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# FABRICATION OF YSZ THIN FILM BY ELECTROCHEMICAL DEPOSITION METHOD AND THE EFFECT OF THE PULSED ELECTRICAL FIELDS FOR MORPHOLOGY CONTROL

# OTRZYMYWANIE CIENKICH WARSTW YSZ METODĄ OSADZANIA ELEKTROCHEMICZNEGO ORAZ WPŁYW PULSACYJNYCH PÓL ELEKTRYCZNYCH NA KONTROLĘ MORFOLOGII

In this study, surface morphology control ions in a precursor solution and patterning the YSZ film has been carried out during deposition of thin film from a precursor solution by applying the electrical field for deposition and the pulsed electrical field. The precursor solution was mixed them of $ZrO(NO_3)_4$, $Y(NO_3)_3$ -$6H_2O$ into deionized water, and then was controlled nearly pH3 by adding $NH_3$(aq). The thin film was deposited on the glass substrate of the minus electrode side by applying the electrical field of 3.0 V for 20 min. In addition, another pulsed voltage was applied to the electrical field along the perdicular direction to the film deposition direction. After annealing samples at 773 K for 6 h in air, the film was crystallized and obtained YSZ film. In the limited condition, the linear patterns of YSZ films due to the frequency of the applied electrical field were observed. It is expected that ions in a precursor solution are controlled by applying the pulsed voltage and the YSZ film is patterned on the substrate.

*Keywords*: yittria stabilized zirconia, thin film, electrochemical deposition method, pulsed electical field, morphology control

W niniejszej pracy cienkie warstwy YSZ otrzymywano metodą elektochemiczną z roztworu. Morfologia otrzymanej warswy była kontrolowana poprzez zastosowanie pulsacyjnego pola elektrycznego. Roztwór prekursora otrzymano poprzez zmieszanie $ZrO(NO_3)_4$, $Y(NO_3)_3$ -$6H_2O$ w wodzie dejonizowanej, przy czym pH roztworu było utzrymywane na stałym poziomie (pH = 3) poprzez dodawanie $NH_3$(aq). Na podłoże szklane naniesiono cienką warstwę po stronie ujemnej elektrody przykładając pole elektryczne o napięciu 3,0 V przez 20 min. Dodatkowo, przyłożono napięcie pulsacyjne do pola elektrycznego w kierunku prostopadłym do kierunku nanoszenia warstwy. Po kalcynacji próbek w 773 K przez 6 godz. w powietrzu, warstwa uległa krystalizacji i otrzymano warstwę YSZ. W tych warunkach zaobserwowano liniowe odwzorowanie warstw YSZ spowodowane częstotliwością przyłożonego pola elektrycznego. Przypuszcza się, że przyłożone napięcie pulsacyjne kontroluje jony w roztworze prekursora, co wpływa na strukturę warstwy YSZ.

## 1. Introduction

Zirconia is transferred to monoclinic near room temperature and tetragonal at about 1170°C. If yitrium is made to dissolve several percent to zirconia, the cubic at a high temperature phase will even become stable at room temperature [1-2]. This is called yittria stabilized zirconia (YSZ). YSZ has high strength, heat resistance, electron insulating properties and chemical stability. Since a part of position of the oxide ion within a crystal serves as a vacancy and the conductivity of an oxide ion increases especially, it is used for an electronic device, such as oxygen sensor. Photolithography is used for the patterning of the semiconductor element's circuit constituting the electronic device [3]. This is technique to pattern the circuit on the substrate with photosensitive agent, called photoresist. If we omit the photolithography in the manufacturing process of the semiconductor element, it leads to reduce environmental burden and lower manufacturing costs. YSZ thin film was fabricated by CVD [4] or PVD methods including RF sputtering [5-8], pulsed laser deposition [9], spin coating [10], electrophoretic deposition [11]. In this study, the film was fabricated by electrochemical deposition method which film was deposited by applying the film deposition voltage and the pulsed voltage. It is expected that ions in a precursor solution are controlled by applying the pulsed voltage and the YSZ film is patterned on the substrate.

