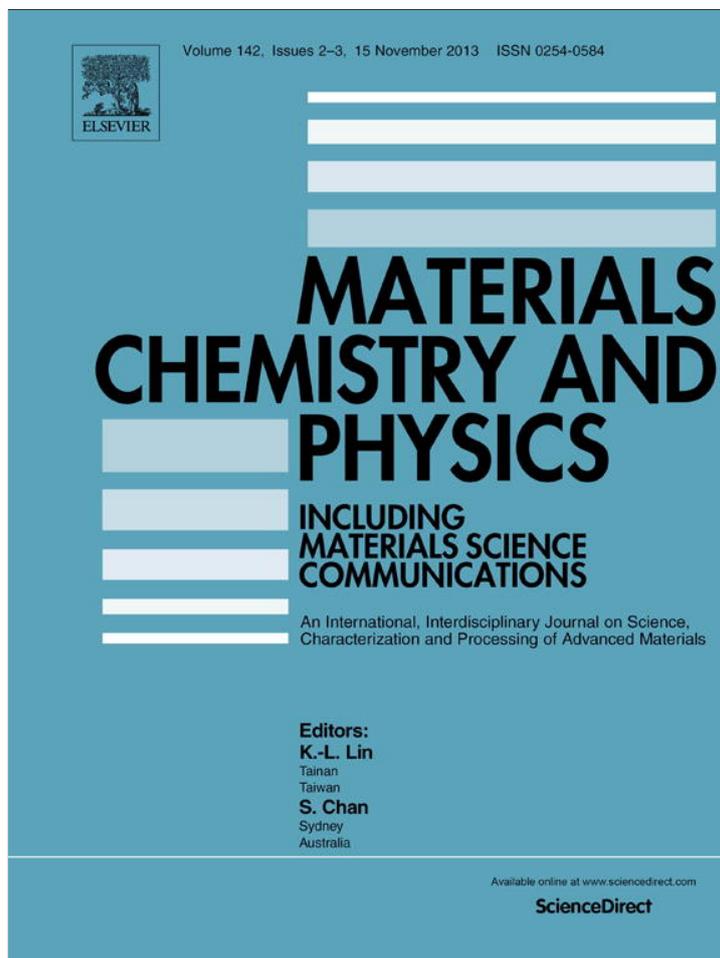


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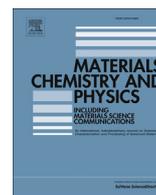
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# Rapid vapor deposition SiO<sub>2</sub> thin film deposited at a low temperature using tris(*tert*-pentoxo)silanol and trimethyl-aluminum

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## HIGHLIGHTS

- The RVD SiO<sub>2</sub> thin films showed a remarkable growth rate (35 nm/cycle) at 120 °C.
- The SiO<sub>2</sub> thin films are carbon-free and perfect composition ratio (O/Si = 2).
- The films exhibited excellent electrical properties (2.5 × 10<sup>-11</sup> A at 8 MV cm<sup>-1</sup>, over 11 MV cm<sup>-1</sup>).

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## ABSTRACT

Rapid atomic layer deposition (ALD) SiO<sub>2</sub> thin film was deposited at various temperatures (below 250 °C) using liquid tris(*tert*-pentoxo)silanol (TPS) as a SiO<sub>2</sub> precursor and trimethyl-aluminum (TMA) as a catalyst. The rapid ALD SiO<sub>2</sub> films showed saturated growth behavior similar to conventional ALD, exhibiting a high growth rate (35 nm/cycle) at 120 °C. As the growth temperature increased to 250 °C, the growth rate decreased slightly to 10.5 nm/cycle. This behavior may have originated from two competing growth mechanisms: the Al catalytic reaction vs. a cross-link reaction. There is no carbon and very little hydrogen in rapid ALD SiO<sub>2</sub> films according to Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD). As the growth temperature increases, the Si–O stretch bond in the Fourier transmittance infrared spectroscopy (FTIR) results increases but the Si–OH stretch bond decreases simultaneously. The rapid ALD SiO<sub>2</sub> films also show an amorphous phase and a smooth surface despite the very high growth rate. In addition, the SiO<sub>2</sub> films exhibited excellent electrical properties despite the low growth temperatures, showing a low leakage current (2.5 × 10<sup>-11</sup> A at 8 MV cm<sup>-1</sup>) and a high breakdown field (over 11 MV cm<sup>-1</sup> at all growth temperatures). The obtained dielectric constant of the SiO<sub>2</sub> films ranged from 6.14 to 4.15 as the growth temperature increased.

