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ScienceDirect
Current Applied Physics 9 (2009) 551–555
Current Applied Physics
An official journal of the KPS
www.elsevier.com/locate/cap
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Characteristics of silicon oxide thin films prepared by sol electrophoretic deposition method using tetraethylorthosilicate as the precursor

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Received 21 September 2007; received in revised form 17 March 2008; accepted 25 March 2008
Available online 15 May 2008

Abstract

Silicon dioxide films were prepared on p-type Si (1 0 0) substrates by sol electrophoretic deposition (EPD) using tetraethylorthosilicate (TEOS) at low temperature. According to the variation of sol dipping conditions, we estimated the characteristics of SiO_2 films, such as composition, surface morphology, wet etch rate, breakdown voltage, etc. The growth rate of the film increased linearly with increasing TEOS quantity in solution. It increased exponentially with the increase in deposition time, and the film thickness was saturated at approximately 200 nm on hydrophilic Si surface after more than 6 days. The growth rate of the EPD SiO_2 films on the hydrophobic Si surface was much lower than that of the film on the hydrophilic Si surface.
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PACS: 68.55.jk

Keywords: Silica (SiO_2); Electrophoretic deposition; Sol–gel; Tetraethylorthosilicate (TEOS); Flexible display

1. Introduction

The technological progression in thin film transistors (TFTs) has been opening up new possibilities in flat panel displays with electronic media. TFTs come in various types and among them the research and development of high-speed and large-scale displays for use as television receivers is now proceeding at a vigorous pace. For the future, there is much anticipation for large displays that provide greater reality for object images; and portable, thin flexible displays is also desirable that allow moving images to be enjoyed anytime and anywhere.

In recent years, the field of flexible displays is ever expanding with many new markets and technologies, and new technologies are in demand for fabricating TFTs and other electronic devices on flexible substrates [1–5]. The challenge is to compose thin silicon and oxide films without deforming or changing the properties of the polymer substrates. In case of the new generation poly-Si TFT using glass substrate, a poly-Si layer with low resistance is formed in a device of top gate style. Therefore, the formation of silicon films at considerably lower temperature has been explored and developed by many researchers [6–10]. However, there has been little research on oxide films as the gate dielectric and inter metal dielectric of TFTs.

Sol–gel deposition of SiO_2 films at lower processing temperature was also studied for the gate oxide of TFT for flexible displays. This sol–gel method has advantages such

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doi:10.1016/j.cap.2008.03.023

as a growth of silicon oxide film at room temperature and controls of film thickness and capacitance through the adjustment of concentration. However, the poor quality of the film deposited by sol–gel method with porous structure has been a serious problem; not only integration in device process may be very difficult due to the higher wet etch rate but also devices by this process are not well working due to the poor electrical properties such as higher leakage current and lower breakdown field.

One method with great potential for the oxide formation of flexible display TFTs and inter dielectric formation between metal to metal in semiconductor device is electrophoretic deposition (EPD). In this method, an electric field is applied to a substrate, which is different to traditional sol–gel deposition. Upon application of an external electric field to a colloidal system or a sol, the constituent charged particles are set in motion in response to the electric field. EPD film shows higher density than that of film deposited by traditional sol–gel deposition methods. This is due to the use of an oriented motion of charged particles to enrich the solid particles from a colloidal dispersion or a sol onto the surface of an electrode [11]. With these advantages, many researchers have been using the EPD method for nanowire and nanorod fabrication [12,13], and the application of the EPD method to SiO_2 film is expected to improve the capabilities of TFT for flexible displays.

In this study, silicon oxide thin films were deposited on p-type Si (1 0 0) substrates by sol EPD using tetraethylorthosilicate (TEOS) in a chemical reactor with a biasing system. The deposition characteristics of the deposited films were estimated with varying TEOS quantity in solution, deposition time, and surface conditions. Physical and electrical properties of the deposited films were comparatively characterized with those of the silicon oxide films deposited by a sol dipping method.

