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Research Article

Influence of Deposition Condition on Y_2O_3 Coatings Produced by Pulsed Electrophoretic Deposition

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Y_2O_3 nanoparticle suspension aqueous solution was prepared using citric acid. Then, Y_2O_3 film was deposited using this solution with pulsed electrophoretic deposition (EPD). A dense Y_2O_3 film of 25.7 μm thickness was obtained with deposition conditions of 0.5 wt% Y_2O_3 concentration, bias voltage of 0.5 V, and bias frequency of 1 kHz. The respective resistivities of the as-deposited film and films heat-treated at 200°C and 400°C were 2.84×10^3 Ω·cm, 5.36×10^4 Ω·cm, and 2.05×10^6 Ω·cm. A 59.8 μm thick dense Y_2O_3 film was obtained using two-step deposition with change of the bias voltage: a first step of 0.5 V and a second step of 2.0 V.

1. Introduction

Recently, semiconductor production equipment systems for dry etching have become widely used [1]. Carbon fluoride gas plasma is commonly used for high-speed etching of silicon wafers [2]. During production in equipment chambers, these plasmas invariably contact ceramic walls made of materials such as SiO_2 or Al_2O_3, thereby causing erosion of the equipment and producing contamination particles [3]. High plasma resistance is therefore necessary for the etching chamber. As a new component of dry-etching equipment, Y_2O_3 is an anticipated candidate because of its excellent resistance to plasma corrosion [4].

Substrate materials of semiconductor production equipment system components are commonly aluminum-based alloys or stainless steel. In fact, Y_2O_3 coatings are applied onto these substrates [5] using coating methods that include CVD [6], plasma spray [7], and aerosol deposition [4]. These coating techniques require vacuum systems, which are expensive resources that entail great difficulty for coating large substrates. However, the substrate materials described above show high electrical conductivity. Electrophoretic deposition (EPD), one candidate for use as Y_2O_3 coating method, enables coatings to be obtained on both planar and complex shape substrates such as spheres and bending metal parts [8]. Furthermore, films can be formed using "powders" alone. Therefore, its limitations are few for source materials. For those reasons, some EPD methods are quite suitable for Y_2O_3 coating onto alloy components of semiconductor production equipment.

In this investigation, Y_2O_3 coating was investigated using Y_2O_3 suspension aqueous solution with a pulsed EPD method. The use of AC or pulsed bias induces very little decomposition of water. Therefore, gas bubble formation in the deposits is eliminated or is greatly minimized [9]. Using a pulsed EPD method to form Y_2O_3 coatings in this investigation, we observed the effects of deposition conditions on Y_2O_3 film formation.

2. Experimental Procedure

As a starting material, Y_2O_3 (Nanophase Technologies Corp., USA) powder was used. It had particle size of 20–90 nm. Y_2O_3 powder was put into a 1.0 wt% citric acid (Wako Pure

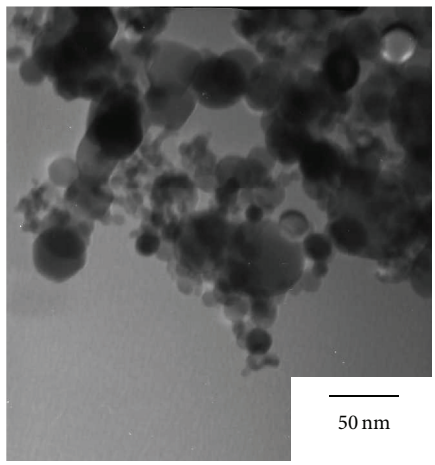


Figure 1: TEM image of the precursor Y_2O_3 nanoparticles.

Chemical Inds. Ltd., Osaka, Japan) aqueous solution with the Y_2O_3 weight ratio of 0.5–5 wt%. Citric acid was used to stabilize the Y_2O_3 suspension aqueous solution [10]. The resulting Y_2O_3 suspension solution was subjected to ultrasonic waves. The suspension solution was stirred. Stainless steel was used as the substrate. It was soaked in the suspension. Y_2O_3 deposition on this substrate was conducted by application of a pulsed bias to substrates using a universal source (HP-3245A; Agilent Technologies Inc.). The bias voltage applied to substrates was −0.5 to −5.0 V (hereinafter, we call a negative bias value simply an absolute bias value). The bias frequency was 10–100 kHz. Deposition was conducted for 1 h. The deposited films were dried at 70°C for 1 day.

