



ALD Process Using Hydrogen Peroxide (H₂O₂mix) for High Aspect Ratio Structures

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As semiconductors become more sophisticated, the conformal deposition on High Aspect Ratio (HAR) structures is a challenge. This paper addresses the applicability of Al₂O₃ ALD with the H₂O₂/H₂O mixture vapor (H₂O₂ mix) on HAR structures. We have investigated the deposition conditions. As a result, the film was formed up to the aspect ratio equivalent 2000. The elucidation of the reaction mechanism suggests that the reaction between H₂O₂ and TMA is thermodynamically more likely to proceed, contributing to higher throughput by shortening the purge time. Compared to other oxidants, H₂O₂ mix can improve the deposition rate and film quality, and is expected to be applied to the manufacturing process of advanced semiconductors.

1. Introduction

As advanced semiconductors become more sophisticated, wiring and mechanical elements fabricated on substrates are rapidly becoming finer, and the film deposition with good step coverage characteristics on high aspect ratio (HAR) structures has become a challenge. Atomic layer deposition (ALD) allows for the self-stopping mechanism of surface chemical reactions and is expected to be the technology that can form films with good coverage characteristics on advanced semiconductors with complex three-dimensional structures.

Al₂O₃ film deposition using ALD is made by oxidation of Al precursor adsorbed on the substrate surface with an oxidant. However, ozone gas (O₃), which is generally used as an oxidant, is an unstable molecule that is easily deactivated, making it difficult to deposit films with good coverage characteristics on the HAR structure^{1,2}.

We have focused on hydrogen peroxide (H₂O₂), which has strong oxidizing power, as an alternative oxidant to O₃, and have developed an ALD process using H₂O₂/H₂O mixed vapor (hereinafter referred to as H₂O₂ mix). Generally, when an aqueous H₂O₂ solution is supplied by bubbling, the H₂O₂ concentration in the solution increases with time, and the

H₂O₂ concentration in the vapor also changes³. On the other hand, RASIRC Peroxidizer[®] (Figure 1) can safely vaporize an aqueous H₂O₂ solution using our proprietary membrane separation technology and can supply H₂O₂ mix at a constant high concentration⁴.

The main features are as follows:

- Can use commercially available 30wt% H₂O₂ aqueous solution as raw material
- Supplies H₂O₂ mix gas (H₂O:H₂O₂ = 4:1) without particles or droplets
- Supplies up to 30 SLM carrier gas flow rate.
- Maximum H₂O₂ concentration up to 50000 ppm

Here, the effectiveness of H₂O₂ mix is discussed by introducing previously reported examples of Al₂O₃ film deposition^{5,6,7}. Figure 2 shows the temperature dependence of the film deposition rates (GPC: Growth Per Cycle) with use of different oxidants⁶. At all deposition temperatures, the highest GPC was obtained with H₂O₂ mix, the second with H₂O, and the third with O₃, and the use of H₂O₂ mix resulted in a GPC increase of about 10-30 % compared to the other oxidants. Figure 3 shows the I-V measured dielectric breakdown strengths of a 0.1 μm-thickness Al₂O₃ film deposited with use of different oxidants⁶. As a result, the highest dielectric breakdown strength was obtained with H₂O₂ mix, the second with O₃, and the third with H₂O. The use of H₂O₂ mix improves the dielectric breakdown properties, which is expected to enable the use of thinner Al₂O₃ films to lead to finer advanced semiconductors. These results were examined in terms of the substrate surface coverage rate of OH groups. Anu Philip et al. found in their

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study that the saturated adsorption of Al precursor in Al₂O₃-ALD is proportional to the OH group coverage rate on the substrate surface⁸⁾. In addition, It was also found that H₂O₂ mix is more effective than H₂O in terminating the substrate surface with OH groups, and therefore it was concluded that the use of H₂O₂ mix contributed to the increase in GPC and the formation of dense, more insulation-resistant Al₂O₃.

In this study, we further confirmed that H₂O₂ mix contributes to the good Al₂O₃ film deposition on HAR structures and elucidated the ALD reaction mechanism.



