

Development of ALD System to Deposit Y, Ba and Zr Complex Metal Oxide Using Alkyl Amidinate Compound Precursors for Micro SOFC

Masafumi Kumano¹, Shuji Tanaka^{1,2},
Kentaro Miyamoto², Kousuke Hikichi² and Masayoshi Esashi^{1,2}

¹Microsystem Integration Center, Tohoku University, Sendai, Japan

²Department of Nanomechanics, Tohoku University, Sendai, Japan

Abstract: We have constructed a laboratory-made atomic layer deposition (ALD) system to deposit yttria-doped barium zirconate (BYZ) for micro solid oxide fuel cells (SOFC). The ALD system uses new types of metal oxide precursors, alkyl amidinate compounds. They sublime or vaporize at relatively low temperature and decompose easily by water vapor. We confirmed the basic operation of the ALD system by depositing zirconia and yttria. This paper mainly describes the handling method of these new precursors in the ALD system and preliminary deposition results.

Keywords: ALD, yttria-doped barium zirconate, SOFC, alkyl amidinate precursor

INTRODUCTION

MEMS-based solid oxide fuel cell (SOFC) is attracting increasing attention, because it produces higher power density and possesses higher compatibility with wafer-level MEMS process than other types of fuel cell[1][2]. From the viewpoints of efficiency, reliability and practical application, it is important to lower the operation temperature and internal resistance. For this purpose, a very thin electrolyte with higher ion conductivity is advantageous. From the viewpoint of system simplicity, a proton conductive membrane is preferable to an oxygen conductive one, because generated water is simply emitted to outside from the cathode. Therefore, proton conductive yttria-doped barium zirconate (BZY) was deposited by atomic layer deposition (ALD) and applied to micro SOFC with a deeply-folded active area [3]. ALD is suitable to deposit a thin, pinhole-free membrane conformally on deep microstructures. However, the detail of the used ALD system was not reported.

In this study, we have developed an ALD system, which uses new types of metal oxide precursors, alkyl amidinate compounds shown in Fig. 1 and Table 1. Among them, yttrium tris(N,N'-diisopropylacetamidinate) was reported to be suited to an ALD precursor [4]. To make the BZY film, similar alkyl amidinate compounds of Zr and Ba might be better as ALD precursors to avoid complex contamination problems. The alkyl amidinate compounds sublime or vaporize at relatively low temperature and decompose easily by water vapor. These characteristics are important to obtain a high quality film by ALD [4]. In addition, these precursors are expected to have vapor pressures in the same order, and thus easy to handle in the same heated oven.

ALD SYSTEM

Figure 2 and 3 are the diagram and photograph of

our ALD system, respectively. The ALD system is also equipped with trimethyl aluminum precursor for Al₂O₃ deposition. The ALD for each oxide can be continuously performed in any sequence. The gas system has separated precursor pathways for BZY and Al₂O₃.

The precursors for BZY are installed in a 140 °C oven with a size of 450 × 450 × 450 mm³. The precursor bottles (200 ml) are made of Pylex glass and have a stainless steel, metal gasket flange, which is connected to Pyrex glass by Kovar sealing. Each alkyl amidinate precursor lines is purged out by a pressure-controlled hot N₂ line ("purge 1" in Fig. 2) with a sampling volume of 25 ml ("SV1" in Fig. 2). "R-N₂" in Fig. 2 is a N₂ hot reservoir of 200 ml, which supplies carrier gas to each precursor sampling volume of 25ml ("S-Ba" for Ba etc. in Fig. 2) and instantaneous push-out purge gas. This push-out purge is done just at the

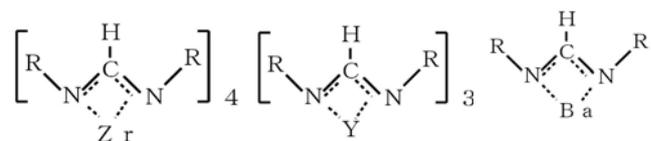


Fig 1. Precursors of Zr-, Y- and Ba-oxides with dimethyl acetamide as a ligand. "R" represents alkyl compound unit.

Table 1. Characteristics of the precursors.