## 2. Experimental

The precursor solution were mixed $ZrO(NO_3)_4$, $Y(NO_3)_3$-$6H_2O$ into deionized water and were adjusted to 92 mol%$ZrO_2$-8 mol%$YO_{1.5}$ and 0.1 mol/dm$^3$. Then, the solution were controlled nearly pH3 by adding $NH_3$(aq) to promote the

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production of $Zr(OH)_4$. Glass substrate ($9.0\times9.0\times0.15$ $mm^3$) were cleaned ultrasonically with an acetone for 15 min and then were washed with deionized water. The glass substrate was placed with the distance of 0.1 mm from the minus electrode. the YSZ thin film was deposited on the minus electrode side of the glass substrate by applying a constant 3.0 V for 20 min. Besides, a triangle square type pulsed voltage of 2.5 V was applied along the perpendicular direction to the film deposition direction at same time. Its frequency was changed from 0 to 5 Hz. Heat treatment was performed to obtain crystallized YSZ. The film morphology was observed by the optical microscope (Microscope BH-2, OLYMPUS) and low vacuum scanning electron microscope (LVSEM, TM-1000, HITACHI). Their chemical composition of the film was determined by EDS (EDS, EAGLE -Probe, EDAX Inc). Elemental map of the film were analyzed by an x-ray fluorescence spectrometer (EPMA, JXA-8230, JEOL) [12].

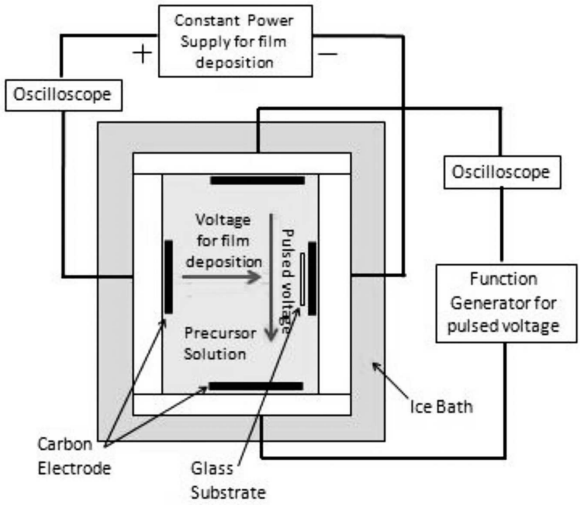



Fig. 1. A schematic diagram of the equipment for thin film deposition

## 3. Result and discussion

Fig. 2 is a qualitative analysis of the results obtained by EDX in the deposition location of the sample. Samples were analyzed by EDX and it was observed that the peak of Zirconium was high. It was found that deposition was contained zirconium.

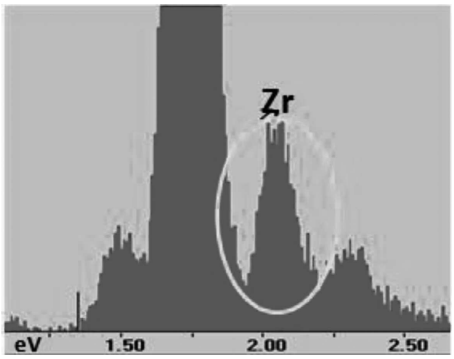



Fig. 2. The result of qualitative analysis obtained by EDX in the deposition location of the sample applied the pulsed voltage of frequency 5 Hz

Also, Fig. 3 is the elemental map of the fabricated samples by EPMA. (a) is the elemental map of Zr, (b) is SEM image of the deposition location. Zr was abundantly detected along the deposition in a line shape that could be observed in SEM image. From these, it was found that Zr was deposited in a line shape by applying the pulsed voltage.

