

# Effect of poly(acrylic acid) on the preparation of thick silica films by electrophoretic sol–gel deposition of re-dispersed silica particles

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Thick silica films were prepared by the electrophoretic sol–gel deposition technique in the presence of poly(acrylic acid) (PAA) using monodispersed silica particles; the particles were prepared by the sol–gel method, pre-heat treated and then re-dispersed in the mixture of H<sub>2</sub>O and ethanol. The weight of deposited silica films was maximized when 0.2 mass % of PAA against the whole amount of sol was added. The particles constructing the thick silica films were packed densely when the amount of added PAA was less than 0.2 mass %. The weight of the film increased with decrease in the content of H<sub>2</sub>O in the sol when a fixed amount of PAA was added. After the heat treatment of deposited films at 800 °C, crack-free silica films of about 30 μm thickness were prepared. © 1998 Chapman & Hall

## 1. Introduction

The sol–gel method has widely been used for the preparation of oxide films by dip-coating or spin-coating procedures [1, 2]. These procedures are suitable for preparing thin films less than 1 μm in thickness. However, it is difficult to obtain films thicker than a micrometre by these procedures. Therefore, a method repeating these procedures is usually employed to obtain thick films of several micrometres in thickness.

Electrophoretic sol–gel deposition is a useful method for preparing thick silica films of several micrometres thickness by only one coating process [3–5]. However, such films tend to be microcracked because of the shrinkage of silica particles in the stage of drying and heat treatment. We have tried to prevent the microcracks in the following two ways.

One is to employ an organic binder such as poly(acrylic acid) (PAA). PAA is useful to improve the adhesion between particles. When silica sols for electrophoretic deposition were prepared in the presence of PAA, the films had no microcracks after drying of the films [3].

The other way to avoid the microcracking is to use much denser silica particles which will not shrink on heat treatment. We separated silica particles from the silica sols prepared by the sol–gel method; the silica particles were heat treated at 600 °C and then re-dispersed in a dispersant to make sols for the electrophoretic deposition. The silica films obtained had no microcracks even after heat treatment at 800 °C [4].

In the present study, we tried to prepare thicker silica films with no cracks after heat treatment by

combining the two ways mentioned above. We investigated the effects of PAA and the mole ratio of H<sub>2</sub>O to ethanol (EtOH) on the weight of silica films deposited on stainless steel sheets. We observed the surface structure of the films and discuss the mechanism of microcracking occurring in the stage of drying and heat treatment.

## 2. Experimental procedure

Silica particles of 0.32 μm and 0.17 μm in average diameter were prepared by hydrolysis of tetraethoxysilane in the same way as we have previously reported [5]. In order to prevent further shrinkage in the drying stage of films, these particles were heat treated at 600 °C for 12 h. Prior to the electrophoretic deposition, H<sub>2</sub>O and EtOH were distilled and the pH of H<sub>2</sub>O was adjusted to be 11.7 by adding ammonium hydroxide. The amount of silica particles was 1 mass % and the amount of PAA added was 0–0.5 mass % with respect to the total amount of the sol. The mole ratio of H<sub>2</sub>O to EtOH was varied from 0.18 to 1.00. The total mass of the sol was 70 g. Silica particles were dispersed in EtOH by ultrasonication. Aqueous ammonium hydroxide containing PAA was also diluted with the same amount of EtOH. The two solutions were mixed. Electrophoretic deposition of thick silica films on the stainless steel sheets (SUS430) was performed in the same manner as reported in a previous paper [4]. Coated substrates were dried at room temperature for 24 h in a silica–gel desiccator. Heat treatment of the films was carried out in air at 800 °C. The masses of deposited silica films were measured with a Mettler M5SA microbalance. The

microstructure of the surface and cross-section of the films was observed using a JEOL JSM-5300 scanning electron microscope. The film thickness was also estimated from the scanning electron microscopy (SEM) photographs.