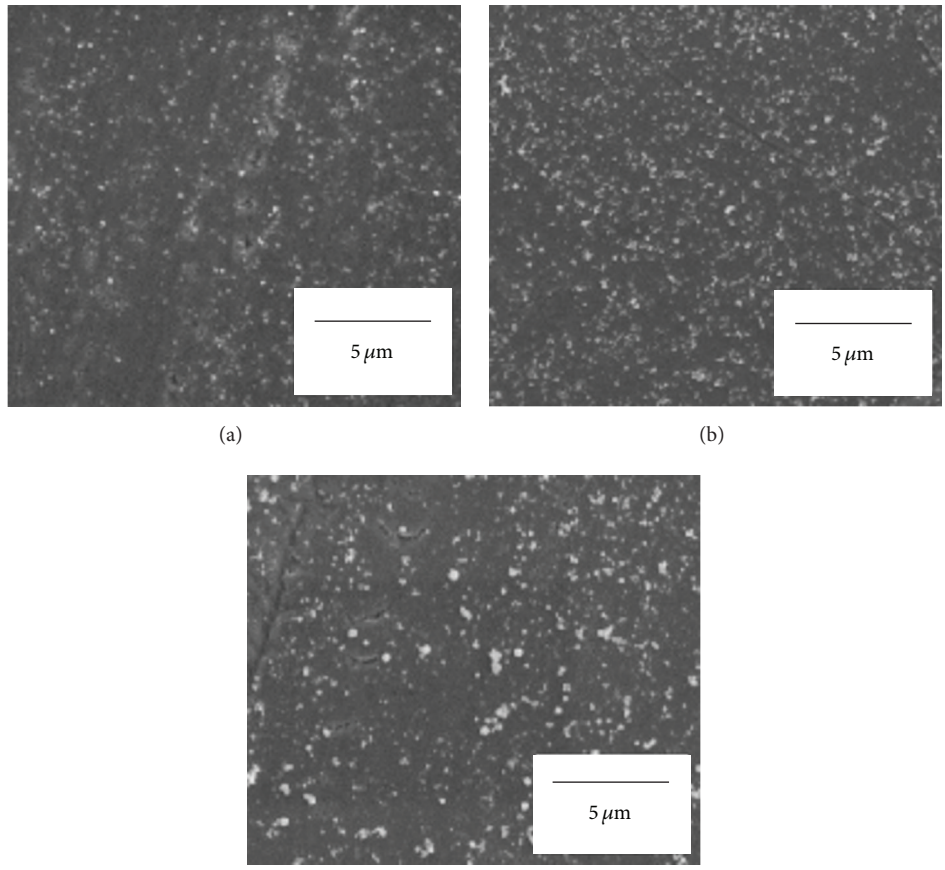
The grain size and form of the Y_2O_3 particles were evaluated using transmission electron microscopy (TEM, EM-002B; Topcon Corp.). The microstructures of the resulting powders were observed using a scanning electron microscope (SEM, JSM-6510; JEOL). Resistivity of the resulting films was evaluated along with the deposition direction using a two-probe method with a DC source (HP-3654; Hewlett Packard Co.) and a digital voltmeter (HP34401; Hewlett Packard Co.).

3. Results and Discussion

The Y_2O_3 particle microstructure was observed using TEM, as presented in Figure 1. The Y_2O_3 particle grain size was 20–90 nm. The form was spheroidal. The Y_2O_3 coatings were applied with different conditions of concentration (wt%) of suspension solution, frequency of applied bias voltage, and the applied bias voltage using Y_2O_3 particles.