Figure 1 RASIRC Peroxidizer[®]

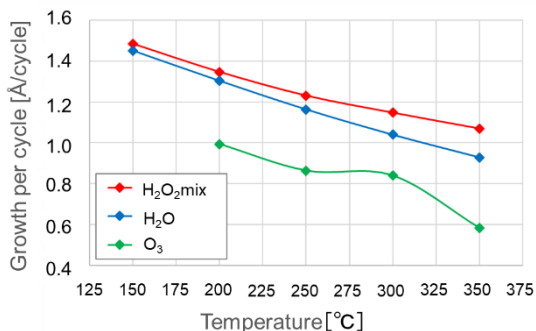


Figure 2 Temperature dependence of Al₂O₃ film GPC

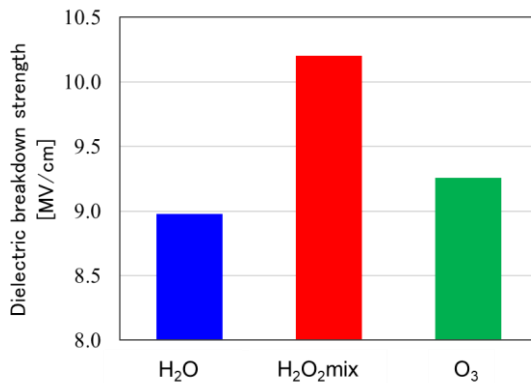


Figure 3 Dielectric breakdown strengths of Al₂O₃ film deposited with use of different oxidants (Al₂O₃ film deposited at 300°C)

2. Experiment

2.1 Film deposition method

We performed ALD of Al₂O₃ on silicon substrates in a hot-wall tubular reactor by supplying trimethylaluminum (TMA) as an Al precursor and H₂O₂ mix or H₂O from Peroxidizer[®] as an oxidant. Figure 4 shows a schematic diagram of the experimental equipment and evaluation samples, and Figure 5 shows the ALD process flow and condition. N₂ purging was performed between the TMA supply and oxidant supply processes to prevent gas-phase reactions in the reactor. The film deposition conditions were set at 300°C, the total pressure at the oxidant supply was 1.33 kPa, and the number of ALD cycles was 200.

In this experiment, the TMA feed rate and oxidant were changed to check the effect on the aspect ratio (AR). Specifically, for conditions A, B, and C, the TMA feed rate per unit time was 8, 12.5, and 25 sccm, respectively, using H₂O₂ mix. For condition D, the TMA feed rate was 25 sccm using H₂O.

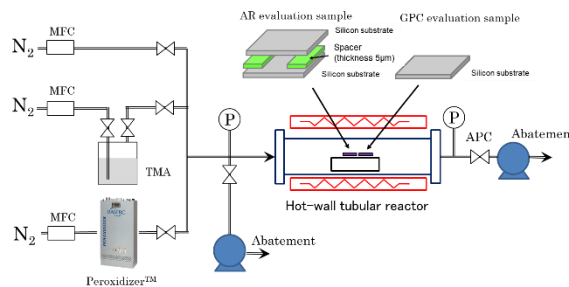


Figure 4 Schematic diagram of ALD equipment and evaluation samples

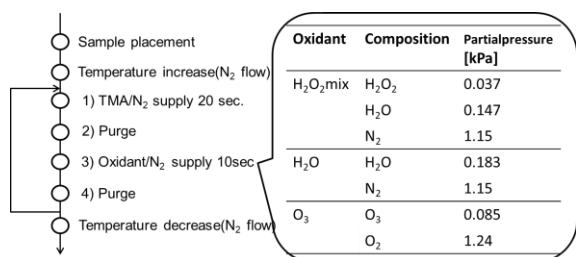


Figure 5 ALD flow and oxidant supply conditions

2.2 Film deposition evaluation method

We measured the thickness of the Al₂O₃ film deposited on the GPC evaluation sample using a spectroscopic ellipsometer, and calculated GPC from the film thickness obtained as the amount of film deposited per cycle.

We used an AR evaluation sample (AR: 0 to 2500, see Figure 4) consisting of stainless steel foil spacers of 5 μm thickness sandwiched between 25 mm square silicon substrates for AR evaluation, and placed it in the reactor so that the slit openings of the spacers were perpendicular to the gas flow. TMA or oxidant was alternately fed through the slit, and the film was deposited by repeated molecular adsorption and oxidation reactions on the substrate. After film deposition, we peeled off the silicon substrate from the AR evaluation sample to check the Al₂O₃ film deposition state, and measured the length L of the film deposition area from the edge to the center direction. Since this length L corresponds to the film deposition depth from the slit opening, AR is defined in this paper as the value obtained by dividing L by 5 μm, the slit width.

