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Description	

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

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Abstract

A low-temperature silcon oxide film was deposited at 160 to 220 ^{o}C using an atmospheric pressure CVD system with silicone oil vapor and ozone gases. It was found that the deposition rate is markedly increased by adding trichloroethylene (TCE) vapor, which is generated by bubbling TCE solution with N_2 gas flow. The increase is more than 3 times that observed without TCE, and any contamination due to TCE is hardly observed in the deposited Si oxide films from Fourier transform infrared spectra.

The low-temperature deposition of silicon oxide films is desired for the fabrication of not only thin film transistors (TFTs) on non-heat-resistant substrates[1)] but also interlayer dielectrics (ILD) in size-minimizing integrated circuits to suppress the disconnection of the interconnect metal, the redistribution of the dopant, and defect generation in the fabricated underlayer.[2)] For low-temperature deposition, plasma-enhanced chemical vapor deposition (PECVD) has been widely carried out as a practical method.[1,3-6)] However, it requires an expensive system consisting of vacuum equipment and high power supply. Also, tetraethylorthosilicate [TEOS: $Si(OC_2H_5)_4$] vapor is commonly used as a deposition gas source.[3-5)] On the other hand, previously, we reported on the deposition of low-temperature Si oxide films using silicone oil (SO) vapor as a deposition source and ozone O_3 gas at a temperature of 200 to 350 ^{o}C at atmospheric pressure without vacuum and pumping systems.[7,8)] SO has advantages over TEOS; the price per unit volume of SO is lower than that of TEOS by about one order, and silicone is not only markedly thermally stable but also a safe material as opposed to TEOS, which is toxic especially to the human eye and throat.[9)]

A deposition mechanism for the silicon oxide film produced using SO and O_3 is described in our previous paper.[8)] This mechanism is similar to that of the TEOS/O_3 system.[10-13)] First, O_3 is decomposed thermally into O_2+O. Then, chemically very active O atoms react with the $–CH_3$ side groups of SO in the gas phase and intermediate products (precursors) are formed together with the by-products CO_2 and H_2O. $–CH_3$ side groups are substituted with hydroxyl –OH groups, and silanol bonds of Si–OH cover the sides of siloxane chains. The surface of a Si substrate or the deposited Si oxide film is terminated by –OH groups through exposure to O_3 gas and H_2O of a by-product. Finally, the –OH groups on the surface are eliminated by dehydration

reaction with the –OH groups of the precursors, Si–OH (surface) + –OH (precursor) → Si–O–Si + H_2O. Then, a $[–Si–O–Si–]_n$ network is constructed on the substrate and the deposition of Si oxide films continues.

However, the deposition rate of the Si oxide films using SO is very low at 3 nm/min,[8] which is not favorable for industrial application. To solve this problem or increase the deposition rate, we attempted to add a certain amount of trichloroethylene (C_2HCl_3: TCE) vapor together with SO and O_3 during deposition. It is well known that an acid catalyst is commonly used to enhance the dehydration reaction. For example, hydrochloric acid (HCl) is used for Fischer esterification reaction.[14] Since H and Cl dissolved from TCE owing to the chemically active O_3 might act as an acid, it is expected that the TCE vapor will enhance the dehydration reaction, markedly increasing the deposition rate.

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

Figure 1 shows a schematic diagram of the deposition system used in this study. The system has a vertical reactor of atmospheric-pressure (AP) CVD instead of the horizontal type used previously.[8] Using this system, film thickness uniformity was much improved, compared with that observed with the previous horizontal reactor. For example, the difference in thickness on a 4 inch Si wafer is about ± 2% for an average Si oxide film thickness of 140 nm. However, the deposition rate is still lower than 5 nm/min at 200 ^{o}C as shown later. The substrate was held face down on a 100-mm-diameter stainless steel holder. As silicone oil, decamethylcyclopentasiloxane ($C_{10}H_{30}O_5Si_5$) was used with a kinematic viscosity of 4.0 mm^2/s. The vapor was

generated by the N_2 gas bubbling of SO, which was heated using a mantle heater to a temperature of 50 ^{o}C. The gas flow rate of N_2 for SO vapor, N_2(SO), was 0.25 to 0.35 lm (liters per minute at 25 ^{o}C). We also added TCE vapor, which was generated by bubbling with N_2 gas with a flow rate of 0.10 lm at room temperature, and then introduced it into the chamber together with SO vapor. Both gases were flown through a 1/4-in.-diameter stainless steel tube heated using a band heater to about 55 ^{o}C to prevent the condensation of SO vapor. O_3 was generated using a silent electric discharge from 99.9995% O_2 gas with a flow rate of 0.50 lm and the O_3 concentration was ~ 150 g/m^3. The SO+TCE vapor and O_3+O_2 gases were introduced individually into the showerhead, where the two groups of gases were mixed. Then, they were directed towards the heated substrate along the stainless steel transport wall with a diameter of ~110 mm. The distance between the showerhead and the substrate was ~100 mm. The films were deposited for 5, 10, or 15 min at a substrate temperature of 160, 180, 200, or 220 ^{o}C. The entire outside of the reactor chamber was made of Pyrex glass.

