substance during particle growth, resulting in small nano-particles. Increased charging voltage leads to increased expansion volume, which may lead to similar effects on crystallite size.

3.3 Nano-particle morphology and size distribution

The typical morphology of SnO_2 particles is shown in **Fig. 6**. Particle morphology of equiaxial shape with a flat surface is most commonly observed. The flat surface is thought to be a habit which becomes evident in large particles. A similar morphology was reported for the nano-particles

Table 1. Crystallographic Information Obtained from X-ray Diffraction

O ₂ pressure [kPa]		charging voltage [kV]		
		2.2	4.2	6.0
6.7	phase	Sn & SnO ₂	Sn & SnO ₂	Sn & SnO ₂
	crystallite size [nm]	15.8 [Sn: 1100]*	13.7 [Sn: 900]	12.4 [Sn: 900]
	a [Å]**	4.735 (1)***	4.7364 (8)	4.736 (1)
	c [Å]**	3.182 (2)	3.1842 (8)	3.186 (1)
26.7	phase	SnO ₂	SnO ₂	SnO ₂
	crystallite size [nm]	22.9	20.2	19.1
	a [Å]	4.7364 (5)	4.7356 (5)	4.7359 (4)
	c [Å]	3.1850 (6)	3.1848 (6)	3.1842 (6)
100	phase	SnO ₂	SnO ₂	SnO ₂
	crystallite size [nm]	35.9	29.5	26.4
	a [Å]	4.7369 (2)	4.7367 (3)	4.7385 (3)
	c [Å]	3.1852 (3)	3.1853 (4)	3.1864 (4)

*) Crystallite size estimated from the broadening of peaks originated in metal Sn.

**) a: 4.738, c: 3.187 [PDF #41-1445]

***) The values are considered reliable to $\pm$ the figure given in parentheses being applicable to the last digit.

Fig. 6. Typical morphology of a synthesized nano-particle. This nano-particle was synthesized under a charging voltage of 4.2 kV and pressure of 26.7 kPa.

derived by precipitation, in which the flat surface becomes more marked with increasing post heat-treatment temperature.¹⁸⁾ It was also reported that defects in liquid-source derived nano-particles are reduced by heat-treatment,^{17),18)} suggesting the change in morphology of these powders is related in some way to crystallinity. The particles synthesized by PWD seem to possess as good crystallinity as same as that of heat-treated nano-particles prepared by wet process.

An example of particle size distribution is shown in Fig. 7. The ordinate indicates frequency, which is normalized as (number of particles)/(total number of particles). The distribution has a long tail toward larger sizes, a characteristic frequently observed in gas phase-derived powders. The data

Fig. 7. Typical particle size distribution. Solid line indicates the curve fitting result using log-normal distribution function.

was fitted to a log-normal distribution, which is shown as a solid line in Fig. 7. Log-normal probability plots are also shown in Figs. 8 and 9. The log-normal distribution is a function in which the Gaussian form is preserved when frequency is plotted against logarithmic scaled particle size. This function is expected to appear for gas-phase derived particles synthesized in the free-molecular regime, which is predicted by a numerical calculation based on a discrete model where chemical reactions and aerosol coagulation are taken in account without assuming any particle size distribution function.¹⁹⁾ It can be seen that the distribution of PWD-synthesized particles follows a log-normal distribution. In a later section, particle size distribution will be discussed with a geometric standard deviation (σ_g) derived from curve fitting to log-normal distribution.

3.4 Particle size distribution

The influence of synthesizing conditions of O₂ pressure and charging voltage on particle size distribution is shown in

Fig. 8. Log-normal probability plots for nano particles synthesized at different charging voltage.

Fig. 11. Variation of particle size distribution at different charging voltages.

Fig. 9. Log-normal probability plots for nano particles synthesized at different oxygen pressure.

Fig. 12. Geometric standard deviation (σ_g) and count mean diameter (d) as a function of O_2 pressure.

Fig. 10. Variation of particle size distribution at different ambient pressures.

Fig. 13. Geometric standard deviation (σ_g) and count mean diameter (d) as a function of charging voltage (V_{ch}).

Figs. 10 and 11. The increase in O_2 pressure tends to broaden the size distribution, as shown in Fig. 10. A low charging voltage also spreads the distribution, as shown in Fig. 11. These geometric standard deviations (σ_g) are summarized as a function of O_2 pressure (P) or charging voltage (V_{ch}) as shown in **Figs. 12 and 13**, respectively. Count mean diameter

(d) is also plotted in the same figures. The geometric standard deviation ranges from 1.4 to 1.8 depending on the synthesizing conditions. The diameter is also influenced by the conditions whose tendency agrees with that of crystallite size, as qualitatively estimated by XRD. A difference between count mean diameter and crystallite size is observed for the

nano-particles synthesized at 4.2 kV under 100 kPa. As shown in Fig. 9, a relatively large amount of huge particles are included in this powder as compared with an expected amount from log-normal distribution. Because the intensity of X-ray diffraction proportionally increases with the fourth power of crystallite size,²⁰⁾ observed crystallite size is strongly influenced by such large particles. This leads the relatively large difference between count mean diameter and crystallite size.