2. Experiments

Boron-doped Si (1 0 0) wafers were used as the substrates for EPD of SiO_2 film. Before film deposition, the surface chemistry of the substrate was modified. Initially, the substrate surface is hydrophobic. In order to obtain a hydrophilic surface, the substrates were immersed in a diluted hydrofluoric acid solution for 5 min to clean and remove a native oxide layer previously formed by air exposure. The substrates were then rinsed with deionized water and dried by blown air.

Initial silica (SiO_2) sol consisted of tetraethylorthosilicate (TEOS), deionized water (DI-H_2O), ethanol (EtOH), and hydrochloric acid (HCl). Hereafter, we will refer to this initial SiO_2 sol as 'TEOS'. In a 50 mL beaker containing a stir bar, 3 mL of DI-H_2O was added with 8 mL of EtOH and stirred at 500 RPM for ~5 min at room temperature. To the above solution, 21 mL of TEOS and 0.09 mL of HCl were added while stirring. The solution was then allowed to stir at 500 RPM for ~2 h at room temperature. After stirring, unused portions of the sol were stored at −20 °C to prevent premature condensation and gelation.

The deposition of SiO_2 film onto Si wafer was initiated by the use of sol electrophoretic deposition (EPD). Before deposition, various amounts of EtOH was added to the TEOS solution to obtain diluted sols with an EtOH:TEOS volume ratio of 2:1, 5:1, or 10:1. Additional amounts of ammonium hydroxide (NH_4OH) were added to the various sols to increase the pH above 2.2 at a pH value between 3 and 4. A titanium (Ti) plate was used as the counter-electrode and the Si wafer substrate (working electrode) was placed ~5 mm apart using an alumina spacer. The Si substrate size was 2 cm × 8 cm. The electrodes were immersed in 10 mL of sol and a potential of 1.2 V was applied to give an applied potential of 2.4 V/cm. After deposition, the films were dried at 100 °C for 1 h.

The thickness and the refractive index of the deposited films were measured using an ellipsometer (Sentech Co. SE400) in five points (top, center, bottom, left and right in a sample), and the uniformity of sample-to-sample was less than 5%. An atomic force microscope (AFM) system was used for measuring the surface. Wet etch rate of the deposited films was evaluated using a diluted 500:1 DI-H_2O:HF solution. To test the breakdown voltage of the oxide films, an aluminum electrode was formed by evaporation. The area of the electrode was 0.78 mm^2, where the I–V data was measured with an HP 4140B system.

3. Result and discussion

The thickness and the refractive index of sol–gel deposited (without bias voltage) films were investigated as a function of the TEOS quantity in solution using an Ellipsometer. As shown in Fig. 1, the thickness and the refractive index of the sol–gel deposited films increased linearly with increasing TEOS quantity. When the EtOH:TEOS volume ratio is 10:1, 5:1, and 2:1, the thickness of the deposited films were 94 nm, 75 nm, and 115 nm, respectively. It was thought that increasing the TEOS quantity in

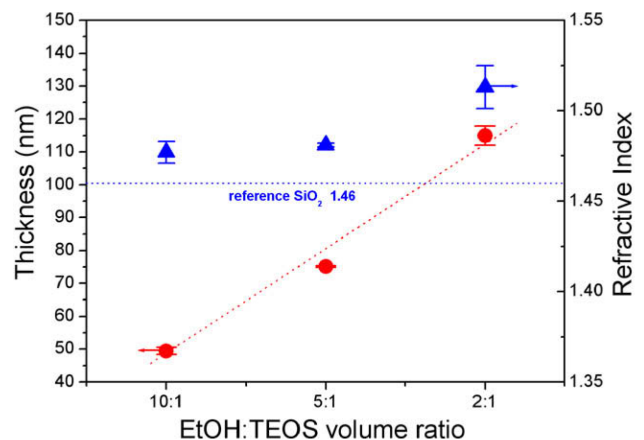

Fig. 1. The thickness and refractive index of sol–gel SiO_2 films ($V_{bias} = 0$) as a function of the EtOH:TEOS volume ratio.