Figures 2 and 3 present surface and cross-sectional SEM images of films deposited under various Y_2O_3 concentrations of a suspension solution (0.5, 2.0, and 5.0 wt%). The dashed circles in the figures indicate the pores or cracks. The coating was conducted under bias voltage of 0.5 V and bias frequency of 1 kHz. The mean thicknesses of films with Y_2O_3 concentrations of 0.5, 2.0, and 5.0 wt% were, respectively, 25.7 μm, 23.4 μm, and 23.0 μm. Increasing the Y_2O_3 concentration in a solution decreased the film thickness slightly, but the film thickness did not depend much on the Y_2O_3 concentration in the solution. The film produced using a 0.5 wt% solution was dense with pores that were free from the cross-sectional image (Figure 3(a)). A few particles were adsorbed onto the film surface (Figure 2(a)). Increasing the Y_2O_3 concentration in the solution increased the adsorbing particles of various sizes including large sizes on the film surface (Figures 2(b) and 2(c)) and an increase in small pores in the films (Figures 3(b) and 3(c)). These large particles were assumed to be the aggregated Y_2O_3 particles. Aggregation of Y_2O_3 particles occurred in a high Y_2O_3 concentration solution. Many large particles were adsorbed onto the growing films' surface at deposition. Presumably, the adsorption of large particles at the growing film surface did not form a dense film because homogeneous Y_2O_3 film growth was prevented by the existence of the adsorbed large particles. Consequently, dense Y_2O_3 films with a few adsorptions were obtained using a low Y_2O_3 concentration solution. The optimal concentration in this study was found to be 0.5 wt%.

To confirm the effects of bias frequency, Y_2O_3 films were deposited to the substrates with different bias frequencies. Figures 4 and 5 show surface and cross-sectional SEM images of the films deposited using various bias frequencies (10 Hz, 1 kHz, and 100 kHz). The dashed circles in the figures indicate the pores or cracks. The coating was conducted with bias voltage of 0.5 V and the Y_2O_3 concentration of 0.5 wt% in a suspension solution. For ease of comparison of the SEM images, an SEM image of the film under bias voltage of 0.5 V is shown in Figures 4(b) and 5(b). The mean thicknesses of the films with bias frequencies of 10 Hz, 1 kHz, and 100 kHz were 36.9 μm, 25.7 μm, and 41.0 μm, respectively. The film thickness depended slightly on the bias frequency. For a film deposited with the bias frequency of 10 Hz, many particles were observed on the film surface (Figure 4(a)). Small pores and voids were observed in the film (Figure 5(a)). Furthermore, gas bubbles were generated during film deposition with the bias frequency of 10 Hz because of electrolysis.



(a) (b)

(c)

Figure 2: Surface SEM images of the films deposited at various Y_2O_3 concentrations in a suspension solution (0.5, 2.0, and 5.0 wt%), with bias voltage of 0.5 V and bias frequency of 1 kHz.

This electrolysis phenomenon caused some damage (pores and voids) to the resulting film. Both films with bias frequencies of 1 kHz and 100 kHz were dense with pores free from cross-sectional images (Figures 5(b) and 5(c)). A few particles were adsorbed onto the film surface (Figures 4(b) and 4(c)). No great differences between films with bias frequencies of 1 kHz and 100 kHz were observed. A low bias frequency prohibited formation of a dense film, although a high bias frequency (higher than 1 kHz in this investigation) causes formation of a dense film with few adsorptions.

To confirm the effects of bias voltage, Y_2O_3 films were deposited onto the substrates with different bias voltages. The Y_2O_3 concentration and the bias frequency were fixed, respectively, as 0.5 wt% and 1 kHz. Figures 6 and 7 present surface and the cross-sectional SEM images of films deposited at various bias voltages: 0.5, 2.0, and 5 V. To compare the SEM images easily, the SEM image of the film under the condition of 0.5 V is depicted again as in Figures 6(a) and 7(a). The dashed circles in the figures indicate the pores or cracks. The mean thicknesses of the films with bias voltages of 0.5, 2.0, and 5 V were, respectively, 25.7 μm, 35.5 μm, and 35.1 μm. The film thickness increased slightly with increased bias voltage. Increasing the bias voltage caused an increase of particle absorbance onto the film surface (Figures 6(a)–6(c)) and an increase of small pores in the films (Figures 7(a)–7(c)). The greater the bias voltage applied to the substrate at deposition, the more the particles in the suspension solution moved to the substrate electrophoretically. Presumably, the adsorption of large particles at the growing film surface does not cause the formation of a dense film because homogeneous Y_2O_3 film growth was prevented by the existence of the large particles that had been adsorbed. Furthermore, these adsorptions presumably caused generation of many pores when growing films at higher bias voltages. Thereby, low bias voltage was shown to be suitable for Y_2O_3 film deposition using a pulsed EPD method.

Results showed that Y_2O_3 dense films were obtainable under the deposition conditions: low Y_2O_3 concentration (0.5 wt%), high bias frequency (higher than 1 kHz), and low bias voltage (0.5 V). We attempted deposition with a longer deposition time (longer than 1 h), but the film thickness did not correspond to the condition described above. In general, the resistivity of Y_2O_3 is 10^{14} Ω·cm [11]. When the film thickness was large, the film resistance was high. The effective electrical field of the film surface decreased with increasing film thickness because of the increased film resistance.