The effect of pressure and charging voltage can be summarized in one parameter in terms of plasma expansion. The volume of plasma expansion is thought to be proportional to the charging energy, if the influence of electromagnetic force is neglected. This assumption is reasonable for the terminal period of the expansion, where charged electric energy is almost completely converted to thermal energy. Based on the above consideration, the work of expansion should show the following relationship,

$$PV_{\text{exp}} \propto \frac{1}{2} CV_{\text{ch}}^2 \quad (1)$$

Here, P is the ambient pressure, V_{exp} is volume of expansion, and C is capacitance. We believe the volume of expansion, which is directly related to the initial number concentration of molecules, to be an accurate index of the synthesizing conditions. In practice, due to losses, some of the charging energy does not contribute to the wire discharge. For an accurate description, it is preferable to adapt the energy consumed by wire discharge (E_t , Fig. 3) to the right-hand side of Eq. (1): $V_{\text{exp}} \propto E_t P^{-1}$. Using the parameter of $E_t P^{-1}$, σ_g and d are summarized as shown in Fig. 14. Both σ_g and d decrease monotonically with increasing $E_t P^{-1}$.

The above dependence of size characteristics on synthesizing conditions can be explained as a natural characteristic of gas phase synthesis in a free molecule regime, where the kinetics of particles approximate those of large molecules. This assumption holds if the particle size is much smaller than the mean free path of the gas. In particular, this assumption holds best for nano-particles manufactured at high temperatures ($>1000^\circ\text{C}$) and low pressures ($<5 \text{ atm}$),¹⁹⁾ which corresponds to Knudsen number more than 10. While coagulation in this regime is normally solved by numerical simulation, an approximate solution in analytical form has been derived.²¹⁾ This analytical solution gives reasonable agreement with numerical simulation within practical conditions. According to the analysis, the progress of σ_g and the geometric mean particle volume (v_g) are expressed as follows.

$$\ln^2 \sigma_g = \frac{2}{15} \ln \left[2 + \frac{\exp \left(\frac{15}{2} Z_0 \right) - 2}{1 + \frac{5}{8} H \bar{t}} \right] \quad (2)$$

and

$$\frac{v_g}{v_{g0}} = \frac{\exp \left(\frac{9}{2} Z_0 \right) \left[1 + \frac{5}{8} H \bar{t} \right]^{6/5}}{\left[2 + \frac{\exp \left(\frac{15}{2} Z_0 \right) - 2}{1 + \frac{5}{8} H \bar{t}} \right]^{3/5}}, \quad (3)$$

where

$$H = \exp \left(\frac{1}{8} Z_0 \right) + 2 \exp \left(\frac{5}{8} Z_0 \right) + \exp \left(\frac{25}{8} Z_0 \right)$$

$$\bar{t} = \text{dimensionless time} = K \tau^{1/2} N_0 t$$

Fig. 14. Geometric standard deviation (σ_g) and count mean diameter (d) as a function of $E_t P^{-1}$. Here, E_t is total energy consumed by wire discharge and P is the O₂ pressure. The parameter of $E_t P^{-1}$ is related to volume of plasma expansion.

Fig. 15. Progress of geometric standard deviation (σ_g) and dimensionless volume of particles (v_g/v_{g0}) simulated for particle growth in a free molecule regime. Coagulation without reaction is denoted as “only coagulation,” as calculated using Eq. (2). The progress of v_g/v_{g0} was obtained using Eq. (3). The curve for “moderate reaction” corresponds to the progress of σ_g in which reaction rate is almost identical to the coagulation rate. In the curve for “slow reaction,” the reaction rate is one-fifth of the coagulation rate. The above curves describing the interplay of reaction and coagulation are taken from the literature.¹⁹⁾

