Experimental Control of Preparation of Thin Film and Fine Particles by CVD†

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Abstract

The formation of TiO₂ thin film and fine particles by the thermal decomposition of titanium tetraisopropoxide (TTIP) vapor was carried out experimentally using a laminar-flow aerosol reactor (LFA R). TTIP vapor and He gas mixture was introduced into a heated pipe in a laminar flow, and the thin films formed and the particles deposited on the pipe wall were observed using an electron microscope under various supplied concentrations of TTIP vapor, reactor temperatures and operating pressure inside the reactor. It has been found that the generation of fine particles is enhanced at higher concentration of TTIP vapor, higher reaction temperature and higher pressure, but the formation of thin films is more enhanced at lower pressure. The observed trends agreed qualitatively with the simulation results obtained by numerically solving the aerosol dynamic equation where the particle formation was evaluated by a simplified reaction and coagulation model.

Introduction

Recently, fine materials are being studied in various fields for the purpose of utilizing their specific function and improving their functions to an even higher degree. Among them, a great deal of attention is paid to the technology for material formation through the process where materials are generated in a solid phase including thin film, fine particles, etc. from the gas phase, i.e., Chemical Vapor Deposition (CVD). A characteristic feature of CVD is that thin film and fine particles that are high in purity are obtainable relatively easily through continuous operation and that thickness and crystalline state for film and size and concentration for particles can be controlled. Particularly, it is qualitatively evident that a change in the pressure condition greatly affects the formation of film and fine particles in a reactor. However, the mechanisms for a gaseous reaction and formation of film and particles have not been fully elucidated, for it is not easy to examine quantitatively the influence of pressure condition upon the formation of film and particles largely due to the experimental difficulties.

Hence, in this study, at first we investigated experimentally how the formation of film and fine particles depend( I ) on pressure inside a reactor(from atmospheric pressure to reduced pressure),( II ) on temperature of the reactor and (III) on supplied TTIP vapor concentration under various conditions by using an aerosol reactor where thin film and fine particles are obtainable through continuous operation.
particles are formed through thermal decomposition of vaporized titanium tetraisopropoxide, hereafter abbreviated as TTIP, fed into a heated tube in a laminar flow.

Second, since it is thought that thin film formation may be governed by the diffusion phenomena of a monomer and cluster and that fine particle formation may be governed by their coagulation phenomena, a diffusion equation considering the particle formation based on a simplified reaction and coagulation model was numerically calculated as a simultaneous equation with a heat energy equation in a non-isothermal field. Then, the results were compared with the experimental results.

1. Formation of TiO₂ Thin Film and Fine Particles through Thermal Decomposition of TTIP Vapor

In this experiment, the formation of a titanium oxide film and the particles through thermal decomposition of titanium tetraisopropoxide (TTIP) vapor was investigated as a reaction system where thin film and fine particles are generated. According to the following overall thermal decomposition, it is simply considered that TTIP vapor is decomposed into titanium oxide with the simultaneous forming of propylene and water.

\[ \text{Ti}(\text{OC}_3\text{H}_7)_4 \rightarrow \text{TiO}_2 + 4\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \]  

(1)

Here, the rate constant for the overall thermal decomposition is found by determining concentration of the propylene by-product using gas chromatography. According to the experimental results of Kanai et al. and those of Okuyama et al., assuming that the above reaction is a first-order reaction, \( K_A \) is approximated to the following equation.

\[ K_A = 3.960 \times 10^{-10} \exp(-7.046 \times 10^{4}/RT) \]  

(2)

In addition, in this experiment, the TiO₂ formation through a reaction between TTIP vapor and the water by-product is thought negligible since the concentration of TTIP vapor is less than about 0.4%.  