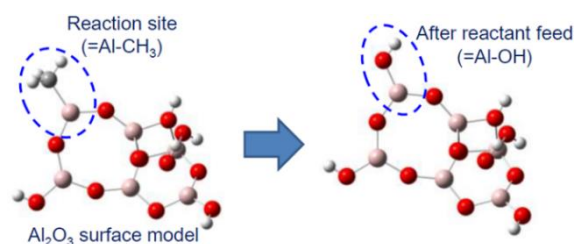
2.3 Exhaust gas analysis

To elucidate the reaction mechanism of Al₂O₃ film deposition, we analyzed the products from ALD in the exhaust gas. Using the ALD equipment shown in Figure 4, exhaust gas discharged from the hot-wall tubular reactor was sampled from the rear side of the automatic pressure control (APC in Figure 4) and analyzed with a quadrupole mass spectrometer.

The sampling condition X is ALD with TMA and H₂O₂ mix, the sampling condition Y is ALD with TMA and H₂O, and the sampling condition Z is supply of H₂O₂ mix only. During the process, the pressure in the reactor was kept at an absolute pressure of 1.33 kPa and the temperature at 300°C. The absolute pressure in the quadrupole mass spectrometer was kept below 10⁻⁴ Pa via differential exhaust.

2.4 Quantum chemical calculation

In order to examine the reaction mechanism of Al₂O₃ film deposition, structural optimization of ALD products was performed using the model shown in Figure 6 in the quantum chemical calculation software Gaussian 16, using the B3LYP density functional theory and cc-pVDZ basis. Here, assuming process 3) in the ALD flow shown in Figure 5, the reaction heat (-ΔH_r) was calculated using the difference in zero-point corrected energies from the optimized structures before and after the reaction.

Figure 6 Quantum chemical calculation model of Al₂O₃

3. Experimental result and examination

Table 1 shows the result of GPC evaluation. In all conditions, thin films were formed by ALD. It can be confirmed that GPC increased more when H₂O₂ mix was used as the oxidant than when H₂O was used.

Table 1 GPC evaluation result (Al₂O₃ film deposited at 300°C)

	Condition A	Condition B	Condition C	Condition D
TMA feed rate [sccm]	8	12.5	25	25
Oxidant	H ₂ O ₂ mix	H ₂ O ₂ mix	H ₂ O ₂ mix	H ₂ O
GPC [Å/cycle]	1.14	1.15	1.15	1.05

Figure 7 shows the appearance of a silicon substrate peeled off from an AR evaluation sample after film deposition to check the AR. The center is the gas penetration area where each reaction gas was adsorbed on the substrate surface and the film was deposited, and the left and right are areas where the stainless steel foil was placed (colored by image processing). As described in the section 2.2, we measured the length L from the edge of the substrate to the boundary of the two areas to calculate the AR. The obtained ARs are added to Figure 7. Figure 8 shows the dependence of AR on TMA supply conditions.

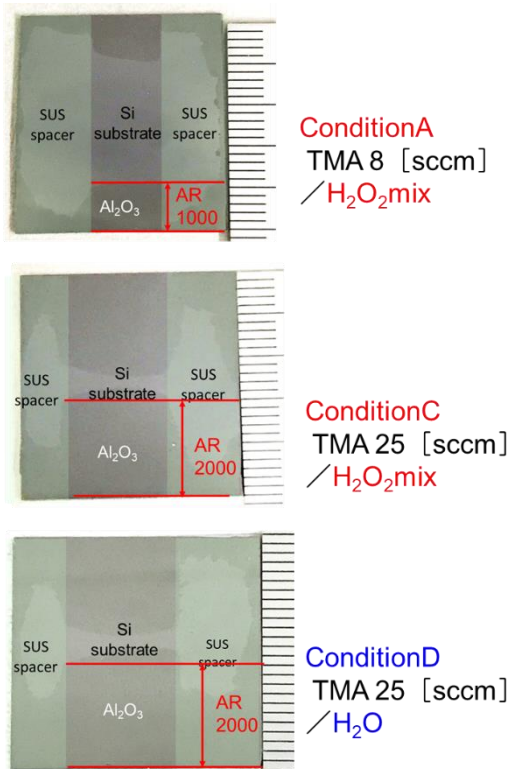


Figure 7 Appearance of AR evaluation samples (conditions A, C, and D)