$$K = \left(\frac{6kT}{\rho} \right)^{1/2}$$

$$Z_0 = \ln^2 \sigma_{g0}.$$

Here, v_{g0} is the geometric mean of initial particle volume, r_{g0} is the geometric mean of the particle radius, N_0 is the initial number concentration of particles, t is time, k is the Boltzmann constant, T is temperature, ρ is the particle density, and σ_{g0} is the initial geometric standard deviation. In addition, this coagulation model assumes that the particle size distribution preserves log-normal distribution through the entire process. The progress of σ_g and v_g/v_{g0} is plotted in Fig. 15 for $\sigma_{g0}=1$, i.e., coagulation starting from a uniform monomer. In this case, σ_g increases from its initial value and reaches an asymptotic value of 1.36 with elapse of time. During this progress, the particles grow monotonically. It is

noted that the abscissa of $\bar{t}$ is a function of N_0 , thought to be in inverse proportion to $E_t P^{-1}$. That is, a large $E_t P^{-1}$ corresponds to a short $\bar{t}$. In addition, temperature and time are also influential factors of $\bar{t}$. Since the coagulation has taken place at certain temperature region during cooling, T is thought to be almost identical even though synthesis conditions are different. In terms of time, low gas pressure may reduce coagulation time, because the period with light emission from vapor was shortened under low gas pressure, which was observed by high speed photography for the synthesis of Al_2O_3 nano-particles.²²⁾ To sum up, low pressure leads to decrease in N_0 and t , and high voltage leads to decrease in N_0 .

In the early stage of coagulation, the particle size distribution spreads with simultaneous particle growth. The particle growth in PWD is thought to correspond to this stage, since the PWD process quenches plasma, resulting in a short growth time. However, σ_g never exceeds the asymptotic value in the simple coagulation model, while the observed value ranges from 1.4 to 1.8. The above contradiction may arise from the use of a simple coagulation model in which the reaction rate is not considered. It is reported that evaporation of SnO_2 occurs mainly by the decomposition according to $\text{SnO}_2(\text{s}) = \text{SnO}(\text{g}) + 1/2\text{O}_2(\text{g})$.²³⁾ This reminds us that the reaction between SnO and $1/2\text{O}_2$ affects the growth kinetics of SnO_2 nano-particles. When the reaction rate is taken into account in growth kinetics, the situation becomes more intelligible. Ladgrebe et al. have numerically calculated the coagulation in a free molecule regime with interplay of chemical reactions.¹⁹⁾ Their results are shown in Fig. 15. When the reaction rate is very much faster than the coagulation rate, the kinetics of particle growth are limited by coagulation, leading to the same results as the simple coagulation model. However, with decreasing reaction rate, particle growth begins to be influenced by the rate of reaction, which retards the creation of monomer, resulting in broadening of the size distribution. Once all the substances have reacted, the size distribution approaches the asymptotic value as a result of the coagulation process. Comparing the simulated solution and the experimental facts, the broadening of σ_g in PWD process is concluded to be caused by the slow reaction rate relative to the coagulation rate.

4. Conclusions

Variation in particle size distribution was studied for SnO_2 nano-particles synthesized by PWD. The chief aim of the study was to elucidate the influence of the synthesizing conditions of ambient pressure and charging voltage on the size distribution. Synthesized particles were observed by TEM to analyze their size distribution, and measured by XRD to obtain crystallographic information. The progress of size distribution was discussed based on the reported simulation results, in which the interplay of coagulation and chemical reaction was taken into account during particle growth in the free molecule regime. We conclude the following.

(1) It was found that the particle size distribution of synthesized SnO_2 nano-particles possessed a geometric standard deviation in the range of 1.4–1.7. Furthermore, it was elucidated that the particle size distribution was broader at high ambient gas pressure and low charging voltage, which was ascribed to small expansion of plasma under these conditions. Because the volume is inversely proportional to initial number concentration for coagulation, a small volume leads to a longer time required for particle growth in terms of dimensionless time. Since the PWD process quenches plasma, the growth process might terminate within the period where σ_g approaches the asymptotic value. In this period, σ_g increased,

accompanied by particle growth. Especially for slow chemical reactions, the broadening of the distribution became more apparent, which is thought to be the case with PWD.

(2) The variation in count mean diameter was also dependent on the expansion volume of the plasma. With increasing plasma volume, the diameter linearly decreased. This tendency could be explained in terms of dimensionless time, which was shortened by a low initial number concentration. In addition, the volume was estimated from the wire discharge condition of $E_t P^{-1}$ which accurately explained the characteristics of the particle size distribution.

(3) Synthesized particles had a count mean average diameter of about 20 nm. Importantly, they were well crystallized, and appears with a particle morphology of equiaxial shape with flat surface. Regardless of the sharp peaks in the XRD pattern, a slight peak shift from standard material was found. This peak shift, i.e., a decrease in lattice constant, was evident for nano-particles synthesized at low O_2 pressure, which might be related to the inclusion of defects such as oxygen vacancies.