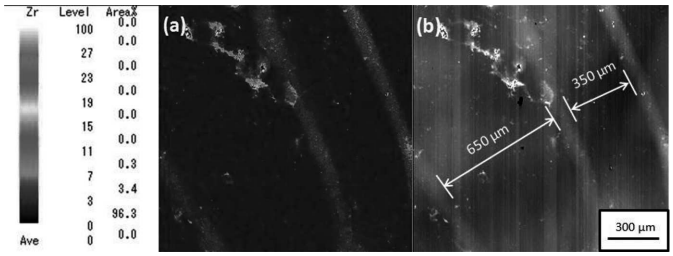
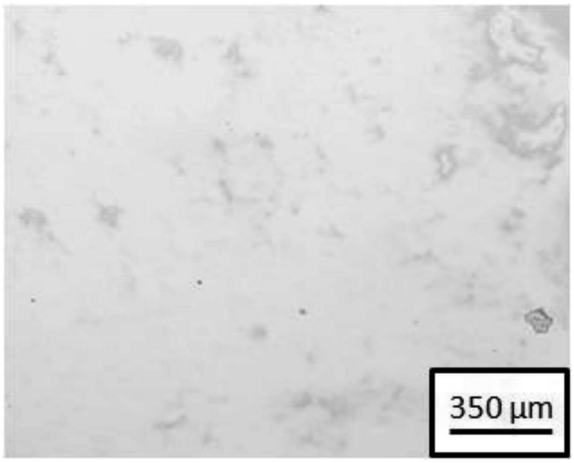



Fig. 3. Elemental map of the fabricated samples by EPMA; (a) Elemental map of Zr, (b) SEM image

Fig. 4 is the result of surface observation with an optical microscope for serface modification[13]. Fig. 4(a) is a sample applied the pulsed voltage of frequency 0 Hz. Samples were applied the pulsed voltage of frequency (b) 1 Hz and (c) 4 Hz. Fig. 5 is the result of surface observation of 1 Hz with the LVSEM. It could be observed the film was deposited in a widely on the substrate, as shown Fig. 4(a).YSZ film in a line shape was deposited in the direction perpendicular to the direction of the applied pulsed voltage, it could be observed that linear films was formed nearly parallel to each other, as shown Fig. 4(b), (c) and Fig. 5. Also, the spacing of the linear films of Fig. 4(b) was 1100 $\mu$m and that of Fig. 4(c) was 750 $\mu$m, 825 $\mu$m. Therefore, this result was that frequency of the pulsed voltage was related to spacing of the deposition location. The relationship was that the higher frequency of the pulsed voltage became, the narrower spacing of the deposition location was.



