

Title	Effect of trichloroethylene enhancement on deposition rate of low-temperature silicon oxide films by silicone oil and ozone
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Description	

1 **Effect of trichloroethylene enhancement on deposition rate of low-temperature**  
2 **silicon oxide films by silicone oil and ozone**

3

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9

**Abstract**

10 A low-temperature silicon oxide film was deposited at 160 to 220 °C using an  
11 atmospheric pressure CVD system with silicone oil vapor and ozone gases. It was found  
12 that the deposition rate is markedly increased by adding trichloroethylene (TCE) vapor,  
13 which is generated by bubbling TCE solution with N<sub>2</sub> gas flow. The increase is more  
14 than 3 times that observed without TCE, and any contamination due to TCE is hardly  
15 observed in the deposited Si oxide films from Fourier transform infrared spectra.

16

1 The low-temperature deposition of silicon oxide films is desired for the fabrication  
2 of not only thin film transistors (TFTs) on non-heat-resistant substrates<sup>1)</sup> but also  
3 interlayer dielectrics (ILD) in size-minimizing integrated circuits to suppress the  
4 disconnection of the interconnect metal, the redistribution of the dopant, and defect  
5 generation in the fabricated underlayer.<sup>2)</sup> For low-temperature deposition,  
6 plasma-enhanced chemical vapor deposition (PECVD) has been widely carried out as a  
7 practical method.<sup>1,3-6)</sup> However, it requires an expensive system consisting of vacuum  
8 equipment and high power supply. Also, tetraethylorthosilicate [TEOS: Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]  
9 vapor is commonly used as a deposition gas source.<sup>3-5)</sup> On the other hand, previously,  
10 we reported on the deposition of low-temperature Si oxide films using silicone oil (SO)  
11 vapor as a deposition source and ozone O<sub>3</sub> gas at a temperature of 200 to 350 °C at  
12 atmospheric pressure without vacuum and pumping systems.<sup>7,8)</sup> SO has advantages over  
13 TEOS; the price per unit volume of SO is lower than that of TEOS by about one order,  
14 and silicone is not only markedly thermally stable but also a safe material as opposed to  
15 TEOS, which is toxic especially to the human eye and throat.<sup>9)</sup>

16 A deposition mechanism for the silicon oxide film produced using SO and O<sub>3</sub> is  
17 described in our previous paper.<sup>8)</sup> This mechanism is similar to that of the TEOS/O<sub>3</sub>  
18 system.<sup>10-13)</sup> First, O<sub>3</sub> is decomposed thermally into O<sub>2</sub>+O. Then, chemically very active  
19 O atoms react with the –CH<sub>3</sub> side groups of SO in the gas phase and intermediate  
20 products (precursors) are formed together with the by-products CO<sub>2</sub> and H<sub>2</sub>O. –CH<sub>3</sub>  
21 side groups are substituted with hydroxyl –OH groups, and silanol bonds of Si–OH  
22 cover the sides of siloxane chains. The surface of a Si substrate or the deposited Si  
23 oxide film is terminated by –OH groups through exposure to O<sub>3</sub> gas and H<sub>2</sub>O of a  
24 by-product. Finally, the –OH groups on the surface are eliminated by dehydration

1 reaction with the –OH groups of the precursors, Si–OH (surface) + –OH (precursor) →  
2 Si–O–Si + H<sub>2</sub>O. Then, a [–Si–O–Si–]<sub>n</sub> network is constructed on the substrate and the  
3 deposition of Si oxide films continues.

4 However, the deposition rate of the Si oxide films using SO is very low at 3  
5 nm/min,<sup>8)</sup> which is not favorable for industrial application. To solve this problem or  
6 increase the deposition rate, we attempted to add a certain amount of trichloroethylene  
7 (C<sub>2</sub>HCl<sub>3</sub>: TCE) vapor together with SO and O<sub>3</sub> during deposition. It is well known that  
8 an acid catalyst is commonly used to enhance the dehydration reaction. For example,  
9 hydrochloric acid (HCl) is used for Fischer esterification reaction.<sup>14)</sup> Since H and Cl  
10 dissolved from TCE owing to the chemically active O<sub>3</sub> might act as an acid, it is  
11 expected that the TCE vapor will enhance the dehydration reaction, markedly increasing  
12 the deposition rate.