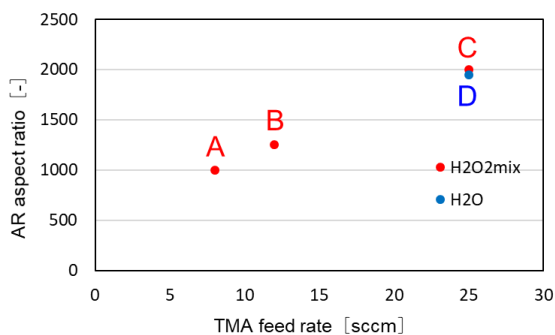


Figure 8 Dependence of AR on TMA supply conditions

As the TMA supply increased, the AR also increased, indicating that the TMA supply limited the rate, i.e., the oxidant was supplied sufficiently deep into the slit of the AR 2000. The oxidant H₂O₂ mix showed good coverage characteristics on the HAR structure as well as H₂O. We plan also to further evaluate the film quality in the future.

Next, the reason why the AR increases as the amount of TMA supplied is increased is discussed from the viewpoint of reaction kinetics ⁹⁾. Here, assuming the process 1) in the ALD flow shown in Figure 5, we discuss the reaction in which the supplied TMA molecules are chemisorbed on the substrate surface. For the

chemisorption reaction to occur, collisions between TMA molecules and OH groups on the surface of the substrate are necessary. The collision frequency between TMA molecules and OH groups, $Z_{TMA-OH\ group}$, can be calculated using Equation (1) and is proportional to the concentration of TMA molecules and the coverage rate of OH groups.

$$Z_{TMA-OH\ group} = \delta \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} n_{TMA} n_{OH\ group} \quad \text{Equation (1)}$$

(δ : collision cross section, n_{TMA} : concentration of TMA molecules, $n_{OH\ group}$: coverage rate of OH groups on film surface, k_B : Boltzmann constant, μ : converted mass)

Figure 9 illustrates the distribution of molecules in the slit. The slit opening ends of an AR evaluation sample are located at two positions symmetrically, but only the area near the opening end on one side is shown in this figure. The upper part of Figure 9 shows diffused TMA molecules (red circles) and OH groups on the substrate surface (blue circles), and the lower part of Figure 9 illustrates the film thickness distribution of Al₂O₃ after the film deposition. TMA molecules diffused into the slit react with OH groups on the substrate surface to form Al-O bonds. The by-product gas generated by this reaction is discharged out of the slit by the purging process.

The inside of the slit is classified into the following four areas.

- Area (1), where TMA molecules are sufficiently supplied to OH groups and a thin film is formed by ALD.
- Area (2), where TMA molecules are insufficiently supplied to OH groups and a thin film is partially formed by ALD.
- Area (3), where OH groups are adsorbed, but TMA molecules do not reach, and a thin film is not formed.
- Area (4), where OH groups are not adsorbed and TMA molecules do not reach, and a thin film is not formed.

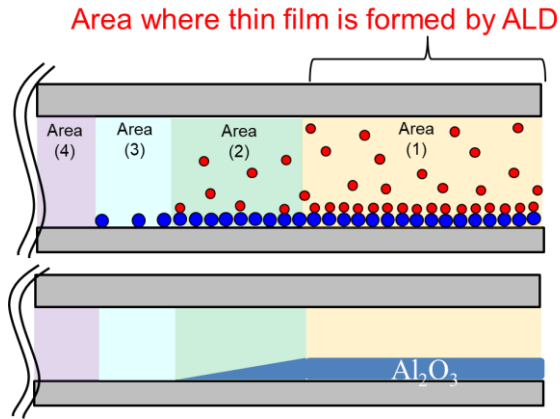


Figure 9 Distribution of molecules in slit
(Upper: Distribution of TMA molecules and OH groups,
Lower: Film thickness distribution of Al₂O₃)

In Equation (1), the coverage rate of OH groups on the film surface, $n_{OH\ group}$, is considered constant because the oxidant in the gas phase is removed in the purging process, so $Z_{TMA-OH\ group}$ is proportional to the concentration of TMA molecules, n_{TMA} . This is shown as Area (2) (green). In deeper areas (3) and (4) (light blue and purple, respectively), n_{TMA} is 0, i.e., $Z_{TMA-OH\ group}$ is 0, so no Al₂O₃ film deposition occurs. On the other hand, in Area (1) (orange), the concentration of TMA molecules, n_{TMA} , becomes higher in the opening, but the thickness of Al₂O₃ film is constant. This is due to the characteristic of ALD process where only one layer is deposited per a cycle due to the self-controlling characteristic of the surface chemical reaction. If $n_{TMA(ALD)}$ is the required concentration of TMA molecules that can form a thin film in ALD mode, in Area (1) (orange), $n_{TMA} \geq n_{TMA(ALD)}$ holds.