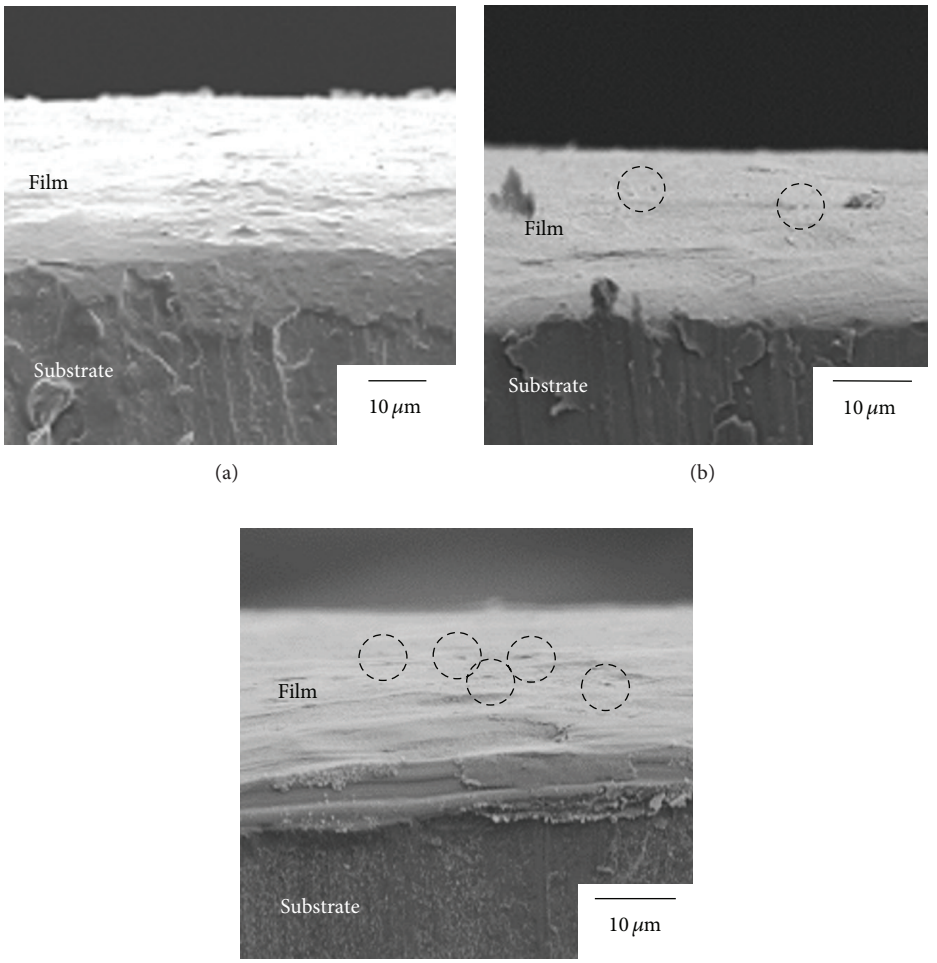


FIGURE 3: Cross-sectional SEM images of films deposited at various Y_2O_3 concentrations in a suspension solution (0.5, 2.0, and 5.0 wt%), with bias voltage of 0.5 V and bias frequency of 1 kHz.