13 In this paper, we report the results obtained by adding TCE vapor during the  
14 low-temperature deposition of Si oxide films, and show a marked improvement in  
15 deposition rate, which is about 3 times that observed without TCE.

16 Figure 1 shows a schematic diagram of the deposition system used in this study. The  
17 system has a vertical reactor of atmospheric-pressure (AP) CVD instead of the  
18 horizontal type used previously.<sup>8)</sup> Using this system, film thickness uniformity was  
19 much improved, compared with that observed with the previous horizontal reactor. For  
20 example, the difference in thickness on a 4 inch Si wafer is about ± 2% for an average  
21 Si oxide film thickness of 140 nm. However, the deposition rate is still lower than 5  
22 nm/min at 200 °C as shown later. The substrate was held face down on a  
23 100-mm-diameter stainless steel holder. As silicone oil, decamethylcyclopentasiloxane  
24 (C<sub>10</sub>H<sub>30</sub>O<sub>5</sub>Si<sub>5</sub>) was used with a kinematic viscosity of 4.0 mm<sup>2</sup>/s. The vapor was

1 generated by the N<sub>2</sub> gas bubbling of SO, which was heated using a mantle heater to a  
2 temperature of 50 °C. The gas flow rate of N<sub>2</sub> for SO vapor, N<sub>2</sub>(SO), was 0.25 to 0.35  
3 lm (liters per minute at 25 °C). We also added TCE vapor, which was generated by  
4 bubbling with N<sub>2</sub> gas with a flow rate of 0.10 lm at room temperature, and then  
5 introduced it into the chamber together with SO vapor. Both gases were flown through a  
6 1/4-in.-diameter stainless steel tube heated using a band heater to about 55 °C to prevent  
7 the condensation of SO vapor. O<sub>3</sub> was generated using a silent electric discharge from  
8 99.9995% O<sub>2</sub> gas with a flow rate of 0.50 lm and the O<sub>3</sub> concentration was ~ 150 g/m<sup>3</sup>.  
9 The SO+TCE vapor and O<sub>3</sub>+O<sub>2</sub> gases were introduced individually into the showerhead,  
10 where the two groups of gases were mixed. Then, they were directed towards the heated  
11 substrate along the stainless steel transport wall with a diameter of ~110 mm. The  
12 distance between the showerhead and the substrate was ~100 mm. The films were  
13 deposited for 5, 10, or 15 min at a substrate temperature of 160, 180, 200, or 220 °C.  
14 The entire outside of the reactor chamber was made of Pyrex glass.

15 Substrates were n-type (111) single crystals with a resistivity of 5–15 Ωcm. Before  
16 setting a substrate on a holder, it was chemically cleaned in hot acid solution and dipped  
17 in dilute HF solution to remove Si oxide. The thicknesses of the as-deposited films were  
18 measured by ellipsometry using a He-Ne laser beam with a wavelength of 632.8 nm. In  
19 the case of a film with a thickness of less than 25 nm, for simplicity, the refractive index  
20 was assumed to be 1.44. Although the refractive index of the silicon oxide film was not  
21 real, the error due to this was estimated to be roughly less than 3%, judging from the  
22 results obtained by a more accurate measurement method with spectroscopic  
23 ellipsometry. The molecular structures of the as-deposited films were analyzed from  
24 Fourier transform infrared spectroscopy (FT-IR) spectra with a resolution of 1 cm<sup>-1</sup>.