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## 1. Introduction

SiO<sub>2</sub> is the most widely used dielectric material in the semiconductor industry. Many researchers have studied the characteristics of SiO<sub>2</sub> for various applications, such as a gate insulator in metal oxide semiconductor field effect transistors (MOSFETs) [1], capacitors for memory devices and an insulation layer [2,3], a gas diffusion barrier [4,5], optoelectronics [6], and in flexible electronics [7], as SiO<sub>2</sub> has excellent properties such as a large gap energy (9.0 eV), a low leakage current, good protection from H<sub>2</sub>O, and low impurity levels in film. For these reasons, SiO<sub>2</sub> is investigated and used mostly commercially to adjust many applications over extended lengths of time.

SiO<sub>2</sub> films are conveniently made by the thermal oxidation of a silicon substrate under very high temperatures. As novel electronic applications such as flexible and transparent devices have been emerging rapidly, deposition methods have become a very important issue to achieve smooth, conformal, particle-free films, and low growth temperature. Unfortunately, conventional plasma-enhanced chemical vapor deposition (PECVD) SiO<sub>2</sub> films still show critical weaknesses such as a comparatively high growth temperature, particle generation, poor step coverage and a slow growth rate. Thus, atomic layer deposition (ALD) has been recently interested as a proper deposition technique for depositing conformal and smooth dielectric films under low-temperature deposition conditions.

ALD is a well-known deposition technique based on sequential and self-limiting surface reactions, exhibiting saturation growth behavior and accurate thickness control. Although ALD has excellent deposition properties, it is still limited when used in practical

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applications due to its low throughput (small growth rate). Also, SiO<sub>2</sub> ALD processes with conventional Si precursors still require a high growth temperature (>350 °C) despite the low growth rate. To ensure feasibility despite the requirements of a high growth temperature and a low growth rate, catalyst SiO<sub>2</sub> ALD has been investigated. Jason W. Klaus and J. D. Ferguson groups reported that SiO<sub>2</sub> film can be deposited at room temperature when pyridine (C<sub>5</sub>H<sub>5</sub>N) and NH<sub>3</sub> are used as a catalyst but that the growth rates are still low in both cases [8,9]. In their investigations of catalytic ALD processes, the Gordon group reported that the growth rate of self-limited SiO<sub>2</sub> film can exceed 12 nm/cycle with Al as a catalyst and Tri(*tert*-butoxy)silanol (TBS), demonstrating that the growth rate of SiO<sub>2</sub> thin film is more than 100 times higher than in previous reports on conventional ALD SiO<sub>2</sub>. A few other groups have also reported that SiO<sub>2</sub> thin film with the Al catalytic ALD process shows a very high growth rate (over 16 nm/cycle) at a low growth temperature (below 150 °C). Although there have been a few reports about rapid ALD SiO<sub>2</sub> films, the details of the film properties, including the physical and electrical properties, have been not investigated systematically thus far.

In this work, we performed rapid SiO<sub>x</sub> ALD using Tri(*tert*-pentoxy)silanol (TPS) as the Si source and trimethyl-aluminum (TMA) as a catalyst and investigated the film properties depending on the growth temperature. As the growth temperature increased from 120 °C to 250 °C, the growth rate of SiO<sub>2</sub> films gradually decreased from 35 nm/cycle to 10.5 nm/cycle. The carbon-free SiO<sub>2</sub> films deposited by rapid ALD are amorphous, transparent and smooth at various growth temperatures. In addition, the SiO<sub>2</sub> films exhibited excellent leakage current and breakdown field properties as well as similar dielectric constant values (~4.0) despite the low growth temperature (120 °C).