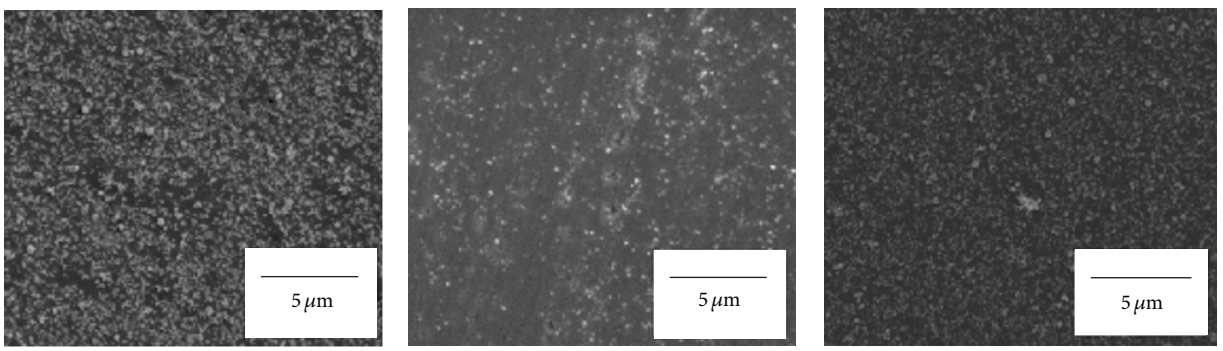
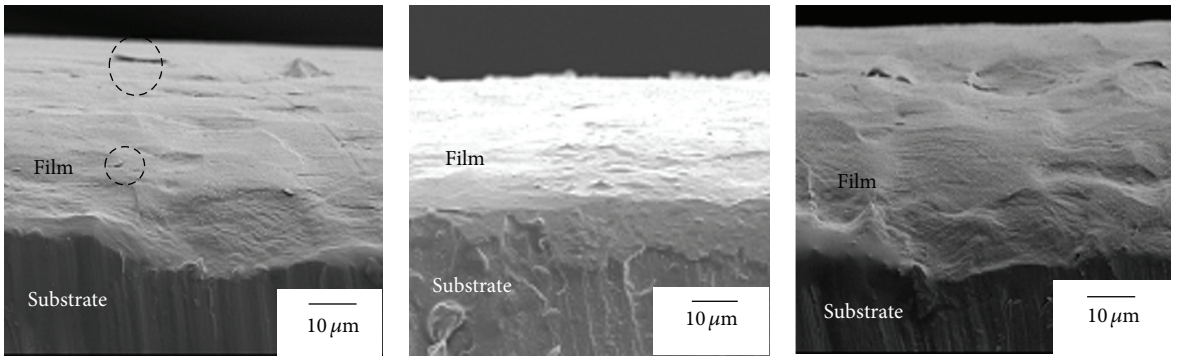
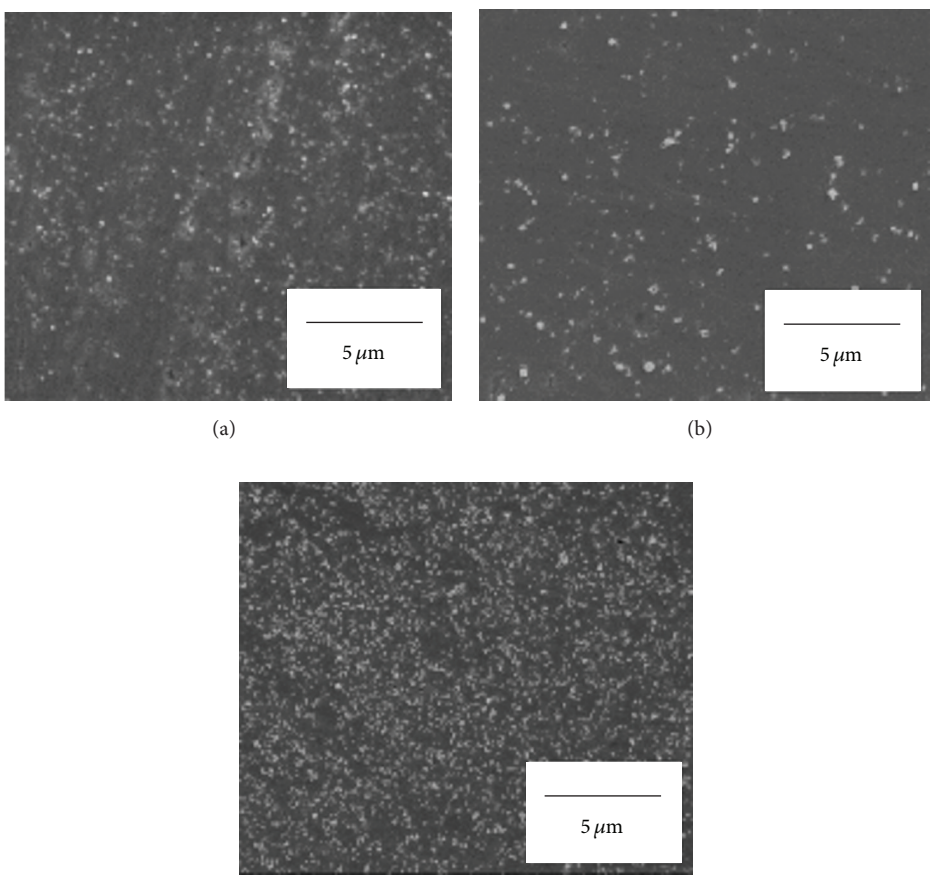


FIGURE 4: Surface SEM images of films deposited at various bias frequencies (10 Hz, 1 kHz, and 100 kHz), with bias voltage of 0.5 V and Y_2O_3 concentration of 0.5 wt% in a suspension solution.