1           Figure 2 shows the typical FT-IR spectra of 194- and 70-nm-thick silicon oxide  
2 films deposited at 200 °C with and without TCE, respectively, where the N<sub>2</sub> flow rate  
3 for SO is 0.35 lm and the deposition time is 15 min. The spectral shape is similar to  
4 those obtained previously using the horizontal furnace.<sup>8)</sup> The peaks at ~800 and 1070  
5 cm<sup>-1</sup> are identified as absorptions due to the bending (TO<sub>2</sub>) and asymmetric stretching  
6 (TO<sub>3</sub>) modes of the Si–O–Si bond, respectively. This indicates that the silicon oxide  
7 film is almost stoichiometric. However, peaks due to the Si-OH and H-OH bonds are  
8 observed at around 960 and 3650, and ~3300 cm<sup>-1</sup>, respectively, indicating that the oxide  
9 films contain a relatively large amount of water. This observation of the OH bond is the  
10 same as that previously reported. It is considered that the OH bonds incorporated in the  
11 films are mainly from the silanol bonds of Si-OH of the precursors where the  
12 dehydration reaction does not occur during the deposition with some possibility in  
13 statistical thermodynamics. By comparing the two spectra, the peak intensity due to the  
14 Si-O-Si bond for TCE is observed to be markedly higher than that obtained without  
15 TCE. This indicates that adding TCE increases the deposition rate of Si oxide films as  
16 expected previously. Furthermore, a peak related to chlorine derived from TCE is hardly  
17 observed. This result indicates that TCE increases the Si oxide deposition rate, but  
18 negligibly affects the chemical composition of the films.

19           Figure 3 shows the comparison of the temperature dependences of deposition rate  
20 obtained with (closed circles) and without (open circles) TCE, where the temperature  
21 ranges from 160 to 220 °C and N<sub>2</sub> (SO) is 0.35 lm. The data plots and error bars indicate  
22 the averages and ranges of deposition rate, respectively, among the three deposition  
23 times of 5, 10, and 15 min. It is seen clearly from Fig. 3 that, in the temperature range,  
24 the deposition rate is higher with TCE than without TCE, as shown in Fig. 2. It is also

1 found that the deposition rate with TCE saturates at the higher deposition temperature,  
2 while that without TCE increases largely with the temperature in a nonlinear fashion.  
3 This will be discussed in detail later.

4 Figure 4 shows the dependence of deposition rate on deposition temperature for the  
5  $N_2(SO)$  flow rates of 0.35 (circles), 0.30 (squares), and 0.25 (triangles) lm with TCE,  
6 where the data for 0.35 lm are the same as those in Fig. 3 and the error bars have the  
7 same meaning. It can be seen that, at any deposition temperature, decreasing the  $N_2(SO)$   
8 flow rate leads to a reduction in deposition rate. This is because the feeding rate of SO  
9 vapor into the reaction chamber is proportional to the flow rate of  $N_2$  required to bubble  
10 SO. Also, it is found that, as the deposition temperature increases above 200 °C, the  
11 deposition rate for any  $N_2$  flow rate saturates as shown in Fig. 3 or tends to decrease  
12 with temperature. This can be explained on the basis of the gas phase and surface  
13 reactions. The gas phase reaction is a chemical reaction that occurs between gaseous  
14 reactants or  $SO + O_3$  near the substrate surface but not on it. Thus, owing to this  
15 reaction, some of the reactants are consumed before reaching the substrate. The surface  
16 reaction is a chemical reaction that occurs between the gaseous reactants on active sites  
17 of the substrate surface. As the temperature increases, the gas phase reaction becomes  
18 more pronounced as reported previously by other researchers.<sup>15-18)</sup> This is because,  
19 owing to the high-temperature radiation from the substrate holder, some reactant gases  
20 react near the substrate surface in the gas phase to produce intermediate species. In the  
21 case with TCE, since its vapor increases the deposition rate or enhances the chemical  
22 reaction, particularly the dehydration reaction, as shown in Figs. 2 and 3, the gas phase  
23 reaction must be promoted also, compared with that in the case without TCE. This is  
24 probably due to the fact that the promoted dehydration reaction occurs even at around

1 200 °C, at which it never occurs without TCE. Most of the SiO<sub>2</sub> particles formed in the  
2 gas phase through the promoted dehydration reaction probably do not contribute to  
3 deposition on the substrate. Thus, with an increase in deposition temperature, the actual  
4 deposition rate of Si oxide films on the substrate is reduced. As a result, the deposition  
5 rate saturates or slightly decreases with an increase in deposition temperature as shown  
6 in Figs. 3 and 4. In contrast, in the case without TCE, since the thermal energy from the  
7 heated substrate in this experiment is insufficient for chemical reaction among reactant  
8 gases, the deposition rate monotonically increases with the deposition temperature as  
9 shown in Fig. 3.