## 2. Experimental details

Rapid ALD SiO<sub>2</sub> films were deposited in the range of 120–250 °C in a viscous flow ALD reactor using TPS and TMA. N<sub>2</sub> gas (99.9999%) was used as a carrier gas for supplying the TPS and TMA. The N<sub>2</sub> flow rate was fixed at 50 sccm and the flow produced a pressure of 0.3 Torr in the reactor. The TPS precursor was held in a stainless steel canister and was maintained at 110 °C, and the TMA was cooled at 10 °C to control the range of vapor pressures. The rapid ALD SiO<sub>x</sub> process sequence used here was as follows: a TMA pulse time (0.3 s) – N<sub>2</sub> purge (10 s) – TPS assist (1.1 s) – TPS pulse (1 s) – N<sub>2</sub> purge (10 s). The thickness and refractive index of the rapid ALD SiO<sub>2</sub> thin films were analyzed using spectroscopy ellipsometry (SE, J. A. Woollam Co.). To obtain the composition ratio and hydrogen impurity, Rutherford back-scattering spectroscopy (RBS) and elastic recoil detection (ERD) were performed. Also, Fourier transform infrared spectroscopy (FTIR) measurements (Model: Vertex 70 from Broker) were carried out from 400 to 4000 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> under an air condition (25 °C and 50%), to confirm the chemical bond states of the deposited films. The acquisition of the FTIR spectra was averaged after over 64 scans. The surface morphology was measured under ambient conditions using an atomic force microscope (AFM, Digital Instruments; Dimension 3100). Current–voltage (*I*–*V*) and capacitance–voltage (*C*–*V*) measurements were performed using HP-4155A and 4284A, respectively, to investigate the breakdown voltage, leakage current, and dielectric constant.

## 3. Result and discussion

The rapid ALD SiO<sub>2</sub> films were deposited on a silicon substrate in a viscous flow ALD reactor. Fig. 1(a) shows the growth rate and refractive index as a function of the TPS exposure time at a substrate

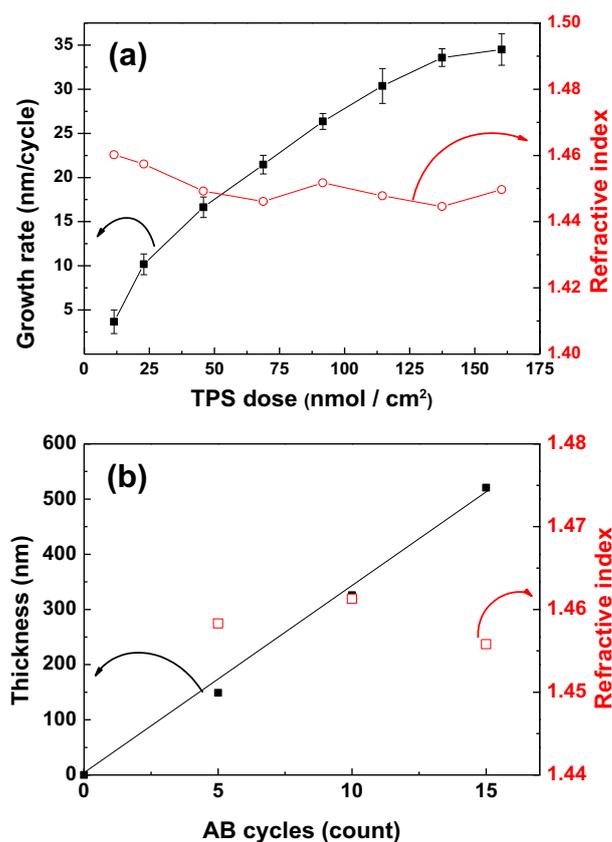


Fig. 1. (a) The growth rate (thickness per cycle) and refractive index of rapid ALD SiO<sub>x</sub> thin film as a function of the exposure times at a substrate temperature 120 °C, (b) film thickness as a function of the number of deposition cycles.