	Melting point	Vapor pressure	State, color
Zirconium tetrakis (N,N' - dimethyl acetamidinate)	165 °C	-	Solid, white
Yttrium tris (alkyl amidinate)	Sublime	5.33 Pa at 150 °C	Solid, white
Barium alkyl amidinate	Sublime	-	Solid, white

end of each precursor transportation cycle to quickly cut the tail flow of precursor vapor. A stationary purge line (“purge 3” in Fig. 2) controls the transmission time of the precursor gas and the pressure gradient of the transportation line. One of key points for this kind of ALD is sufficient purge, because the vapor pressure of these precursors are much lower (a few Pa at 140 °C) than that of water.

Temperature at the inlet of the reactor is set at 200 °C, which is necessary to avoid the accidental deposition of precursor materials and to minimize the H₂O back diffusion to the precursor transportation lines. The transportation line between the oven (140 °C) and the reactor inlet (200 °C) is heated as it has temperature gradient.

The precursor for Al₂O₃, Al(CH₃)₃, and H₂O, which is used for both BZY and Al₂O₃, are kept at room temperature, because they have the same order of relatively-high vapor pressure at room temperature.

The Al(CH₃)₃ bottle is a conventional stainless steel bottle with a stop valve, which is connected to the line by a metal gasket joint. The H₂O bottle is a glass flask with a glass-PTFE stop valve, which is connected to the metal line using an O ring. The lines except the precursor and water bottles are separately wound by heaters, and the temperature is controlled as it has gradient from 120 °C around the reservoir bottle to 200 °C at the reactor inlet.

All precursor vapors and N₂ purge gas are measured by each sampling volume (“S-X” in Fig. 2; X is each gas molecule) to control the number of transported gas molecule. To switch the gas flow, high-temperature-

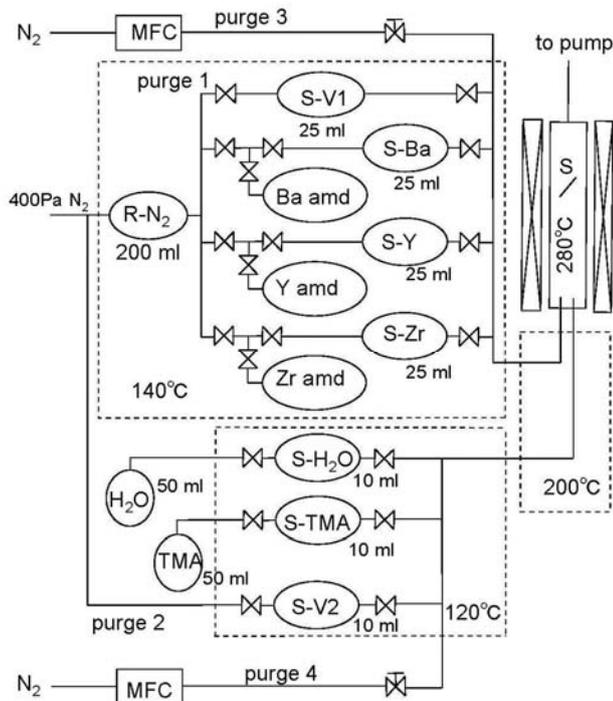


Fig. 2. Diagram of the ALD gas system with one reactor for 4 element metal oxides. “TMA” and “amd” denote trimethyl aluminum precursor and alkyl amidinate complex of Ba, Y and Zr respectively..

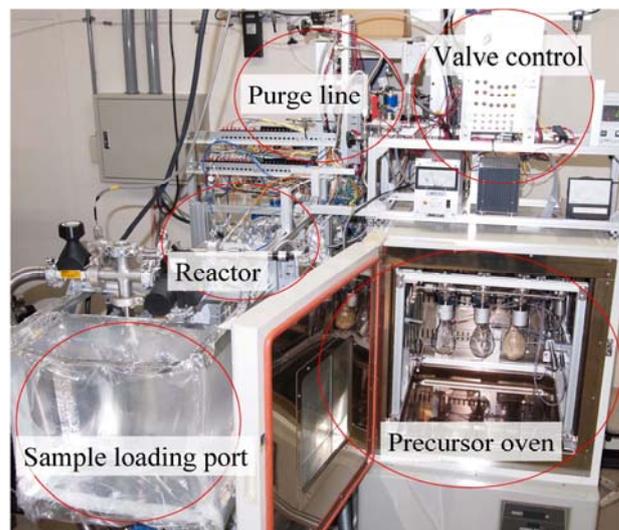


Fig. 3 Photograph of the completed ALD system.

resistive, high-speed pneumatic valves (6LVV-ALD3FR4-P-CV, Swagelok Co. and FPR-NHD-71-6, Fujikin Co.) are used. The valve sequence and system temperatures are controlled by a personal computer using original software.