1.1. Apparatus and Method for Experiment

A flow diagram of the experimental apparatus is shown in Figure 1. Passing He gas with mass flow rate \( Q \) determined by mass-flow meter MF which indicates \( Q \) converted into the gas, flow rate at 239K under 1.01 x 10⁵ Pa, it is introduced into an evaporator containing TTIP liquid to be saturated with TTIP vapor and the resulting gas is red into a reactor heated in a furnace. Quantity of generating TTIP vapor, i.e., concentration, can be varied by adjusting the water bath temperature. Temperature of the heating furnace can be controlled with a thermocouple inserted in a reactor tube. Pressure of the reactor tube is regulated by a vacuum pump installed after the reactor and is measured with a vacuum gauge. Furthermore, to avoid condensation of the effluent gas from the evaporator before flowing into the reactor, the connecting tubes are warmed to about 323K with heating tapes.

The reactor tube is a stainless steel pipe having a 0.025m I.D. and a 0.7m length and both of its ends have O-rings sandwiched between flanges in construction to keep the tube airtight. A thin plate of aluminum, 0.02m in width and 0.7m in length, is mounted in the lower part of the reactor as the basal plate. Then, it is taken out after each experiment for observation of film and deposited particles generated on the basal plate through the
Table 1. CVD experimental condition.

| Run | Pressure P [Pa] | Volume flow Q [m³/s] | TTIP concentration C [%] | Furnace temperature T [K] |
|-----|-----------------|-----------------------|--------------------------|---------------------------|
| a   | 1.01 × 10⁵      | 1.67 × 10⁻¹           | 0.1                      | 523                       |
| b   | 1.13 × 10⁵      |                       |                          |                           |
| c   | 1.13 × 10⁵      |                       |                          |                           |
| d   | 1.01 × 10⁵      |                       | 0.025                    | 523                       |
| e   | 1.13 × 10⁵      |                       | 0.4                      |                           |
| f   | 1.13 × 10⁵      |                       |                          |                           |
| g   | 1.01 × 10⁵      |                       | 0.025                    | 523                       |
| h   | 1.13 × 10⁵      |                       | 0.4                      |                           |
| i   | 1.13 × 10⁵      |                       |                          |                           |
| j   | 1.13 × 10⁵      |                       |                          |                           |

*1) This value was calculated from the saturated vapor pressure Pₐ of TTIP vapor shown in the below.

| Temperature [K] | 312 | 323 | 351 |
|----------------|-----|-----|-----|
| Pₐ [Pa]        | 25.3 | 101.3 | 404.0 |

*2) Pₐ of TTIP is referred to the catalog of articles printed by TRI CHEMICAL LABORATORY INC..

reaction. In addition, a filter unit, using a GB100R filter paper supplied by TOYO ROSHI, is fitted closely after the outlet of the reactor to collect particles.

The experimental procedure is as follows. Experiments were carried out under atmospheric or reduced pressure. In both cases, He gas is passed through a by-pass beforehand by switching with the V₁ valve so that He gas alone flows through the reactor tube. Then, the V₁ valve is opened to the side of TTIP evaporator and the TTIP vapor accompanied by He gas is introduced into the reactor tube to be decomposed thermally in the tube, resulting in the generation of titanium oxide. Experimental conditions, i.e., operating conditions of the reactor are shown in Table 1. Particularly under reduced pressure as shown in Table 1, the flow rate of He gas is lowered considering its cubic expansion due to a pressure drop so that TTIP vapor concentration at the tube inlet and the gas residence time in the tube are adjusted similarly to those under atmospheric pressure. Accordingly, in these experiments, the flow rate of He gas is regulated with the mass flow meter so that the gas residence time in the tube is adjusted to 20.6 sec. independently of the pressure.

1.2 Results and Discussion

As shown in Table 1, the experiments were conditioned in the following cases. Pressure inside the reactor is chosen from (I) 1.01 × 10⁵ Pa (= 1 atm), (II) 1.13 × 10⁵ Pa and (III) 1.13 × 10⁶ Pa. The TTIP concentration is chosen from 0.025, 0.1 and 0.4%. The flow rate of the reactant gas is 1.67 × 10⁻⁵ m³/s calculated considering the cubic expansion due to reduced pressure inside the reactor tube as mentioned previously. Set temperature of the reactor tube is chosen from 523, 623 and 723K, where the temperature distribution is in a convex form (see Fig.2).