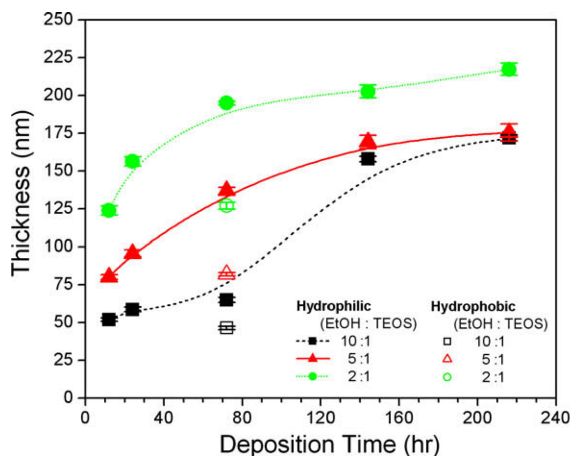

Fig. 2. The thickness of the sol–gel EPD SiO_2 films ($V_{bias} = 1.2$ V) as a function of the deposition time and the TEOS quantity.

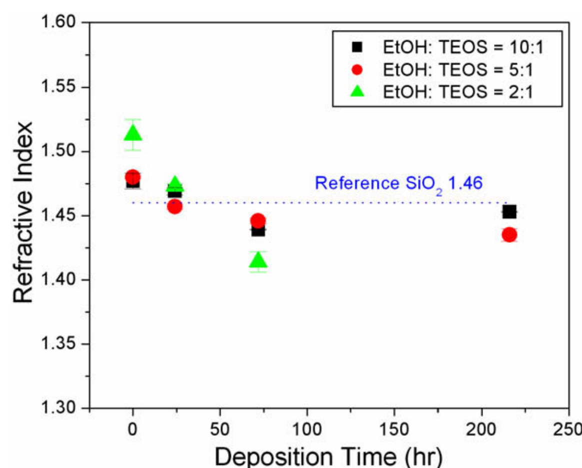

Fig. 3. The refractive index of the sol–gel EPD SiO_2 films ($V_{bias} = 1.2$ V) as a function of the deposition time and the TEOS quantity.

solution leads to an increase in the deposition rate. Therefore, an estimation in the deposition rate as a function of the variation of TEOS quantity in solution was made.

Fig. 2 shows the thickness of the deposited film as a function of TEOS quantity and the deposition (=dipping) time by EPD using a bias voltage of 1.2 V. In general, as shown in Fig. 2, the thickness of the deposited films increased with increasing TEOS quantity and dipping time. Specifically, with the variation of the dipping time before 12 h, the thickness of the deposited films hardly changed. However, after 24 h, the thickness increased exponentially with increasing dipping time, and eventually becomes saturated when over 6 days (>144 h). The results showing no thickness change before 12 h could be due to the fact that an incubation time is required in order to deposit SiO_2 film using the EPD method. In addition, the saturation point after 6 days, where the film growth is stopped by an abrupt decrease in the deposition rate and where the thickness does not change any further, could be due to a voltage drop.

Furthermore, the thickness of the deposited SiO_2 films by EPD in relation to the surface properties of the substrate (i.e. hydrophobic surfaces versus hydrophilic surfaces), is also shown in Fig. 2. As shown, the SiO_2 film does not grow sufficiently on a hydrophobic surface, but effectively grows on a hydrophilic surface. On the hydrophilic surface, film deposition is more likely to occur because the substrate surface is "water-like" with the presence of surface –OH groups that help the attachment of oxide particles to the substrate surface through the bondage of –SiO groups (oxide particles) to the –OH groups (substrate surface). Therefore, it is assumed that the difficulty in the deposition of the SiO_2 film on the hydrophobic surface, as shown by the limited number of points in Fig. 2, is due to the less likely attachment of the oxide particles to a surface that is not "water-like."