### 3. Results and discussion

Fig. 1 shows the mass of silica films deposited on stainless steel sheets against the concentration of PAA for the deposition times of 5 and 20 min. The silica particles used were  $0.32\ \mu\text{m}$  in average diameter and the applied voltage was 40 V. The  $\text{H}_2\text{O}$ -to-EtOH mole ratio of the dispersing medium was 1.00. The films prepared under the above conditions had no microcracks after drying. The mass of the deposited films is maximized at the PAA concentration of 0.2 mass % for any deposition time. When the concentration of PAA is lower than 0.2 mass %, the mass of the deposited silica film increased with increasing PAA. In this region, PAA must act as a binder and promote the deposition of the silica particles. When the concentration of PAA added is higher than 0.2 mass %, the mass decreased with increase in the PAA concentration; this is caused by the fact that the pH of the sol was decreased by the addition of the weak acid PAA and the surface negative charge of dispersed silica particles was decreased.

Fig. 2 shows the SEM photographs of the thick silica films prepared using various amounts of PAA. All the films were free from cracks in the stage of drying. Without PAA, silica particles are regularly arranged and densely packed to form a film with a smooth surface (Fig. 2a). When 0.2 mass % PAA is

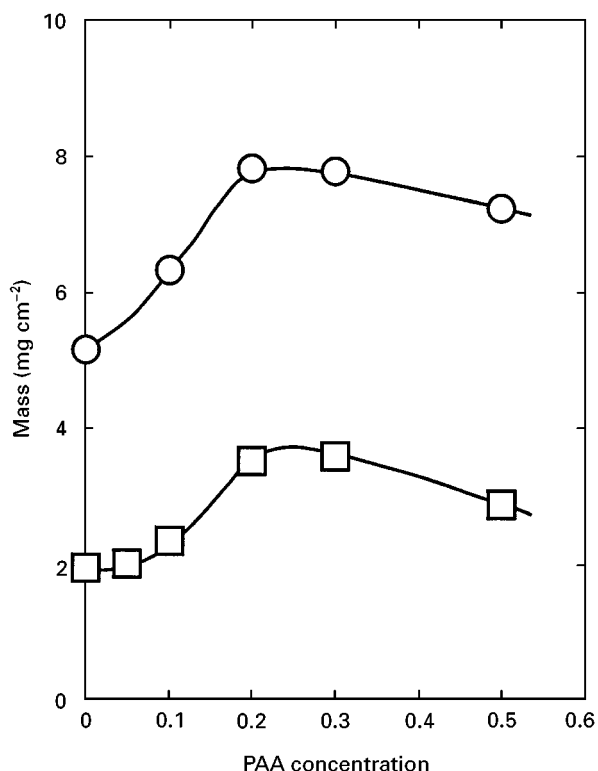


Figure 1 Mass of deposited silica films as a function of PAA added. The deposition times were 20 min (○) and 5 min (□).