Running time in each experiment is 2 hr. A standard operating condition selected for the reactor is a combination of 1.01 × 10⁵ Pa for pressure, 0.1% for TTIP vapor concentration, 1.67 × 10⁻⁵ m³/s for the flow rate of reactant gas and 523K for the setting temperature of the reactor. Then, the formation of thin film and fine particles was investigated experimentally.
Fig. 2 Temperature distributions of the reactor

Fig. 3 Schematic representation of CVD experimental results

| Run | Deposition pattern of TiO₂ film and particles on aluminum plate |
|-----|---------------------------------------------------------------|
| (a) | ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ }
Second, in the experiment under the reduced pressure $1.13 \times 10^4 \text{Pa}$, a striped film emitting similar interference fringes to the above mentioned was formed from the point about 0.04m to 0.47m from the inlet as shown in Fig.3(b), while the white fine powder of TiO$_2$ was observed over the whole interval. Figure 5(a) shows a SEM photo of film, the blue part, obtained in the experiment on the aluminum plate. According to this, the film surface is found having similar aspects to those of the experiments under atmospheric pressure(Fig. 4(b)). Figure 5(b) shows the white fine powder of TiO$_2$ deposited at the point 0.47m distance from the inlet in same condition. This powder consist of granular particles almost uniform in size, which is the similar results as the above-mentioned CVD experiment under atmospheric pressure.

The films and particles obtained in the above experiments were observed with a transmission electron microscope(TEM) and results are shown in Figs.4(d), 5(c). These figures indicate that mean diameter of the particles generated under atmospheric pressure and the reduced pressure of $1.13 \times 10^4 \text{Pa}$ is about 0.06$\mu$m and about 0.03$\mu$m, respectively.

Next, the experiment under the reduced pressure of $1.13 \times 10^4 \text{Pa}$ gave a striped film
emitting interference fringes changing from yellow to red over the interval from a point about 0.11m to the point 0.17m from the inlet. The interval of the stripes was found to be wider than of the above-mentioned 1.13×10^4 Pa case and the film emitting blue interference fringes was observed over the interval from a point about 0.17m to 0.51m from the inlet. The film emitting interference fringes changing from red to yellow over the interval from the

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**Fig. 5** EM photographs of TiO₂ film and particles on Aluminum plate by low-pressure CVD (at 1.3×10^4 Pa) { (a), (b): SEM photographs, (c): TEM photograph }

**Fig. 6** EM photographs of TiO₂ on film Aluminum plate by low-pressure CVD (at 1.13×10^4 Pa) { (a): SEM photograph, (b): TEM photograph }
successive point to a point 0.55m from the inlet. **Figure 6** (a) shows a SEM photo. of the film, the blue part, on an aluminum plate in the experiment under the above pressure condition. There are stripes like the above 2 experimental results, while the film surface evidently has no granular unevenness to be smoothed. **Figures 6** (b) shows a TEM photo. of the film cross section, the blue part and indicates in which thickness is about 300nm and that it is formed uniformly without space.

The aforementioned results clarify that by reducing the pressure in the reactor, the film formation becomes more favored that of particles. This is considered because diffusion phenomena of monomer and clusters including dimer, trimer, etc., become predominant due to the effect of reduced pressure.

(II) Effect of Operating Temperature in the Reactor

Experimental results at a setting temperature of 623 and 723K under atmospheric pressure are schematically shown in **Figs.3** (d),(e), respectively. As is evident from each figure, film and particles have formed in reactor tube at each operating temperature. Furthermore, by a comparison of **Figs.3**(a),

![EM photographs of TiO2 particles on Aluminum plate by CVD](image_url)
(d) and (e), as the temperature of the reactor tube is raised, the depositing end of the film and particles is shifted toward the inlet, the film area reduces and the interval of the stripes is narrowed, while the depositing part of particles is evidently extended. This is considered because raising the temperature in the reactor tube enhances the reaction rate of TTIP vapor, so that the generated monomer increases as the distance from the inlet decreases, resulting in an increases in the particles formed thereafter by immediate coagulation.