Under conditions of constant total pressure, the amount of material of TMA molecules passing through a unit area of the cross section of TMA molecules per unit time, N_{TMA} , can be expressed by Equation (2).

$$N_{TMA} = \frac{D}{RT} \left(\frac{dp_{TMA}}{dx} \right) \propto n_{TMA} \quad \text{Equation (2)}$$

(D: diffusion coefficient, p_{TMA} : partial pressure of TMA molecules)

Based on the above, it is considered that increasing the TMA feed rate in this experiment leads to a higher partial pressure and concentration of TMA molecules in Equation (2), and thus to an elongation of Area (1) where $n_{TMA} \geq n_{TMA(ALD)}$ holds, and the length of the Al₂O₃ film

deposition area ((1)+(2)), i.e., the film deposition length from the slit opening is extended as a result.

Here the reaction mechanism of ALD with TMA and H₂O₂ mix is discussed based on the results of exhaust gas analysis using a quadrupole mass spectrometer (Figure 10) and quantum chemical calculations (Table 2).

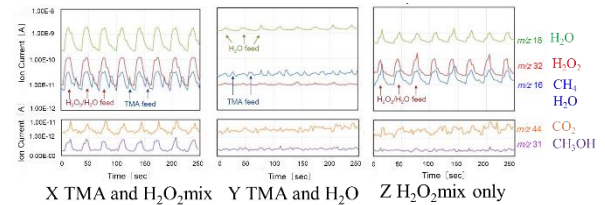


Figure 10 Exhaust gas analysis result by quadrupole mass spectrometer

Under the condition X, chemical species with $m/z = 32$ and 44 were observed synchronously with the H₂O₂ mix supply. A chemical species with $m/z = 16$ increased both with H₂O₂ mix and with TMA supply. From the above behavior, the CH₃ group bonded to Al is considered to react with H₂O₂ or H₂O, so the species with $m/z = 16$ can be attributed to CH₄ and H₂O, the species with $m/z = 32$ to CH₃OH, and the species with $m/z = 44$ to CO₂.

In the condition Y, only a species with $m/z = 16$ was observed in synchronization with the H₂O supply and can be attributed to CH₄. Unlike in the condition X, species with $m/z = 32$ and 44 were not observed.

In the condition Z, H₂O ($m/z = 16$ and 18) and H₂O₂ ($m/z = 32$), which were the compositional components of H₂O₂ mix, were observed.

Table 2 Enthalpy calculation results for each condition

ALD condition	Reaction equation for surface adsorbed TMA	$-\Delta H_r$ [kJ/mol]
Condition X Oxidant: H ₂ O ₂ Temp.: 300°C	$=Al-CH_3 + H_2O_2 \rightarrow =Al-OH + CH_3OH$	256
	$CH_3OH + 3H_2O_2 \rightarrow CO_2 + 5H_2O$	993
Condition Y Oxidant: H ₂ O Temp.: 300°C	$=Al-CH_3 + H_2O \rightarrow =Al-OH + CH_4$	40

For the condition X, it was found through theoretical calculation that the enthalpy change ($-\Delta H_r$) of the surface reaction of TMA ($=Al-CH_3$) adsorbed on the substrate

and H₂O₂, by which CH₃OH was formed, was -256 kJ/mol, indicating that the reaction was thermodynamically likely to proceed. In addition, the enthalpy change (-ΔH_r) of the reaction in which CH₃OH was oxidized by H₂O₂ to form CO₂ was even larger, indicating that the reaction was easier to proceed.

For the condition Y, the theoretical calculation showed that the enthalpy change (-ΔH_r) of the surface reaction of H₂O and adsorbed TMA (=Al-CH₃), which formed CH₄, was -40 kJ/mol. Thermodynamically, the reaction proceeds although the ease of reaction was inferior to the condition a.

Table 3 shows the diffusion coefficients of the gases relevant to the reaction in a nitrogen environment at 1.33 kPa and 300°C¹⁰⁾.