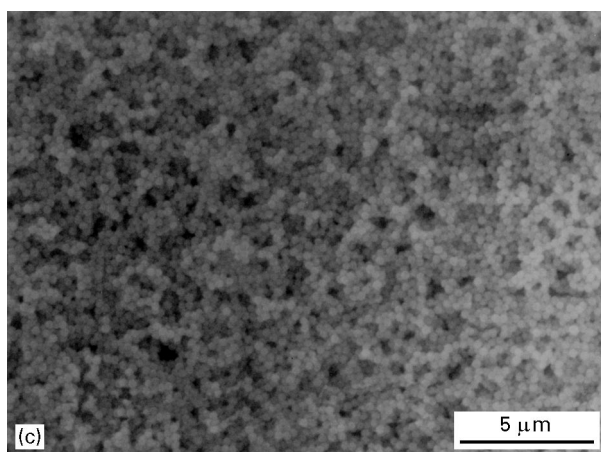
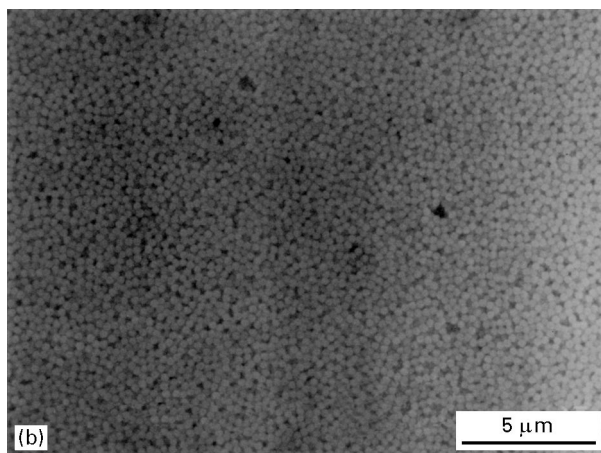
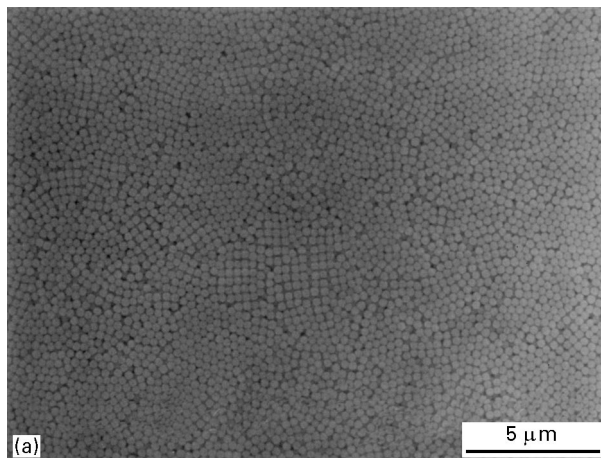


Figure 2 SEM photographs of the surface of thick silica films. The amounts of PAA added were (a) 0, (b) 0.2 mass % and (c) 0.5 mass %.

added, the arrangement of the particles is slightly irregular. However, a dense and smooth surface structure is still observed (Fig. 2b). When the concentration of PAA added is higher than 0.2 mass %, a densely packed structure is no longer observed (Fig. 2c). Without PAA, adhesion between the particles in the as-deposited films was so small that particles in the film could be rearranged to the more stable positions. Consequently, a dense, smooth and well-arranged structure was obtained, as shown in Fig. 2a. When 0.2 mass % PAA was added, as-deposited particles could also be rearranged. However, the particles could

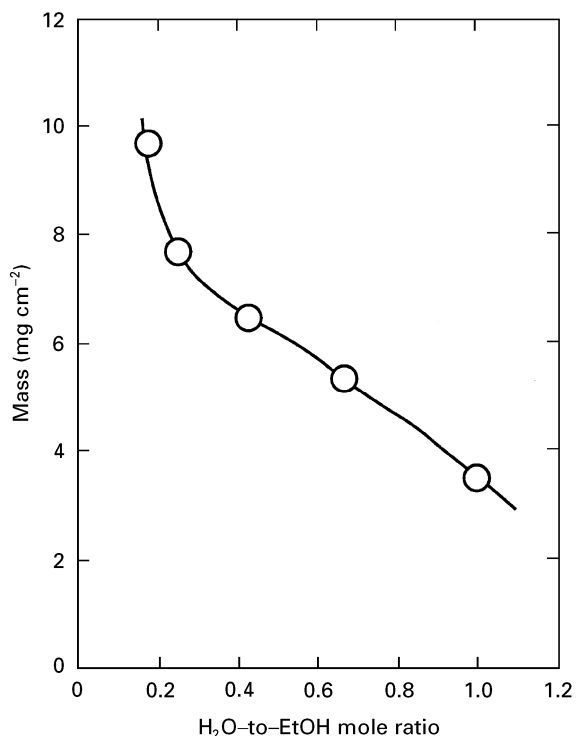


Figure 3 Mass of deposited silica films as a function of H<sub>2</sub>O-to-EtOH mole ratio of dispersing medium. The amount of PAA added was 0.1 mass%.