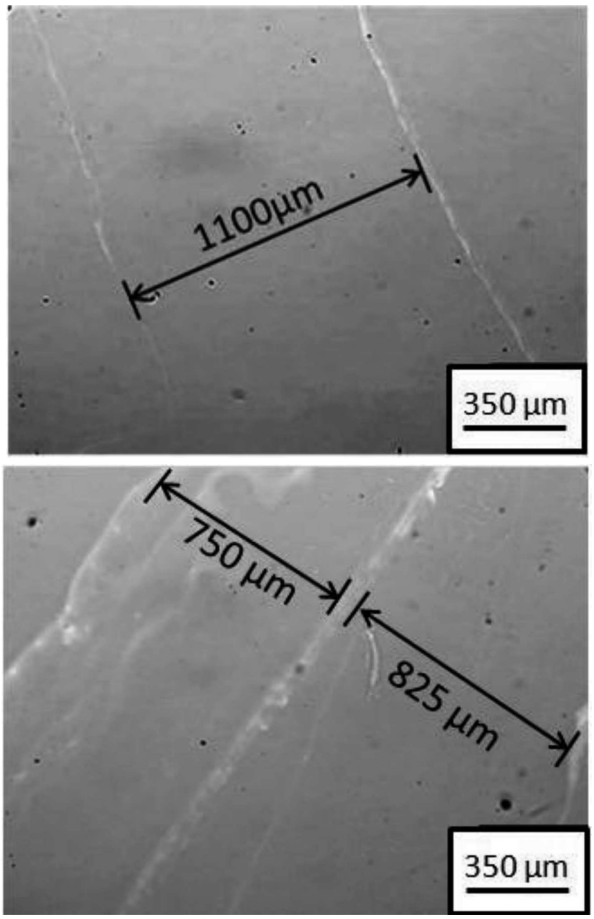



Fig. 4. The optical microscope images of surface observation; (a) 0 Hz (b) 1 Hz (c) 4 Hz

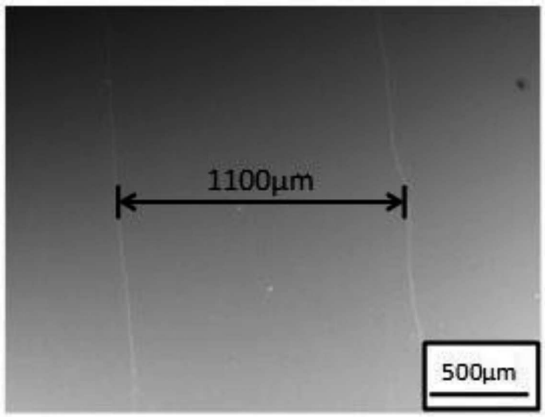
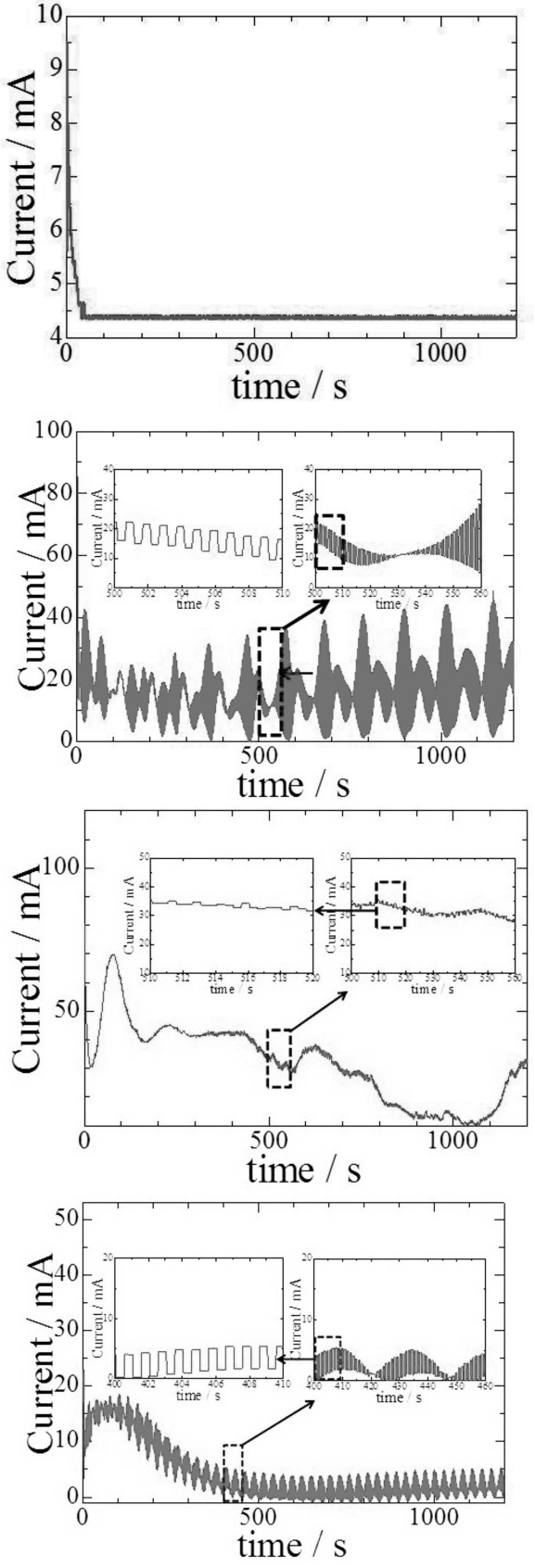