Fig. 3 shows the variation of the refractive index as a function of deposition time and TEOS quantity. For all the film samples, the refractive index approaches a standard value (1.46) of thermal oxide with increasing deposition time. Specifically, for the film samples in which the volume ratio of EtOH:TEOS is 2:1 and 5:1, the refractive index decreases linearly with increasing thickness of the oxide layer, as shown in Fig. 2. However, for the film samples in which the volume ratio of EtOH:TEOS is 10:1, the refractive index decreases linearly with increasing thickness of the oxide layer for the first 72 h, but then approaches the standard value of 1.46 after 72 h. From these results, it is assumed that the decrease in the refractive index is due to the formation of a porous film by an abrupt increase in the film thickness of the oxide layer.

According to the variation of the volume ratio of EtOH:TEOS, the surface morphology in the film samples formed by EPD and sol–gel methods was measured by AFM, as shown in Fig. 4. Before heat treatment, the surface morphology of all the film samples by sol–gel deposition in which the EtOH:TEOS volume ratio is 10:1, 5:1, and 2:1 is rough, as shown in Fig. 4a, d, and g, respectively. In addition, the number and the size of the pores in the film sample in Fig. 4a formed using a sol with EtOH:TEOS volume ratio of 10:1 are larger and smaller, respectively, than that in the film sample in Fig. 4g formed using a sol with EtOH:TEOS volume ratio of 2:1. After heat treatment for 1 hour at 100 °C for these film samples, the pores are clearly shown in Figs. 4b, e, and h; and the trend is similar to the results before heat treatment, as shown in Fig. 4a, d, and g, respectively. However, after heat treatment for the film samples by the EPD method, as shown in Fig. 4c, f, and i, the pores nearly disappear.

The wet etch rates of the films were estimated with a diluted 1000:1 DIH_2O:HF solution to investigate the density and the integrity of the films. Fig. 5 shows the results of the etch rate in annealed film samples prepared by electrophoretic deposition and sol–gel methods. The etch rate in the films prepared by the EPD method decreased by about 50–60% in comparison with that of the films made by typical sol–gel methods. From these results, it is