10 Although adding TCE during the deposition increases the deposition rate  
11 effectively as mentioned previously, its effect on the reduction in OH content seems to  
12 be smaller as shown in Fig. 2, which shows that the peaks due to the OH bond are much  
13 larger with TCE than without TCE. One of the reasons for this is the markedly larger  
14 thickness in the TCE case. Another reason might be that, as mentioned previously, since  
15 the residual OH bonds in a Si oxide film are mainly due to the non-dehydration reaction  
16 between the silanols and OH bonds terminated at the substrate surface, a higher  
17 deposition rate could lead to a lower possibility in their dehydration reaction such that  
18 the number of unreacted OH bonds should become larger in the deposited film.  
19 However, at present, we hardly know not only the deposition rate dependence of the  
20 incorporation rate of OH bonds but also the effect of TCE on the reduction in  
21 incorporation rate in a deposited film. Thus, we will investigate them and report our  
22 results about this in the future.

23 In this study, we showed that adding TCE vapor markedly increases the  
24 deposition rate more than 3 times that observed without TCE for the low-temperature

1 deposition of Si oxide films using silicone oil and ozone in an APCVD system, where  
2 the deposition temperature was around 200 °C. We found that TCE negligibly affects  
3 the chemical component of Si oxide or produces few amount of impurity in the films.  
4 Thus, we can conclude that adding TCE in the deposition gas source, e.g., organic  
5 silicon, is markedly effective in increasing the deposition rate of Si oxide films in a low  
6 deposition temperature range.

7

#### 8 **Acknowledgment**

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10 JP16K06257.

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1 **Figure Captions**

2

3 Fig. 1. Schematic diagram of the APCVD system used in this study. The system  
4 consists of a vertical reactor, a substrate holder, a transport wall, a showerhead, and a  
5 reactant gas supply system. The N<sub>2</sub> gas flow rate is 0.25, 0.3, or 0.35 lm for SO and the  
6 substrate temperature ranges from 160 to 220 °C.

7

8 Fig. 2. (Color online) Typical FT-IR spectra of 70- and 196-nm-thick silicon oxide films  
9 deposited with and without TCE, respectively, for the deposition time of 15 min at the  
10 substrate temperature of 200 °C.

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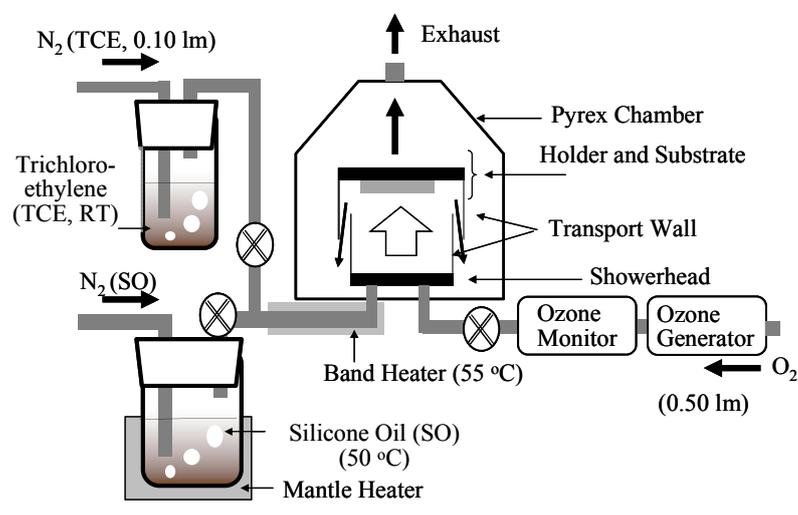
12 Fig. 3. Comparison of deposition temperature dependences of deposition rate obtained  
13 with and without TCE, where the temperature ranges from 160 to 220 °C and N<sub>2</sub> (SO) is  
14 0.35 lm. The plots and error bars indicate the averages and ranges of deposition rate,  
15 respectively, among the 3 deposition times of 5, 10, and 15 min.