Fig. 5. The LVSEM image of surface observation in the deposition location of the sample applied the pulsed voltage of frequency 1 Hz

Fig. 6 is the deposision current change during the film deposition at each frequency of the pulsed voltage was measured by an oscilloscope. During applying the voltage, deposition current was reduced, as shown in Fig. 5 (a). It could be considered that ions in the solution were moved by applying the voltage and then the reaction to produce hydroxide after equilibration was reached. Also, the current change could be observed regularly waveform when the 1,3,4,5 Hz, the frequency of the pulsed voltage. But the current change could be observed irregularly waveform when 2 Hz, the frequency of the pulsed voltage.



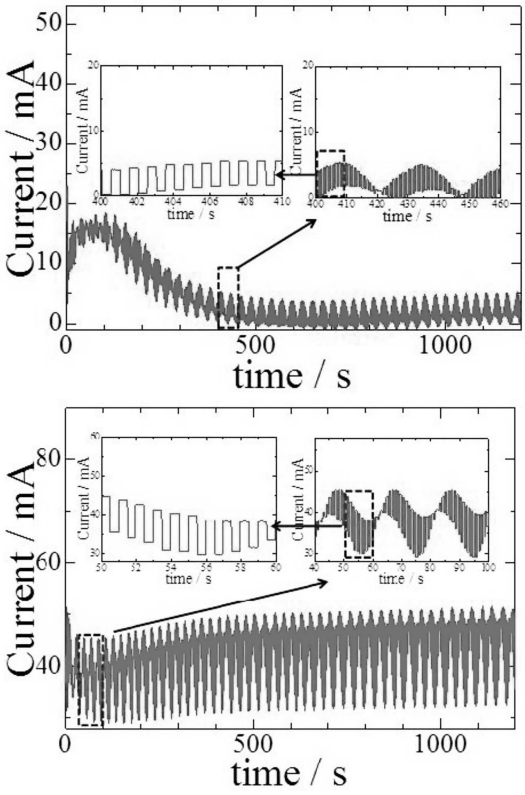



Fig. 6. The deposision current change during the film deposition at each frequency of the pulsed voltage was measured by an oscilloscope; (a) 0 Hz (b) 1Hz (c) 2 Hz (d) 3 Hz (e) 4 Hz (f) 5 Hz

The movement of ions between glass substrate and the minus electrode was considered as following. Negative ions were moved to the plus electrode side, the positive ions such as hydrogen ion were moved to the minus electrode side by applying a deposition voltage. Hydrogen was gradually generated, and pH in the solution was risen and the hydroxide ion moved to the plus electrode. Then hydroxide of zirconium was formed and the film was deposited on the glass substrate surface. In this study, the pulsed voltage was also applied, and it was caused wave in the solution near film deposition location. The wave by applying pulsed voltage was deposited the linear films because the wave by the pulsed voltage was influence on movement of ions in the solution.

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## 4. Conclusions

In this study, the film was fabricated by electrochemical deposition method which film was deposited by applying the film deposition voltage and the pulsed voltage.

Samples were analyzed by EDX and it was found that deposition was contained zirconium, as shown Fig. 2.

The relationship between frequency of the pulsed voltage and spacing of the deposition location was considered that the higher frequency of the pulsed voltage became, the narrower spacing of the deposition location was, as shown Fig. 4, 5.

This was because the wave by the pulsed voltage was influence on movement of ions in the solution.

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