원자층 증착법과 스퍼터링법을 이용한 고체산화물 연료전지용 YSZ 전해질 증착에 관한 연구

Comparison of Yittria Stabilized Zirconia Electrolytes for Solid Oxide Fuel Cell by Atomic Layer Deposition or Sputtering

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1. Introduction

Solid Oxide Fuel Cells are getting increasingly popular as the demand for producing environmentally friendly devices that can produce electricity at high energy conversion efficiency increases. However, high operating temperatures limit further expansion of applications due to thermal stresses and rapid degradation of cell components. For this reason, extensive research has been conducted to reduce electrolyte resistance at reduced temperatures. One approach is to use a new electrolyte material that shows high oxygen ion conductivity at temperatures below 800°C, comparable to that of YSZ at 1000°C. Another is to reduce thickness of electrolyte, as by reducing thickness of electrolyte one can reduce the ohmic loss.

Many methods have been utilized previously to deposit thin as well as conformal layers of Yittria Stabilized Zirconia. Some of them are ; dip-coating, Chemical Vapor Deposition(CVD), magnetron sputtering. This work is dedicated to the optimization of thin layers obtained by two selected techniques namely (sputtering and atomic layer deposition), to analyze their performance and compare them in different configurations. Atomic layer deposition (ALD), also referred to as atomic layer CVD (ALCVD), is a modified CVD method based on alternating chemisorptions of the reacting precursors on the substrate surface. Sputtering on the other hand, is a thin film deposition technique in which a thin film of material is formed on the substrate, by the aid of atoms induced due to bombardment of the target (YSZ in this case) with high energy electrons. The atoms coming out from the target construct a beam or plasma incident on the substrate, resulting in formation of thin conformal layers as time goes on.

2. Experimental

Ultrathin layers of YSZ were elaborated by two techniques in laboratory namely; Atomic Layer Deposition and Sputtering. Substrate used for deposition was single side polished $SiO_{2.}$

A commercial ALD chamber composed of a main chamber and a loadlock chamber was used. Film depositions were carried out at *0.031 Torr* pressure. (Tetrakis[dimethylaminozirconium] Commercial $ZrN(Me_2)_4$ Sigma-Aldrich Inc) was used as Zirconium precursor, where as $Y(MeCp)_3$ (Tris[methylcyclopentadienyl] yittrium (99%-Y) Strem Chemicals, Inc.) was used as yittrium precursor. O_2 was used as the reactant and high Purity *Ar* gas (>99.999%), was used as carrier and purging gas. The standard pulsing sequence in one cycle combines *7* pulsing sequences of $ZrN(Me_2)_4$ (*Pulses 1-4*) followed by *1* pulsing sequence of $Y(MeCp)_3$ (*Pulses 5-8*). The deposition temperature was *250°C.* The volatilization temperatures of precursors were *190°C* for $Y(MeCp)_3$ and *80°C* for $ZrN(Me_2)_4$.

Sputtering of YSZ films was done at room temperature, *8at% Y-Zr* target in a reactive Ar atmosphere. The experimental device is a sputtering chamber pumped down *via* turbo-molecular pump, allowing a base vacuum of 10^{-4} *Pa*.

Table 1. ALD YSZ single cycle recipe

Pulse No.	Pulse 1 *1st Precusor*	Pulse 2 *1st Purge*	Pulse 3 *Reactant*	Pulse 4 *2nd Purge*
Time	$ZrN(Me_2)_4$ 5s	Ar 30s	O_2 1s	Ar 20s
Pulse No.	Pulse 5 *2nd Precusor*	Pulse 6 *3rd Purge*	Pulse 7 *Reactant*	Pulse 8 *4th Purge*
Time	$Y(MeCp)_3$ 6s	Ar 30s	O_2 1s	Ar 20s

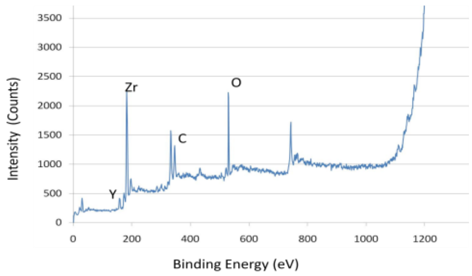

Fig 1. X-ray Photoelectron Scopy of YSZ ALD for 500 cycles

Table 2. Atomic Concentration of YSZ-ALD 480 cycles

Substance	Y 3d	Zr 3d	C 1s	O 1s
Atomic Conc%	3.02	26.18	14.96	52.07

The 2in diameter target was fixed on an unbalanced magnetron with its centre at *80mm* from the rotating substrate-holder axis. Continuous deposition was done for *10 hrs* and then resulting sample was extracted.

3. Results & Discussions

X-Ray Photoelectron Microscopy (XPS) has been shown in Fig 1. The comparison of atomic Percentages of Yittria and Zirconia show a ratio of nearly 1/9 which is consistent with the previous published results.

The results obtained by FIB of the YSZ deposited on SiO_2 wafer by ALD have been shown in Fig 2. Deposition rate of almost *1.0A°/cycle* was achieved, with ALD deposition.

Ionic conductivity measurement is most important feature for YSZ electrolyte. Schematic of the planned apparatus setup has been shown in Fig 3. The result for best composition of YSZ will be decided and then that Specimen will be tested using impedance spectroscopy method.

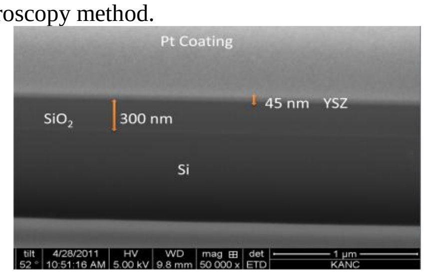

Fig. 2 FIB results of YSZ for 480 ALD cycles

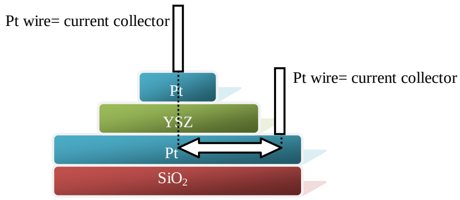

Fig 3. Schematic Conductivity measuring apparatus

4. Conclusion

Conformal thin-layers of nanometer size were formed by ALD and sputtering techniques. The micro-nanostructure and conductive properties of YSZ layers were investigated and tested. This study confirmed that YSZ thin films deposited via ALD are more uniform and show better ionic conductivity than the ones deposited through Sputtering. The deposition rate is also faster in case of ALD than in Sputtering.

References

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