The reactor chamber is a glass tube (34 mm in diameter and 350 mm in length), which is set horizontally in an electric furnace heated at 280 °C. All gas lines are made of a 1/4” stainless tube to balance the inner surface area and conductance of the tubes between the reservoir bottles and the reactor. In addition, sufficiently short transmission time of the gases can be achieved using the 1/4” stainless tube at moderate flow rate. All gas flow is pumped out by a 50 l/s turbo molecular pump. Without gas flow, the back pressure of the reactor is lower than 2.6×10^{-4} Pa.

EXPERIMENTAL AND DISCUSSION

Observation of Precursors

The vapor pressure of yttrium tris-alkyl amidinate is 5.33 Pa at 150 °C and 4 Pa at 90 °C. For Zr and Ba alkyl amidinate compounds, no information about vapor pressure is known. Fig. 4 shows the three precursor bottles kept at 140 °C in the oven. All bottles were pumped out and held in vacuum at this temperature for 48 h or longer. It is observed that the Y and Zr precursors sublimed and recrystallized on the inside surface of the bottle due to a small temperature difference in the oven. The Y precursor made large crystals of 3-5 mm in diameter. The Zr precursor also recrystallized at higher growth rate than the Y precursor. The Ba precursor showed only a small change in the bottle, and no large recrystallization was observed.

The atomic number of gas in the 200 ml precursor bottle is estimated to be 2.82×10^{17} at 5.33 Pa, which is the vapor pressure of yttrium tris-alkyl amidinate at 150 °C. Thus, the constant volume cell of 25 ml might contain 3.5×10^{16} molecule, which is comparable to the maximum number of absorbed molecules on the

whole surface area of the transportation tubes and the reactor (ca. 380 cm²). To assure the transfer of each precursor molecule from the reservoir to the reactor and to shorten the purge time, it is necessary to optimize the number of molecules transported in each ALD cycle. For this purpose, two methods of precursor transportation were tested; with and without introducing N₂ gas to the precursor bottles.

Without introducing N₂ gas, the number of precursor molecule to be fed can be easy to estimate from the equilibrium pressure. However, the equilibrium pressure must be higher than pressure in the transportation tube. From the observed difference in sublimation behavior in the bottle for each precursor, it was found that the Zr precursor has higher vapor pressure than that of the Y precursor, which is 5.33 Pa at 150 °C. Therefore, pressure in the transportation tubes connected to the bottles must be lower than 5.33 Pa. Fig. 5 shows the measured relationship between stationary purge gas flow rate and pressure in the transportation tube. The stationary purge N₂ flow rate should be lower than 0.017 sccm, which is near the lower limit of the mass flow controller used.

Test Deposition

ALD with the Zr precursor was tested at stationary N₂ purge rate of 0.018 sccm. The equilibrium pressure in the reactor was 5×10^{-2} Pa. After 600 ALD cycles, the thickness of the film was 330 Å, which is reasonable because each ALD cycle corresponds to ca. 0.5 Å. The as-deposited film showed a refractive index of 2.144, which is close to a value for bulk ZrO₂ (2.05 at 500 nm).

In this condition, however, the Y and Ba precursors could not flow out from the bottle sufficiently, and no deposition was observed even after 1000 ALD cycles. At present, the tube length from the precursor bottles to the reactor inlet is 70-90 cm, which is effective to block H₂O back diffusion from the reactor to the precursor bottle, but limits the achievable vacuum level of the transportation tubes. To overcome this problem, the tube length should be shortened to ca. 30 cm and the tube diameter should be changed from 1/4" to 3/8". However, the influence of H₂O back diffusion must be reconsidered.