Figures 7 (a), (b) show SEM-observed results of white fine powder TiO₂ on aluminum plates obtained in the experiments. In each case, the particle size and deposition condition on the aluminum plates become quite clear. TEM-observed results of these particles are shown in Figs. 7(c), (d). In both cases, the particle size is found to be about 0.06 μm through the TEM photos. Therefore, the operating temperature in the reactor could not greatly influence the size of the resulting particles.

Fig. 3 (f) shows the experimental results at the setting temperature of 623K under reduced pressure of 1.13 x 10⁴ Pa. This indicates that
only film is formed and Figs. 3(c),(f) clarify that the depositing place film is shifted toward the inlet as in case under atmospheric pressure as previously mentioned. This is because of the increase in conversion results from raised temperature in the reactor tube.

### (III) Effect of Reactant Vapor Concentration

Fig. 3 (g) and (h) show the experimental results for TTIP vapor concentration 0.025 and 0.4% respectively under atmospheric pressure. As is evident from each figure, film and particles have formed in the reactor tube in each case. Furthermore, by a comparison of Fig. 3 (a),(g) and (h), as the reactant vapor concentration in the reactor tube increases, the depositing end of particles is shifted toward the inlet with a reduction in the film area. This shows that the coagulation of the monomers and clusters become predominant as the vapor concentration increases, which tend to from particles. Figures 8 (a),(b) show SEM-observed results of white fine powder TiO₂ on aluminum plates obtained under those conditions. In each case, particles size is found to be almost uniform. TEM-observed results of these particles are shown in Fig. 8(c),(d). In both cases, it is found that the particles are in spherical in form and the particle size is about 0.5 μm for 0.4% concentration and about 0.04 μm for a 0.025% concentration. Therefore, the TTIP vapor feed concentration evidently has a great influence on the size of the resulting particles.

Figures 3(i) and (j) show the experimental results for TTIP vapor concentration 0.025% and 0.4% respectively under the reduced pressure of 1.13×10⁻¹ Pa. As is evident from each figure, only film has formed in each vapor concentration. By comparison of Figs. 3(e),(i) and (j), the film area tends to extend with increasing the vapor concentration. This is because the higher vapor concentration enhances the generation of monomers, resulting in an increased deposit on the reactor tube wall.

### 1.3 Comparative Study of Experimental Results and Numerical Calculation on the Formation of Thin film and Particles

It is quite difficult to evaluate correctly the process of formation for TiO₂ thin film and fine particles in an aerosol reactor, so that we cannot help approaching it by using an appropriate model at present. Okuyama et al. have elucidated the process of formation for clusters and fine particles through the reaction of gas flowing laminarily in a tube by solving numerically the aerosol dynamic equation which is derived from the diffusion equation for evaluating the deposition of clusters and fine particles by incorporating a simplified reaction and coagulation model. Comparative study of experimental results and numerical calculation results obtained by the same method were made in this paper. In this theoretical analysis, the monomer formation through thermal decomposition, Brown coagulation of monomers, clusters and fine particles and transport by laminar flow are taken into consideration with the following assumptions.

1. At the tube inlet, gas flows with a well-developed laminar-flow velocity distribution which is not influenced by any temperature change.
2. Particles are in spherical form and electrically neutral, ignoring their thermal migration.
3. Particles coagulate to from a new spherical particle which has weight equal to the sum of each particle weight.
4. All of the particles which collided with the reactor tube’s wall are deposited on the wall surface.
5. The molecules of TTIP vapor do not be deposited on the tube wall surface.
6. The axial diffusion of monomers, clusters and fine particles in a tube are negligible compared with their convection.
7. The heat of reaction for TTIP vapor and the heat of condensation for TiO₂ particles are negligible.