temperature of 120 °C. When the TPS dose exceeds 150 nmol cm<sup>-2</sup>, the growth rate of the SiO<sub>x</sub> films becomes saturated at about 33 nm/cycle. The growth rate of SiO<sub>2</sub> films using TPS precursor exhibits 10 times higher than that in an earlier study using TBS as a precursor [11]. A previous report using TPS as a precursor [12], it has reported the growth rate (16 nm/cycle) with very long exposure and purge times per cycle. However, in term of process throughput, the growth rate is not effective in previous report because process time is too long (1 cycle = over 1000 s). Also, the long exposure time leads to a larger precursor dose, which means that the precursor was wasted. To solve these problems, we developed the rapid ALD SiO<sub>2</sub> process with a short process time and a low precursor dose. As a result, the growth rate shows a dramatic improvement, such as 35 nm/cycle under a reduced process time (1 cycle = 155.5 s). The refractive index (R.I.) of the SiO<sub>2</sub> films is about 1.45–1.46. All of refractive index values were extracted at 550 nm wavelength. This value implies that the physical/chemical properties of the SiO<sub>2</sub> films are very similar to those of other conventionally processed SiO<sub>2</sub> films (R.I. = 1.46). In addition, a self-limiting characteristic was demonstrated at the growth temperature, as shown in Fig. 1(b). Fig. 1(b) exhibits the total thickness of the SiO<sub>2</sub> films depending on the number of cycles, which is a characteristic of the conventional ALD process. This is believed to result from the growth of siloxane polymer chains at the Al-catalytic sites and the cross-linking of these polymer chains to form a dense SiO<sub>2</sub> film [11,12]. Although the origin of the increasing growth rate is still unclear, this might induce from the decomposition of TPS due to the long exposure time and the different ALD process chamber schematics.

Fig. 2 shows the growth rate and R.I. value of SiO<sub>2</sub> films at different growth temperatures (120 °C–250 °C). The growth rate

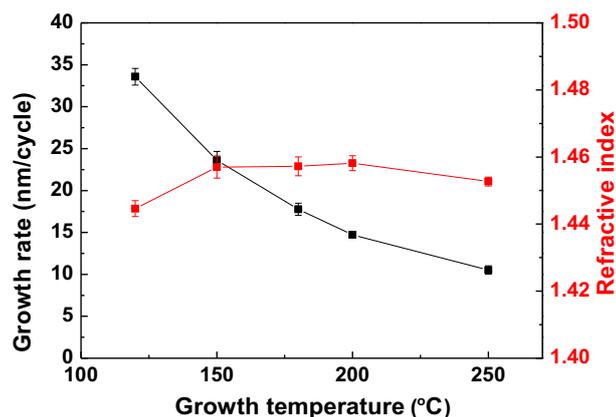


Fig. 2. The growth rate and refractive index depending on the growth temperatures.

decreases rapidly from 35 nm/cycle to 10.5 nm/cycle as the growth temperature increases from 120 °C to 250 °C. A similar tendency in the growth behavior was observed in several earlier results involving catalyzed SiO<sub>2</sub> ALD [8,10–13]. The explanation was that the decrease in the growth rate was caused by higher cross-linking rates, which limit the diffusion of silanol reactants through the growing film to the Al catalytic center [10,11]. Interestingly, the R.I. exhibits a constant value (about 1.46) at various growth temperatures, unlike the previous result using TBS as a precursor [11].

To investigate the stoichiometry and impurity of the SiO<sub>2</sub> films, SiO<sub>2</sub> films deposited at various growth temperatures were measured by and RBS and ERD. Fig. 3(a) displays a typical RBS result of the SiO<sub>2</sub> films. No carbon content in the SiO<sub>2</sub> films was detected at any growth temperature (under the detection limit of 1 at%). There was also no significant change of the Si–O ratio depending on the growth temperature, resulting in a Si:O ratio of 1:2. This indicates that the rapid ALD SiO<sub>2</sub> films were formed by a complete catalytic reaction between the TPS and the TMA. The film composition and Si/O ratio are summarized in Table 1. Interestingly, the hydrogen content in the SiO<sub>2</sub> films gradually increased from 4 at% (150 °C) to 10 at% (250 °C) with an increase in the growth temperature, as shown in Fig. 3(b). This results are reasonable prepared with previous report [12], and can be considered with the following two possibilities. One is related to the decomposition of TPS, as the films are oxygen-rich or undergo silicon deficiency at 250 °C. An increase in the hydrogen level can be predicted based on the decomposition of the TPS precursor. The other is that a by-product such as an O–H group could become incorporated into the SiO<sub>2</sub> films by means of cross-linking reactions due to the high cross-link rate.