(a) (b) (c)

FIGURE 5: Cross-sectional SEM images of films deposited at various bias frequencies (10 Hz, 1 kHz, and 100 kHz), with bias voltage of 0.5 V and Y_2O_3 concentration of 0.5 wt% in a suspension solution.



(a) (b)

(c)

FIGURE 6: Surface SEM images of the films deposited at various bias voltages (0.5, 2.0, and 5 V), with bias frequency of 1 kHz and the Y_2O_3 concentration of 0.5 wt% in a suspension solution.

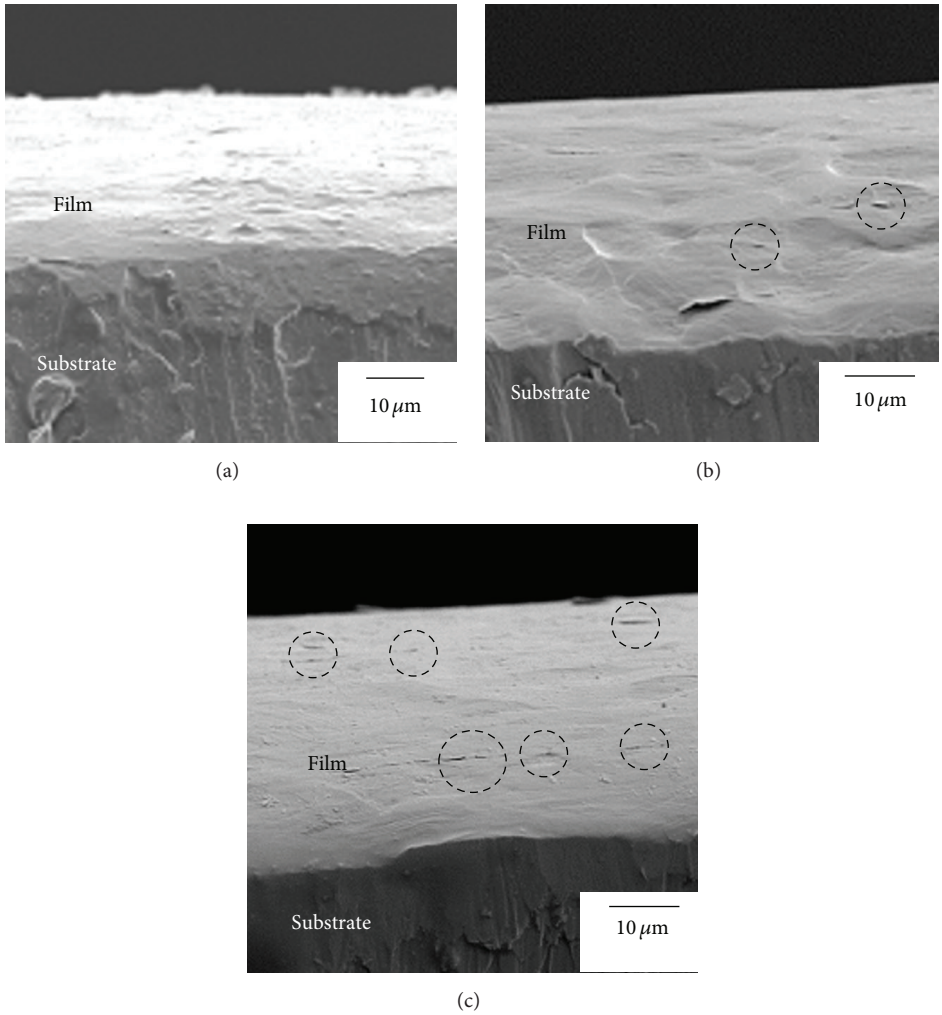


Figure 7: Cross-sectional SEM images of films deposited at various bias voltages (0.5, 2.0, and 5 V), with bias frequency of 1 kHz and the Y_2O_3 concentration of 0.5 wt% in a suspension solution.