Acknowledgments The suggestions and experimental support of Dr. Yasumasa Takao and Kenichi Tazoe of the National Institute of Advanced Industrial Science and Technology are gratefully acknowledged.

References

- 1) Kruis, F. E., Fissan, H. and Peled, A., *J. Aerosol Sci.*, Vol. 29, pp. 511–535 (1998).
- 2) Trindade, T., O'Brien, P. and Pickett, N. L., *Chem. Mater.*, Vol. 13, pp. 3843–3858 (2001).
- 3) Chace, W. G., "Exploding Wires," Ed. by Chase, W. G. and Moore, H. K., Plenum, New York (1959) pp. 7–14.
- 4) Karioris, F. G. and Fish, B. R., *J. Colloid Sci.*, Vol. 17, pp. 155–161 (1962).
- 5) Ivanov, V., Kotov, Y. A., Samatov, O. H., Böhme, R., Karow, H. U. and Schumacher, G., *Nanostructured Mater.*, Vol. 6, pp. 287–290 (1995).
- 6) Kotov, Y. A., Azarkevich, E. I., Beketov, I. V., Demina, T. M., Murzakaev, A. M. and Samatov, O. M., *Key Engineering Mater.*, Vol. 132–136, pp. 173–176 (1997).
- 7) Jiang, W. and Yatsui, K., *IEEE Trans. Plasma Sci.*, Vol. 26, pp. 1498–1501 (1998).
- 8) Suzuki, T., Keawchai, K., Jiang, W. and Yatsui, K., *Jpn. J. Appl. Phys.*, Vol. 40, Pt. 1 [2B], pp. 1073–1075 (2001).
- 9) Kinemuchi, Y., Ishizaka, K., Suematsu, H., Jiang, W. and Yatsui, K., *Thin Solid Films*, Vol. 407, pp. 109–113 (2002).
- 10) Kinemuchi, Y., Ikeuchi, T., Suzuki, T., Suematsu, H., Jiang, W. and Yatsui, K., *IEEE Trans. Plasma Sci.*, Vol. 30, pp. 1858–1862 (2002).
- 11) Kotov, Y. A. and Samatov, O. M., *Nanostructured Mater.*, Vol. 12, pp. 119–122 (1999).
- 12) Sangrai, C., Kinemuchi, Y., Suzuki, T., Jiang, W. and Yatsui, K., *Jpn. J. Appl. Phys.*, Vol. 40, Pt. 1 [2B], pp. 1070–1072 (2001).
- 13) Cho, C., Kinemuchi, Y., Suematsu, H., Jiang, W. and Yatsui, K., *Jpn. J. Appl. Phys.*, Vol. 42, Pt. 1 [4A], pp. 1763–1765 (2003).
- 14) Kinemuchi, Y., Murai, K., Sangrai, C., Cho, C., Suematsu, H., Jiang, W. and Yatsui, K., *J. Am. Ceram. Soc.*, Vol. 86, pp. 420–424 (2003).
- 15) Saunders, W. A., Sercel, P. C., Atwater, H. A., Vahala, K. J. and Flagan, R. C., *Appl. Phys. Lett.*, Vol. 60, pp. 950–952 (1992).
- 16) Standard formation enthalpy of gas from "NIST Chemistry Webbook," <http://webbook.nist.gov/chemistry/>. Enthalpy change from room temperature to the boiling point was referred from "Thermochemical properties of inorganic substances," Ed. by Barin, I. and Knacke, O., Springer-Verlag, Berlin

- Heidelberg, New York (1973) pp. 697.
- 17) Yu, K. N., Xiong, Y., Liu, Y. and Xiong, C., *Phys. Rev. B*, Vol. 55, pp. 2666–2671 (1997).
- 18) Diéguez, A., Rodriguez, A. R., Morante, J. R., Weimar, U., Berberich, M. S. and Göpel, W., *Sensors and Actuators B*, Vol. 31, pp. 1–8 (1996).
- 19) Landgrebe, J. D. and Pratsinis, S. E., *Ind. Eng. Chem. Res.*, Vol. 28, pp. 1474–1481 (1989).
- 20) Ida, T., Shimazaki, S., Hibino, H. and Toraya, H., *J. Appl. Crystallogr.*, Vol. 36, Part 5, pp. 1107–1115 (2003).
- 21) Lee, K. W., Curtis, L. A. and Chen, H., *Aerosol Sci. Technol.*, Vol. 12, pp. 457–462 (1990).
- 22) Komson, K., Master Thesis, Nagaoka University of Technology (1999).
- 23) Zimmermann, E., Königs, S. and Neuschütz, D., *Zeitschrift für Physikalische Chemie*, Vol. 209, pp. 271–280 (1999).