Another way to assure the transportation of the precursor molecules from the precursor bottle to the reactor is to introduce N₂ gas to the precursor bottle. In this case, the precursor molecules are carried by N₂ gas, and thus there is no limitation about pressure in the transportation tube. However, N₂ pressure must be optimized to supply appropriate number of the precursor molecules for surface reaction.

In this test run, pressure in the N₂ reservoir (R-N₂) was controlled at ca. 400 Pa, and the whole N₂ gas (200 ml) in the reservoir was introduced to the Y precursor bottle. After 600 ALD cycles, the thickness of the film was 1400 Å, and the as-deposited film showed a refractive index of 1.75, which is close to



Y amidinate Zr amidinate Ba amidinate

Fig. 4 Photograph of the precursor bottle after heated at 140 °C for 48 h or longer in the oven.

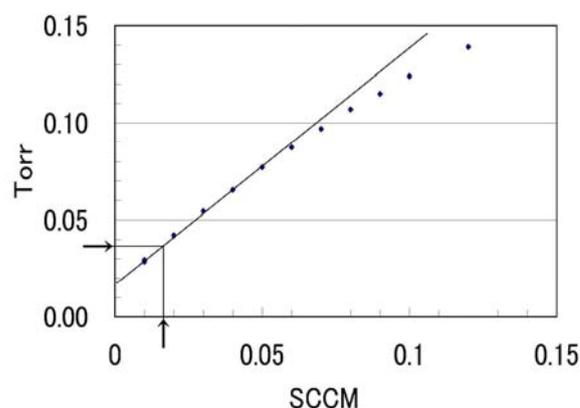


Fig. 5 Relationship between stationary purge N₂ gas flow rate and estimated pressure in the transportation tube in the oven.

a value for bulk Y₂O₃ (1.87 at 550nm). The film thickness corresponding to each ALD cycle is 2.3 Å, which is much larger than reported value (0.8 Å [2]). This high growth rate might come from the partial decomposition of the Y precursor at a reactor temperature of 280 °C. Further optimization about pressure, carrier gas flow rate and reactor temperature is necessary to realize pure ALD process. At present, ALD with the Ba precursor is not confirmed. The Ba precursor bottle should be kept at higher temperature than 140 °C, which needs the modification of the system.

CONCLUSION

An ALD system for BZY thin film as the ion conductive layer of micro SOFC was developed. New precursors, alkyl amidinate compounds of Y, Zr and Ba were used. This paper first reported the handling method of these precursors in the ALD system. We confirmed the deposition of zirconia and yttria, and the former was found to be ALD process from deposition rate. However, the deposition of barium oxide was not confirmed. The Zr and Y precursors can be handled in the same oven at 140 °C, while the Ba precursor might need higher temperature to sublime sufficiently. After confirming each oxide deposition separately, BZY films will be deposited using an

appropriate sequence like (Ba × 5, Zr × 4 and Y × 1) × *n* cycles.

ACKNOWLEDGEMENT

This study was performed partly in R&D Center of Excellence for Integrated Microsystems, Tohoku University under the program “Formation of Innovation Center for Fusion of Advanced Technologies” supported by Special Coordination Funds for Promoting Science and Technology, and partly as a topic of Creative Scientific Research Program No. 18GS0203 “Nano-energy System Creation” supported by the Ministry of Education, Science, Culture and Sports.

REFERENCES

- [1] Evans A, Bieberle-Huetter A, Rupp J and Gauckler L 2009 Review on microfabricated micro-solid oxide fuel cell membranes *Journal of Power Sources* 194 119-129
- [2] Huang H, Nakamura M, Su P, Fasching R, Saito Y and Prinz F B 2007 High-performance ultrathin solid oxide fuel cells for low -temperature operation *Journal of The Electrochemical Society* 154 B20-B24
- [3] Shim J H, Park J S, An J, Guer T M, Kang S and Prinz F B 2009 Intermediate-Temperature Ceramic Fuel Cells with Thin Film Yttrium-Doped Barium Zirconate Electrolytes *Chem. Mater.* 21 3290-3296
- [4] Rouffignac P, Park J S and Gordon R G 2005 Atomic Layer Deposition of Y₂O₃ Thin Films from Yttrium Tris(N,N'-diisopropylacetamidinate) and Water *Chem. Mater.* 17 4808-4814