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17 Fig. 4. (Color online) Dependence of deposition rate on the deposition temperature for  
18 the N<sub>2</sub> (SO) flow rates of 0.35 (circles), 0.30 (squares), and 0.25 (triangles) lm with  
19 TCE.

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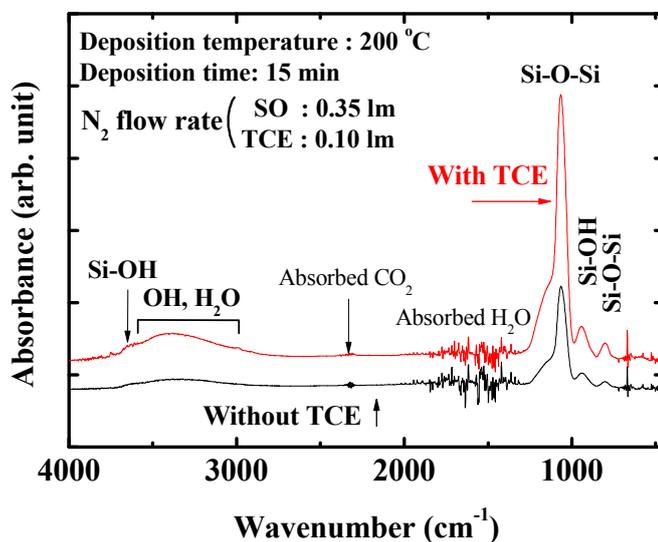
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**Fig. 1**

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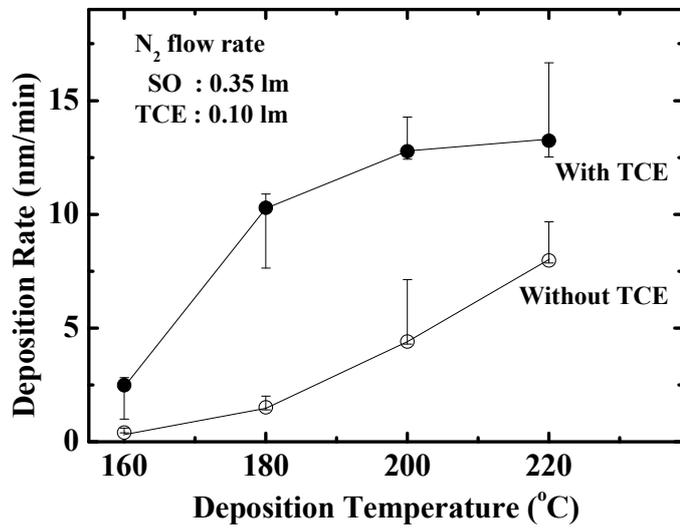
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**Fig. 2**

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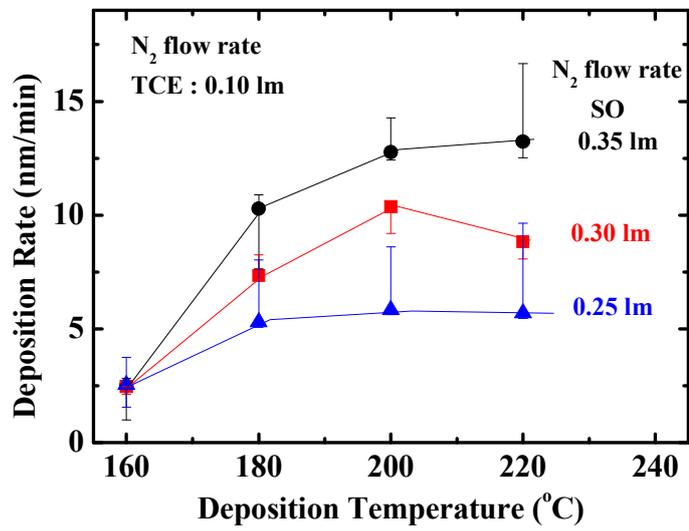
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**Fig. 3**

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**Fig. 4**

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