To confirm the chemical bonding states in the SiO<sub>2</sub> films, Fig. 4(a) and (b) shows the FTIR spectra of the O–H, Si–O and Si–OH bonding states at various growth temperatures. A Si–O stretching peak at 1060 cm<sup>-1</sup> and a Si–OH stretching peak at 920 cm<sup>-1</sup> were detected [13,14]. The absorbance of O–H stretching vibrations (3000–3700 cm<sup>-1</sup> range) was observed as shown Fig. 4(a). An increase in the absorbance of the O–H species with increasing growth temperature was observed. This might be due to residual O–H species by cross-linking reactions. The cross-linking reactions are occurred more at high temperature than low temperature, and then residual O–H ligands in films through cross-linking reactions also remain large quantities with increasing temperature. Also, the higher hydrogen content at higher growth temperatures would mainly originate from the incorporation of a by-product during the cross-linking reactions. As shown in Fig. 4(b), an increase in the Si–O stretching peak correlates with an increase in the growth temperature. In contrast to Si–O stretching,

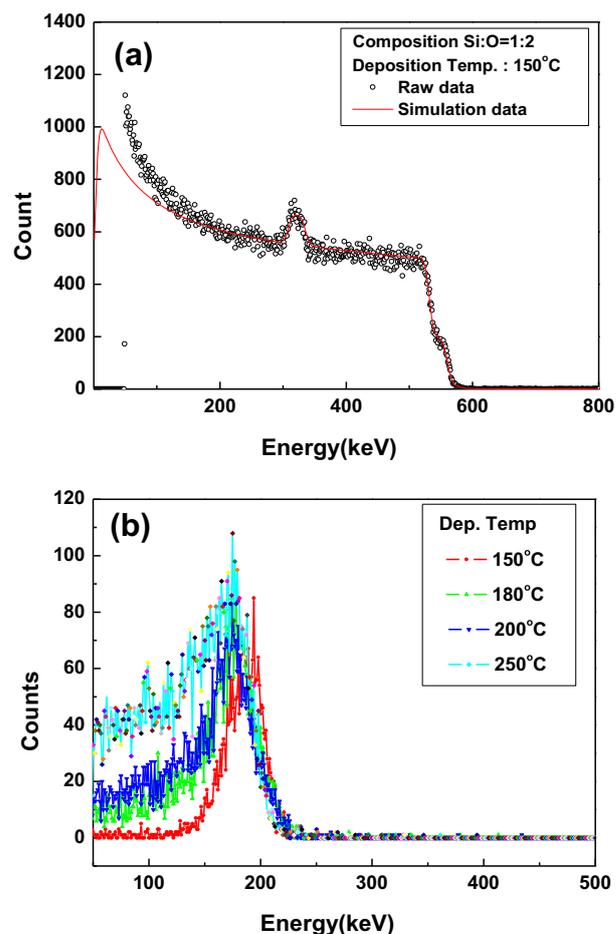


Fig. 3. (a) Rutherford backscattering spectrum and (b) elastic recoil detection from SiO<sub>x</sub> samples grown at various substrate temperatures.

the Si–OH stretching peak decreased with an increase in Si–O stretching simultaneously. This suggests that Si–OH bonds become Si–O bonds through cross-linking reactions, as cross-linking reactions occur between Si–OH bonds and Si–OH bonds. Fig. 5 shows AFM images of SiO<sub>2</sub> films at different growth temperatures. The RMS values at various growth temperatures are summarized in Table 1. The RMS values of SiO<sub>2</sub> films are relatively high compared to previously reported SiO<sub>2</sub> thin films [15–17]. This could result from the different growth mechanism and the existence of hydrogen-related species. It has generally been reported that hydrogen-related bonds including Si–OH and O–H bond degrade the surface morphology [15]. This phenomenon may be correlated with the FTIR spectra, as mentioned in Fig. 4.