not be rearranged completely because of the adhesion of PAA. The surface structure of the film was thus slightly irregular compared with the film obtained

without PAA. When the PAA concentration was as high as 0.5 mass%, the particles once deposited on the substrate could not be rearranged because of strong adhesion between the particles. The rough surface structure was thus obtained as shown in Fig. 2c.

Fig. 3 shows the mass of silica films deposited on the stainless steel sheet as a function of the H<sub>2</sub>O-to-EtOH mole ratio. The average diameter of silica particles was 0.32 μm. The concentration of PAA was 0.1 mass%. The applied voltage was 40 V and the deposition time was 10 min. Films obtained had no microcracks after drying at any H<sub>2</sub>O-to-EtOH ratio. The mass of deposited silica films decreases as the H<sub>2</sub>O-to-EtOH mole ratio increases. When the amount of H<sub>2</sub>O in the dispersing medium was large, the silica particles once deposited on the substrate would be peeled off because of the O<sub>2</sub> generated by electrolysis of H<sub>2</sub>O at the coating electrode [6–8].

Fig. 4a and b shows SEM photographs of the surface and cross-section of thick silica films with and without PAA, respectively. Both films were heat treated at 800 °C. The average particle diameter was 0.17 μm. The H<sub>2</sub>O-to-EtOH mole ratio was 0.25. The applied voltage was 40 V and the deposition time was 5 min in Fig. 4a and 10 min in Fig. 4b. These deposition times were adjusted to obtain the thickness shown in the SEM photographs. When 0.1 mass% PAA was added, as shown in Fig. 4b, a thick silica film of about 30 μm thickness was obtained and no cracks were generated in the surface. However, silica films prepared without PAA were cracked in spite of the