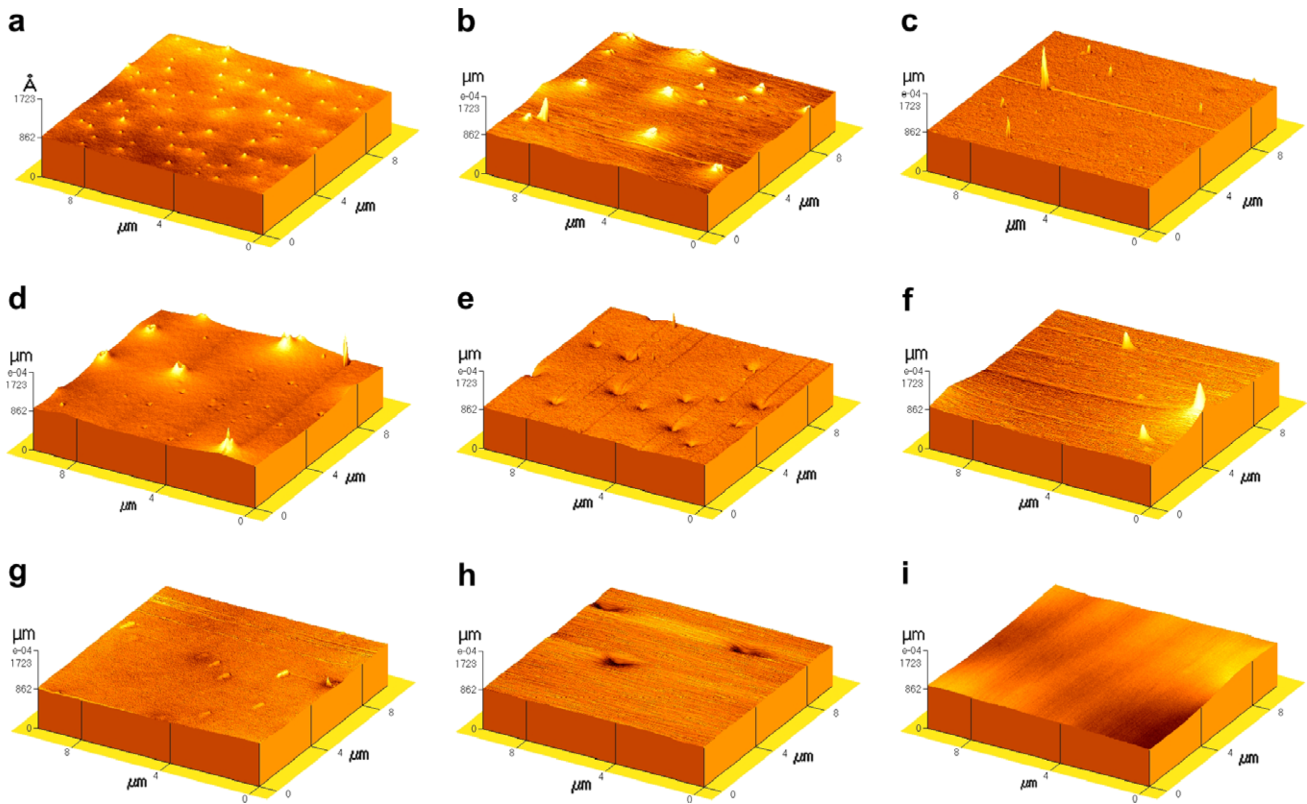

Fig. 4. The surface morphology of the sol–gel and the EPD SiO_2 films. The films were processed using the following conditions: (a) EtOH:TEOS volume ratio of 10:1, sol–gel deposition without annealing, (b) EtOH:TEOS volume ratio of 10:1, sol–gel deposition with annealing for 1 h at 100 °C, (c) EtOH:TEOS volume ratio of 10:1, EPD for 72 h with annealing for 1 h at 100 °C, (d) EtOH:TEOS volume ratio of 5:1, sol–gel deposition without annealing, (e) EtOH:TEOS volume ratio of 5:1, sol–gel deposition with annealing for 1 h at 100 °C, (f) EtOH:TEOS volume ratio of 5:1, EPD for 72 h with annealing for 1 h at 100 °C, (g) EtOH:TEOS volume ratio of 2:1, sol–gel deposition without annealing, (h) EtOH:TEOS volume ratio of 2:1, sol–gel deposition with annealing for 1 h at 100 °C and (i) EtOH:TEOS volume ratio of 2:1, EPD for 72 h with annealing for 1 h at 100 °C.

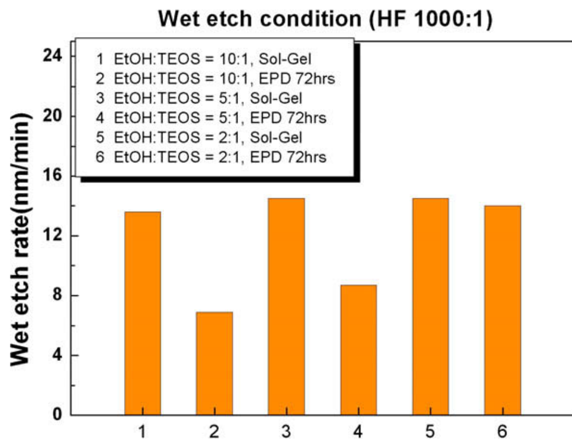

Fig. 5. Wet etch rate of sol–gel and EPD SiO_2 films.