Table 3 Diffusion coefficients of gases

	H ₂ O ₂	H ₂ O	CH ₃ OH	CH ₄	CO ₂
Diffusion coefficient [cm ² /sec] (1.33[kPa], 300[°C])	37.8	50.8	34.5	36.7	37.3

The diffusion coefficient of CH₃OH formed under the condition X is smaller than that of H₂O and CH₄. Therefore, in a previously published study⁶⁾, it was speculated that although there is concern about the reaction of CH₃OH and TMA (=Al-OH) during the purging process, the reaction is thermodynamically unfavorable and the reverse reaction is unlikely to occur. On the other hand, the diffusion coefficient of CH₄ formed under the condition Y is smaller than that of H₂O, and the enthalpy change is smaller than that under the condition X. Thus, the reaction of CH₄ and TMA (=Al-OH) proceeds during the purging process, and H₂O may be re-formed. Therefore, a long purge time is necessary to prevent the gas-phase reaction with the next supplied TMA.

If the reaction between CH₄ and TMA (=Al-OH) proceeds during the purging process, the film quality (electric breakdown strength) is considered to decrease because C remains in the film as an impurity. Furthermore, even if TMA is supplied, the residual C decreases the adsorption point of TMA, which has an effect on the decrease in GPC.

Based on the above, it was found that in ALD using H₂O, a reversible reaction, in which H₂O is regenerated during the subsequent purging process, may proceed.

Since the surface reaction in ALD using H₂O₂ is irreversible, H₂O₂ mix may be a promising reactant to increase the throughput of the ALD process from a chemical point of view.

4. Conclusion

As advanced semiconductors become more sophisticated, wiring and other devices fabricated on substrates are becoming finer, and step coverage characteristics on high aspect ratio structures has become a challenge. We fabricated Al₂O₃ by atomic layer deposition using trimethylaluminum (TMA) and H₂O₂/H₂O mixed vapor (H₂O₂ mix) supplied from a high concentration H₂O₂ gas supply system. Through experiments, we demonstrated that H₂O₂ mix allows film deposition on structures with an aspect ratio equivalent to 2000 without deactivation on an evaluation sample with a fine structure. Through quantum chemical calculations and exhaust gas analysis, it was found that H₂O₂ has a thermodynamic advantage in the reaction of TMA with H₂O₂ or H₂O, and because the reaction proceeds irreversibly, H₂O₂ mix can contribute to high throughput of high aspect ratio structures by reducing purge time. As a result, H₂O₂ mix can improve the film deposition rate and film quality compared to other oxidants, and is expected to be applied to the manufacturing process for advanced semiconductors with increasingly high functionality.

References

- 1) G. Prechti et al, "A model for Al₂O₃ ALD conformity and deposition rate from oxygen precursor reactivity" IEEE international ELECTRON DEVICES meeting, Session 9.6, (2003)
- 2) Véronique Cremers et al, "Conformality in atomic layer deposition: Current status overview of analysis and modelling", Appl. Phys. Rev. 6, 021302 (2019)
- 3) J.J. Van Laar. Z. Physik. Chem. 72: 723 (1910)
- 4) Keisuke Adachi, "High Concentration Hydrogen Peroxide Gas Delivery System - Peroxidizer[®]", Taiyo Nippon Sanso Technical Report No. 38, (2019)
- 5) Gaku Tsuchibuchi et al. "Al₂O₃ Atomic Layer Deposition Using a Novel High Concentration H₂O₂ Gas Delivery System (Peroxidizer[®])", Taiyo Nippon Sanso Technical Report No. 38, pp. 16-21 (2019)
- 6) Hideharu Shimizu et al. "Enhanced Throughput of High-Aspect-Ratio ALD using Al(CH₃)₃ and Hydrogen Peroxide", ALD2021 USA (2021)
- 7) Dan Alvarez Jr. et al., "Anhydrous Hydrogen Peroxide Gas Delivery for Semiconductor Manufacturing: Optimal Delivery Condition for ALD Processes", ALD2017 USA, AM-MoP1 (2017)
- 8) Anu Philip et al., "Calculation of GPC of atomic layer deposited aluminium oxide nanolayers and dependence of GPC on surface OH concentration", Pramana - J. Phys., Vol. 82, No. 3, pp. 563-569 (2014)
- 9) Noriaki Wakao, "Gas Diffusion in Pores", Journal of Chemical Engineering of Japan Vol. 28, No. 6, (1964)
- 10) Shuzo Oe, "Physical Properties Estimation Method", Databook Publishing Co., 2002