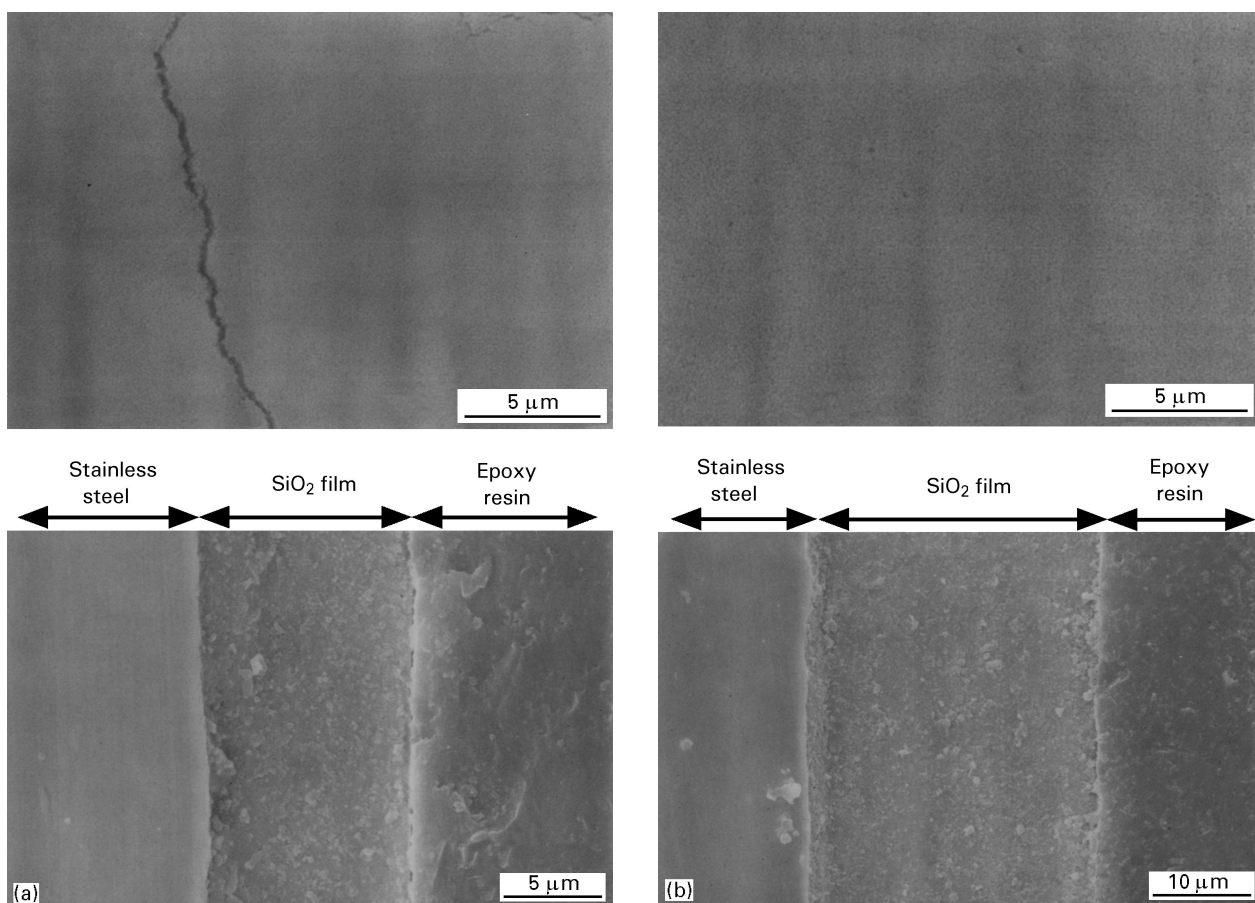


Figure 4 SEM photographs for the surface and cross-section of thick silica films after heat treatment at 800 °C. The amounts of PAA added were (a) 0 and (b) 0.1 mass%.

fact that the film thickness was thinner than the film with PAA. Such cracks must be generated in the stage of heat treatment because no cracks were observed in both films before heat treatment. In a green body, the adhesion between particles is not so strong. However, the adhesion between the particles must be increased in the stage of heat treatment. Without PAA, silica particles strongly adhered to each other in the stage of heat treatment, which caused the crack generation. In contrast, when PAA was present at the stage of heat treatment, adhesion between the silica particles was relatively small.

The sintering behaviour of ceramics in relation to the burning out of organic binders has already been reported [9]. When the binder was burn-out beforehand, the shrinkage of ceramic body was reported to occur easily. However, when burn-out and sintering occurred as a simultaneous step, the shrinkage was not so large [9]. In the present study, heat treatment of films without PAA is considered to correspond to the case when burn-out has occurred prior to the heat treatment. In contrast, the films with PAA probably corresponds to the case of the simultaneous step. Therefore, such microcracks could be prevented in the presence of PAA.

#### 4. Conclusions

Thick silica films of about 30  $\mu\text{m}$  thickness without cracks after heat treatment at 800  $^{\circ}\text{C}$  were prepared by electrophoretic deposition using silica particles of 0.17  $\mu\text{m}$  diameter and PAA; the silica particles were prepared from tetraethoxysilane. When the  $\text{H}_2\text{O}$ -to-

EtOH mole ratio of dispersing medium was fixed at 1.00, the mass of deposited silica films was maximized at the PAA concentration of 0.2 mass %. The surface structure of the films was smooth when the concentration of PAA was lower than 0.2 mass %. However, the silica particles constructing thick films were loosely packed and the surface structure became rough when the amount of added PAA was higher than 0.2 mass %. When the amount of PAA was fixed at 0.1 mass %, the mass of deposited silica particles increased with decrease in the  $\text{H}_2\text{O}$ -to-EtOH mole ratio.

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