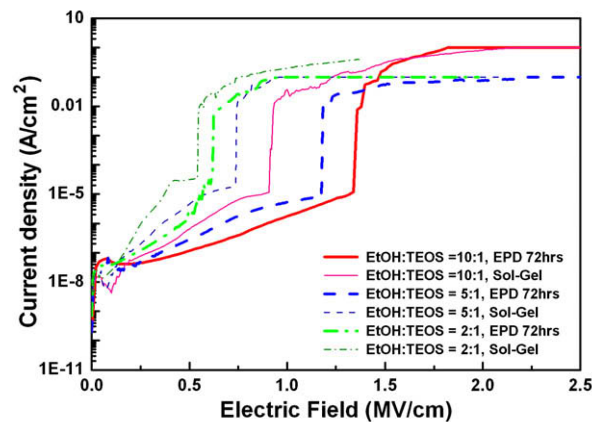

Fig. 6. Current–voltage characteristics of sol–gel and EPD SiO_2 films.

assumed that the EPD films are denser than the sol–gel deposited films due to the use of the EPD method, in which an oriented motion of charged particles are used to grow the films by enriching the solid particles from a colloidal dispersion or a sol onto the surface of an electrode.

In order to evaluate electrical properties of the films formed by sol–gel and EPD methods, we measured the current–voltage (I–V) characteristics. The results obtained from the I–V curves and the breakdown voltages in the film samples are shown in Fig. 6 and Table 1. From the results, the leakage current in the films prepared by the EPD method is lower than that in the films prepared by the sol–gel method, except for the sample using the a sol with a EtOH:TEOS volume ratio of 2:1. In addition, the breakdown voltage in all the film samples prepared by the EPD method is higher than that in the film samples prepared by

Table 1
Breakdown fields of various SiO_2 thin films determined by the *I–V* curve measurements in Fig. 6

EtOH:TEOS	Deposition process			
	Sol–gel deposition, no annealing (MV/cm)	Sol–gel deposition, annealing at 100 °C for 1 h (MV/cm)	72 h EPD, no annealing (MV/cm)	72 h EPD, annealing at 100 °C for 1 h (MV/cm)
10:1	0.79	0.91	0.92	1.33
5:1	0.66	0.74	0.71	1.19
2:1	0.45	0.53	0.52	0.63

typical sol–gel deposition. From these results, it was found that the films prepared by the EPD method is denser and has better integrity than the films prepared by sol–gel deposition. However, the films may be difficult to use as an insulator gate for TFT devices since the maximum value of the breakdown voltage in the film sample prepared using a sol with a EtOH:TEOS volume ratio of 10:1 is about 1.33 MV/cm. The low value of the breakdown voltage may be due to the weak reaction-like pore formation, as shown in the AFM results in Fig. 4. This problem may be solved by stuffing the pores through ambient control at temperatures over 100 °C.

4. Conclusion

Silicon dioxide thin films were deposited on p-type Si (100) substrates by sol electrophoretic deposition using TEOS at room temperature. In addition, the deposition characteristics of these film samples were estimated. The growth rate of the deposited films increased linearly as a function of the TEOS quantity in solution, increased exponentially as a function of time, and was saturated at about 200 nm in over 6 days. The films were selectively deposited onto the hydrophilic surface of the substrates by electorphoresis. The SiO_2 thin films prepared by the EPD method using TEOS at room temperature performed better than the deposited films using sol–gel deposition when comparing the chemical composition, wet etch rate, leakage current, and breakdown voltage. These films prepared by the EPD method would be difficult to use as an insulator gate for TFT devices due to the maximum value of breakdown voltage of 1.33 MV/cm.

This research may be the primary study which is done by applying the electrophoretic mechanism to the deposition of SiO_2 film. Therefore, the application feasibility in TFT LCD panel process is not yet studied enough. However, we suggest that these EPD films have great potential in application to TFT LCD panel process through this study. With more advanced research in regards to the EPD process and possible methods to eliminate pores in the film to accomplish better electrical characteristics, more advanced research in EPD oxide films is required for device applications.

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