The electrical properties of SiO<sub>2</sub> films, including the leakage current and breakdown field, were investigated at the growth temperatures. To measure the electrical properties of SiO<sub>2</sub> films, the metal–oxide–semiconductor structures were applied: 100 nm thick Al electrode/20 nm thick SiO<sub>2</sub> films/Si substrate. Fig. 6(a)

Table 1  
The film composition and RMS roughness values as measured by RBS and AFM.

	Si	O	C	Si/O ratio	RMS roughness
120 °C	33	67	N/D	0.50	2.31
150 °C	33	67	N/D	0.50	2.89
180 °C	33	67	N/D	0.50	2.50
200 °C	33	67	N/D	0.50	2.46
250 °C	32	68	N/D	0.48	4.29

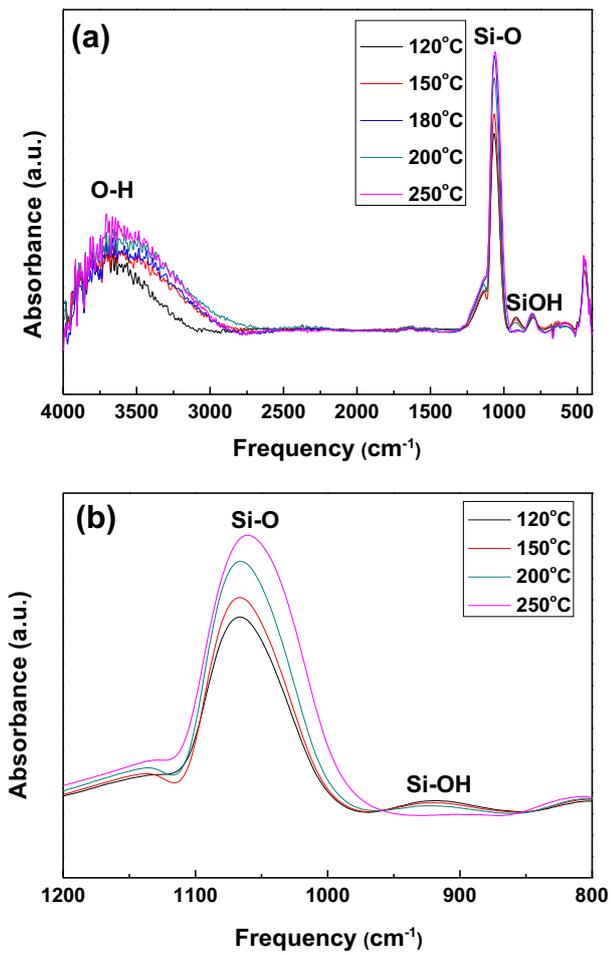


Fig. 4. (a) FTIR vibrational spectra and (b) the Si–O and Si–OH stretching vibration region for 100 nm SiO<sub>x</sub> films grown at various substrate temperatures.