The present study showed a limitation of Y_2O_3 film thickness that exists when using the pulsed EPD method with constant bias voltage.

To evaluate the electric insulation of the resulting Y_2O_3 film, the resistivity was measured for an as-deposited film. Furthermore, the resistivity of a film that was heat-treated at 200°C and 400°C was measured. The resistivity of the as-deposited film and the films heat-treated at 200°C and 400°C was, respectively, 2.84×10^3 Ω·cm, 5.36×10^4 Ω·cm, and 2.05×10^6 Ω·cm. Although the resistivity of the as-deposited film was lower than the reported value of 1×10^{14} Ω·cm [11], the as-deposited film showed sufficient electrical insulation, which suggests that some limitation of Y_2O_3 film thickness exists in relation to pulsed EPD method because of the film's high resistivity. The resistivity of the film that had been heat-treated at 200°C increased corresponding to that of the as-deposited film. This result is assumed to be attributable to residual water removed from films by heat treatment at 200°C. The resistivity of the film that was heat-treated at 400°C increased more than that of the film heat-treated at 200°C, presumably because of the removal of residual citric acid in the films. The resistivity of the film that had been heat-treated at 400°C was 2.05×10^6 Ω·cm, which was much less than the reported value of 1×10^{14} Ω·cm. The resulting films require some other heat or vacuum treatment to obtain pure Y_2O_3 films.

A dense Y_2O_3 film with film thickness of 25.7 μm was obtained using pulsed EPD method under deposition conditions of Y_2O_3 concentration of 0.5 wt%, bias frequency of 1 kHz, bias voltage of 0.5 V, and deposition time of 1 h, but a thicker Y_2O_3 film is necessary for application to semiconductor production equipment. Therefore, we attempted fabrication of a dense, thick film using two-step deposition with different bias voltages. The first step was deposition with conditions of 0.5 wt% Y_2O_3 concentration, bias voltage of 0.5 V, bias frequency of 1 kHz, and 1-hour deposition.

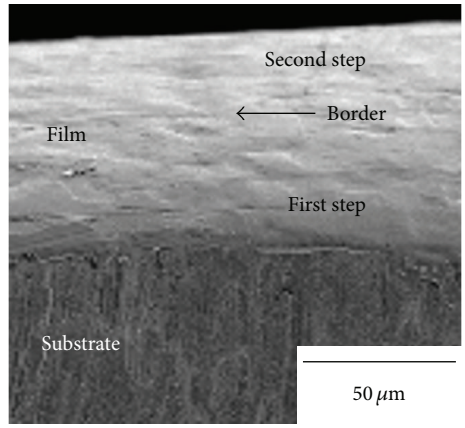


Figure 8: Cross-sectional SEM images of the films with two-step depositions. The first-step deposition condition was 0.5 wt% Y_2O_3 concentration, with bias voltage of 0.5 V, bias frequency of 1 kHz, and deposition time of 1 h. The second-step deposition condition was 0.5 wt% Y_2O_3 concentration, with bias voltage of "2.0 V," bias frequency of 1 kHz, and deposition time of 1 h.

The second step was increased bias voltage (2.0 V). Other deposition conditions were identical to those of the first deposition. Figure 8 presents SEM images of the films deposited with the second-step bias of 2.0 V. The film thickness produced with the second-step bias of 2.0 V was about 59.8 μm. A borderline between the first-step deposition and the second-step deposition was observed at around 30.3 μm from the substrate. This result suggests that Y_2O_3 dense and thick film can be deposited using two-step deposition with changing of the bias voltage. To obtain a dense, thick film using pulsed EPD, two or more deposition steps with different bias voltages are very useful.

4. Conclusion

Using pulsed EPD, Y_2O_3 films were deposited. To obtain a dense Y_2O_3 film using that method, the effective deposition conditions were found to be the following: low Y_2O_3 concentration solution, high bias frequency, and low bias voltage. Increasing the Y_2O_3 concentration in a solution slightly decreased the film thickness. The resulting Y_2O_3 films contain water and some organics derived from the Y_2O_3 suspension solution. Heat treatment was necessary to remove the residual water and organics from the resulting Y_2O_3 films. Results show that Y_2O_3 dense film thickness can be controlled through deposition while changing the bias voltage in two or more steps.

Competing Interests

The authors declare that they have no competing interests.

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