For numerical calculation, we treated a
substance composed of 5 molecules or under as a cluster and one composed of 6 molecules or more as a particle, since numerical calculations become more difficult with a raise in the reaction temperature or with an increase with TTIP vapor concentration. Furthermore, to determine the number of axial and radial steps, the calculation was repeated by changing the number of axial partitions from 70000 to 700000 and by changing the number of radial partitions from 30 to 100. By comparing the obtained results, 350000 for the number of axial partitions and 50 for the number of radial partitions was found to give sufficient accuracy. Hence, most of calculations were made with 350000 axial partitions and with 50 radial partitions through the solution by the Crank-Nicolson method.

Among the above assumptions, assumption (1) seems to be hardly realized in the reactor shown in Fig. 1 due to the influence of the inlet part, existence of temperature distribution in the reactor, etc., so that the following numerical calculation results can be compared with the experimental results qualitatively.

The results of the numerical calculation based the experimental condition mentioned previously (see Table 1) are shown in Figures 9-12.

Figures 9-11 show the distribution of
deposition rate onto the reactor wall for the TiO$_2$ monomer, cluster and particle, where the axis of the abscissas expresses the distance from the reactor inlet and the axis of the ordinate expresses the deposition rate onto the reactor wall. Figure 12 shows the change in the volume mean diameter of deposited particles, where the curve of (a)-(e),(g) and (h) express the calculation results corresponding to those in Figs. 9–11. Comparative studies of the experimental results and numerical results and numerical calculation results on the formation of thin film and fine particles are mentioned below.

(1) Effect of Operating Pressure inside the Reactor

Fig.9(a)–(c) show the numerical calculation results for operating pressure in the reactor $1.01 \times 10^5$Pa, $1.13 \times 10^5$Pa and $1.13 \times 10^6$Pa, respectively. In each figure, the distribution of the deposition rates for the TiO$_2$ monomer, cluster and particle are of a convex form, which is known to be very much related to the temperature distribution in the reactor (see Fig.2).

In the reaction under atmospheric pressure, as is evident from Fig.9(a), monomers are deposited in a small quantity at the inlet and outlet of the tube and in a large quantity at around the middle part of the tube. Since the particles are formed through the coagulation of the clusters including monomers, dimers, trimers, etc., their deposition quantities are increasing gradually toward the middle of tube from the inlet similar to the case of the monomers. Furthermore, it was found that they are deposited in a large quantity even around the outlet. Accordingly, judging from the deposition distribution, the film formation in the experiments under atmospheric pressure may be attributed to the deposition of clusters including monomers, dimers, trimers, etc., so that, in particular, the deposition of monomer has a significant influence on the film formation. On the other hand, particles are estimated to be deposited in a large quantity from the middle part of the tube to the outlet, which evidently agrees with the above experimental results as a tendency. From Fig.12(a) the particle diameter at the outlet of tube was found to be about $0.3\mu m$ for a calculated value which is considerably greater than the experimental value, about $0.06\mu m$ given by the TEM photo. The reason for this may be that a coagulum is formed from particles without fusion and collision between particles does not cause adhesion in all cases since the melting point rises or approaches that of the bulk material with increasing particle diameter.

Next, in case of $1.13 \times 10^5$Pa as shown in Fig.9(c), an increase in the diffusion rate of the monomers and clusters due to a reduction in the pressure causes more and wider deposition than in case under atmospheric pressure. In addition, in this case, particles are deposited in small quantities. This is because the particles formation is difficult to occur due to the rapid deposition of the monomers and clusters onto the tube wall before they are coagulated to form a particle.