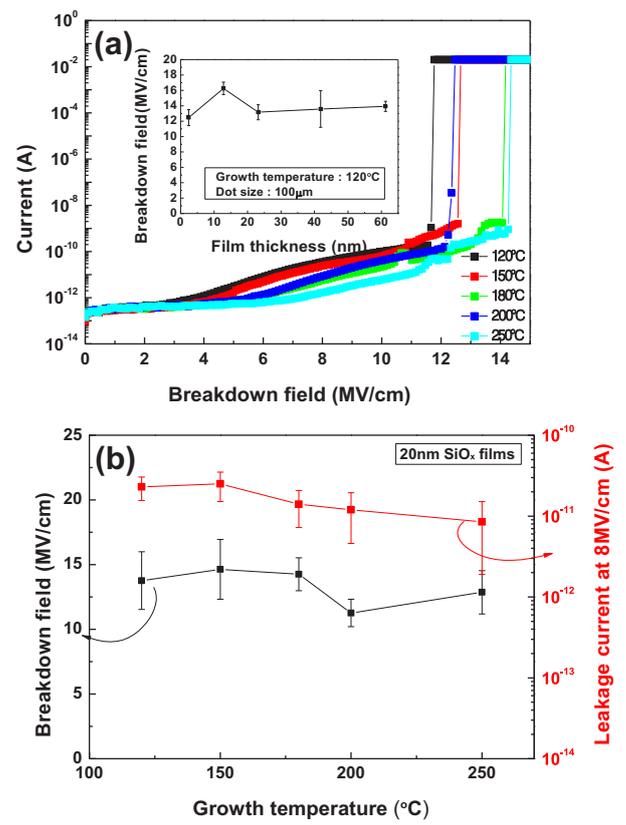


Fig. 6. (a) The representative leakage current curves of 20 nm thick SiO<sub>x</sub> films as a function of growth temperature and the average breakdown field values (inset) at 120 °C depending on film thickness (b) the average breakdown field and leakage current values on growth temperatures.

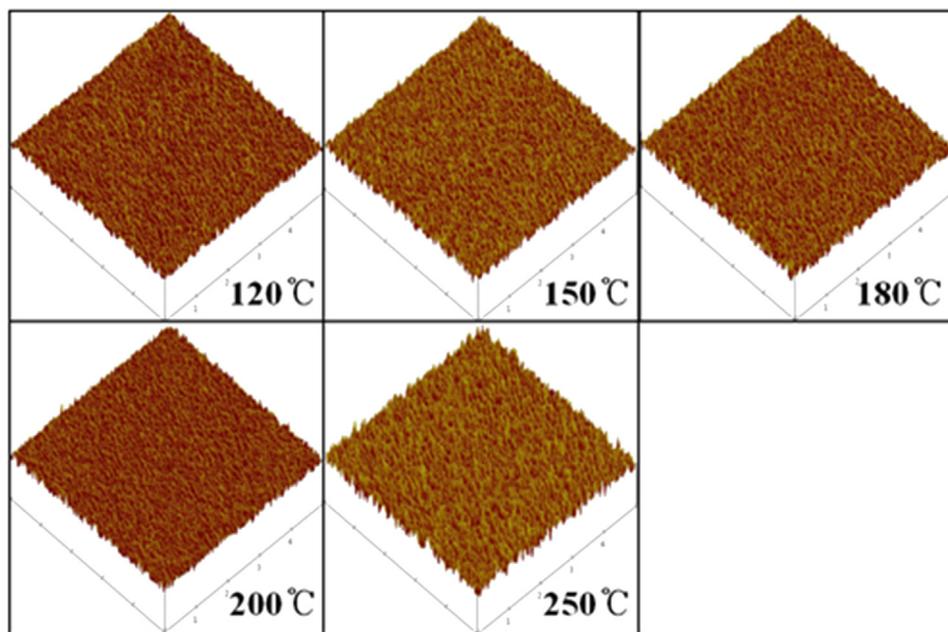


Fig. 5. AFM images of SiO<sub>x</sub> thin film surfaces grown from 120 °C to 250 °C.

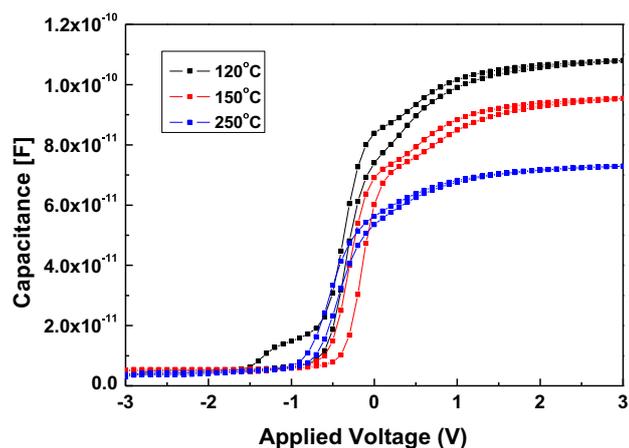


Fig. 7. Representative C–V curve of rapid ALD SiO<sub>x</sub> films deposited at 120, 150, 250 °C.

shows the representative *I*–*V* curves depending on the growth temperature. The behavior of the breakdown field shows no significant differences on growth temperatures, measuring 13.1 and 12.9 MV cm<sup>-1</sup> at 120 and 250 °C, respectively. Generally, the electrical properties of oxide films are very dependent on the film thickness. In the case of Rapid ALD SiO<sub>x</sub> films, the average breakdown filed values showed the reasonable behavior (12–13 MV cm<sup>-1</sup>) at least over 20 nm as shown in Fig. 6 (a) inset. The electrical properties of the 20 nm thick SiO<sub>2</sub> films are summarized in Fig. 6(b). The average breakdown field and leakage current values were extracted from 10 samples. As the growth temperature increases to 250 °C, the leakage current of the SiO<sub>2</sub> films also improves gradually to 8.5 × 10<sup>-12</sup> A under a high electrical field (8 MV cm<sup>-1</sup>). Generally, a higher growth temperature can lead to the formation of dense rapid ALD SiO<sub>2</sub> films [11] due to the decreasing film porosity. In the case of SiO<sub>2</sub> films, a high growth temperature may decrease the film porosity; moreover, the buildup of additional siloxane networks also tends to decrease the film porosity in SiO<sub>2</sub> films [18]. This implies that films deposited at a higher growth temperature are denser, leading to an improvement in their electrical properties, such as the breakdown and insulator strength. Unlike rapid ALD SiO<sub>2</sub> films with TBS as a precursor, these SiO<sub>2</sub> films show an outstanding breakdown field (over 12 MV cm<sup>-1</sup>) and leakage current values (below 1 × 10<sup>-11</sup> A at 8 MV cm<sup>-1</sup>) throughout the range of growth temperatures compared to previous results [19–21]. This may originate from the accurate Si/O ratio (0.5) and clean composition such carbon-free and less hydrogen contents.

Fig. 7 shows the representative capacitance–voltage (C–V) curves of SiO<sub>2</sub> films depending on the growth temperature. A voltage sweep was conducted from positive to negative first, and then in the reverse order. As the growth temperature increases, the hysteresis of the SiO<sub>2</sub> films decreased from 0.25 to 0.1 V, and the dielectric constant of the SiO<sub>2</sub> film also decreased from 6.14 to 4.15. In previous report [13], Si–OH and Si–CH bonds may play roles as charge trap states, degrading the dielectric properties such as hysteresis and dielectric constant. Interestingly, it may correlate with FTIR spectra result (Fig. 4.), showing that the amounts of Si–OH are changed to Si–O bonds. Thus, it would lead to decrease the hysteresis (Δ*V*) and the dielectric constant of the SiO<sub>2</sub> film on the

growth temperature, suggesting that the decrease of Si–OH states may improve the electrical properties of SiO<sub>2</sub> films.

#### 4. Conclusion

High-throughput ALD SiO<sub>2</sub> films were deposited at low growth temperatures (120–250 °C) using tri(*tert*-butoxy)silanol as a silicon oxide source and trimethyl-aluminum as a catalytic agent. The growth rate of the SiO<sub>2</sub> films is about 30 nm/cycle at 120 °C, showing a self-limited reaction mechanism. The rapid ALD SiO<sub>2</sub> growth is highly dependent on the growth temperature, showing that the growth rate decreases drastically at a high growth temperature due to the fast cross-linking reaction rate. The Si–OH bonds in SiO<sub>2</sub> films gradually decrease with an increase in the amount of Si–O stretching as the growth temperature increases. The SiO<sub>2</sub> films here exhibited outstanding electrical properties despite the low growth temperature, showing a low leakage current (2.5 × 10<sup>-11</sup> A at 8 MV cm<sup>-1</sup>) and a high breakdown field (over 11 MV cm<sup>-1</sup> at all growth temperatures) and the dielectric constant decreased from 6.14 to 4.15 with an increase in the growth temperature. High throughput ALD SiO<sub>2</sub> using TPS has strong potential as an insulator/passivation material for a low-temperature process for application to next-generation electronics.

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