Therefore, in the experiment under reduced pressure $1.13 \times 10^5$Pa, it is expected that the film is chiefly formed while spreading axially in a tube, which is considered to agree with
the experimental results as a tendency. As for particle diameter, it is about $8 \times 10^{-4} \mu m$ as a calculated value through the whole inside of tube as seen from Fig.12(c), and is of the order of a cluster. This agrees with none of the observations of particles in the experiments. Furthermore, in case of $1.13 \times 10^4 Pa$ as shown in Fig.9(b), evidently deposition of the monomer and cluster amounts to the quantities between the cases of atmospheric pressure and $1.13 \times 10^4 Pa$, while deposition of the particle is larger than in the case in Fig.9(a), which explains well the tendency of the experimental results. As for the particle diameter, it is found about $0.15 \mu m$ as a calculated value at the tube outlet as seen from Fig.12(b) and is quite different from the experimental results, about $0.04 \mu m$ from the TEM photo, which is by similar reasoning as mentioned previously.

(II) Effect of Operating Temperature in the Reactor

Figure 10(d),(e) show the numerical calculation results for set temperature in the reactor 623 and 723K, respectively. In Fig.9(a) and Figs.10(d),(e), as the set temperature is raised, the deposition distributions of monomer, cluster and particle are shifted toward the inlet, which evidently agrees with the experimental as a tendency. As for the particle diameter, there is not so large a difference between the calculation and experimental results, while the coagulation effect becomes predominant as the operating temperature is raised, so that the particles grow.

(III) Effect of Reactant Vapor Concentration

Figure 11(g) and (h) show the numerical calculation results for TTIP vapor concentration 0.025 and 0.4% respectively under atmospheric pressure. Fig.9(a), and Fig.11(g) and (h) indicate that the deposition of particles and also the monomer and cluster increase as the TTIP vapor concentration increases, which evidently agrees with the experimental results. As for the particle diameter, Figs.12(g),(h) indicate that it grows as the TTIP vapor concentration increases due to the predominant coagulation effect.

2. Conclusion

The following was clarified after investigating the formation of thin film and fine particles through the experiments by using a laminar flow aerosol reactor.

(1) The CVD experiments under atmospheric and reduced pressure elucidated that with reducing pressure the formation of film becomes more favored than that of particles and the interval of their stripes increases in the axial direction of the tube. Regarding the particles, spheres almost uniform in size are formed, while for film, the interference fringe due to the diffraction of visible light is observed. Since its color varies with stripes, there appeared a distribution of film thickness.

(2) Since the conversion inside the reactor increases as the operating temperature of the reactor tube is raised, the rate of monomer formation increases in the inlet part, so that film and particles are apt to be formed on the side of the reactor inlet.

(3) Since the monomer formation increases as the concentration of the vapor supplied to the reactor is increased, in case of atmospheric pressure large particles are formed through coagulation and in case of reduced pressure the area of film extends.

(4) The above experimental results agree well qualitatively with the numerical solution of the diffusion equation including the terms for particles formation based on a simplified reaction and coagulation model, so that it became possible to estimate the influence of changes in the reactor condition including the pressure and temperature and in the concentration of vapor supplied to the reactor on the formation of film.
and particles to some extent.

**Nomenclature**

C = supplied concentration of TTIP vapor into the reactor [\%]

K = reaction rate constant [s⁻¹]

L = distance from the reactor inlet [m]

P = pressure gauge in the reactor [Pa]

Q = flow rate of carrier gas with TTIP vapor [m³/s]

T = setting value of temperature in the reactor [K]

**References**

1) Kanai, T., H. Komiyama and H. Inoue: *Kagaku Kagaku Ronbunshu*, 11, 317 (1985)

2) Okuyama, K.: *J. Soc. Powder Technol., Japan*, 26, 3 (1989)

3) Okuyama, K., R. Ushio, Y. Kousaka, J.H. Seinfeld and R.C. Flagan: *Kagaku Kagaku Ronbunshu*, 16, 526 (1990)

4) Okuyama, K., Y. Kousaka, N. Tohge, S. Yamamoto, J.J. Wu, R.C. Flagan and J.H. Seinfeld: *AIChE J.*, 32, 2010 (1986)

5) Okuyama, K., J.J. Jeung, Y. Kousaka, H.V. Nguyen, J.J. Wu and R.C. Flagan: *Chem. Eng. Sci.*, 44, 1369 (1989)