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

Figure 2 shows the typical FT-IR spectra of 194- and 70-nm-thick silicon oxide films deposited at 200 ^{o}C with and without TCE, respectively, where the N_2 flow rate for SO is 0.35 lm and the deposition time is 15 min. The spectral shape is similar to those obtained previously using the horizontal furnace.[8)] The peaks at ~800 and 1070 cm^{-1} are identified as absorptions due to the bending (TO_2) and asymmetric stretching (TO_3) modes of the Si–O–Si bond, respectively. This indicates that the silicon oxide film is almost stoichiometric. However, peaks due to the Si-OH and H-OH bonds are observed at around 960 and 3650, and ~3300 cm^{-1}, respectively, indicating that the oxide films contain a relatively large amount of water. This observation of the OH bond is the same as that previously reported. It is considered that the OH bonds incorporated in the films are mainly from the silanol bonds of Si-OH of the precursors where the dehydration reaction does not occur during the deposition with some possibility in statistical thermodynamics. By comparing the two spectra, the peak intensity due to the Si-O-Si bond for TCE is observed to be markedly higher than that obtained without TCE. This indicates that adding TCE increases the deposition rate of Si oxide films as expected previously. Furthermore, a peak related to chlorine derived from TCE is hardly observed. This result indicates that TCE increases the Si oxide deposition rate, but negligibly affects the chemical composition of the films.

Figure 3 shows the comparison of the temperature dependences of deposition rate obtained with (closed circles) and without (open circles) TCE, where the temperature ranges from 160 to 220 ^{o}C and N_2 (SO) is 0.35 lm. The data plots and error bars indicate the averages and ranges of deposition rate, respectively, among the three deposition times of 5, 10, and 15 min. It is seen clearly from Fig. 3 that, in the temperature range, the deposition rate is higher with TCE than without TCE, as shown in Fig. 2. It is also

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

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

200 ^{o}C, at which it never occurs without TCE. Most of the SiO_2 particles formed in the gas phase through the promoted dehydration reaction probably do not contribute to deposition on the substrate. Thus, with an increase in deposition temperature, the actual deposition rate of Si oxide films on the substrate is reduced. As a result, the deposition rate saturates or slightly decreases with an increase in deposition temperature as shown in Figs. 3 and 4. In contrast, in the case without TCE, since the thermal energy from the heated substrate in this experiment is insufficient for chemical reaction among reactant gases, the deposition rate monotonically increases with the deposition temperature as shown in Fig. 3.

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

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

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

Acknowledgment

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Figure Captions

Fig. 1. Schematic diagram of the APCVD system used in this study. The system consists of a vertical reactor, a substrate holder, a transport wall, a showerhead, and a reactant gas supply system. The N_2 gas flow rate is 0.25, 0.3, or 0.35 lm for SO and the substrate temperature ranges from 160 to 220 ^{o}C.

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

Fig. 3. Comparison of deposition temperature dependences of deposition rate obtained with and without TCE, where the temperature ranges from 160 to 220 ^{o}C and N_2 (SO) is 0.35 lm. The plots and error bars indicate the averages and ranges of deposition rate, respectively, among the 3 deposition times of 5, 10, and 15 min.

Fig. 4. (Color online) Dependence of deposition rate on the deposition temperature for the N_2 (SO) flow rates of 0.35 (circles), 0.30 (squares), and 0.25 (triangles) lm with TCE.

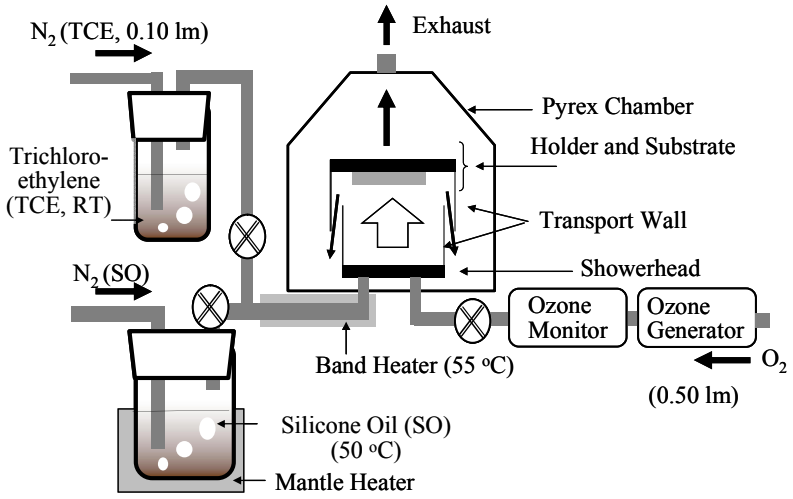
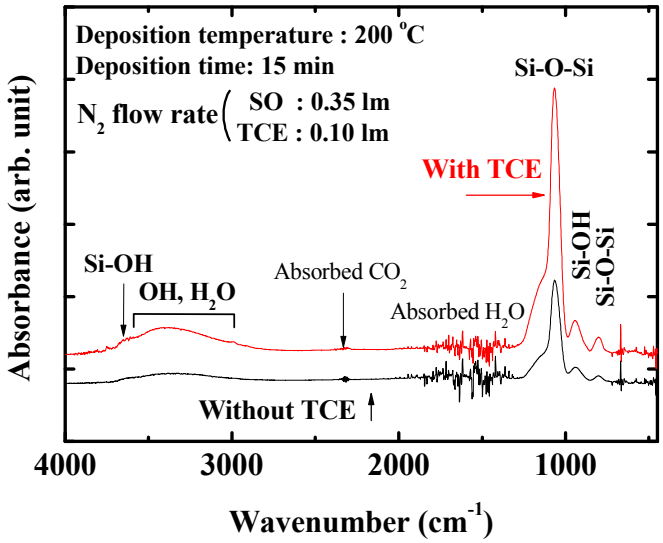


Fig. 1 **BN of JJAP, S. Horita et al.**



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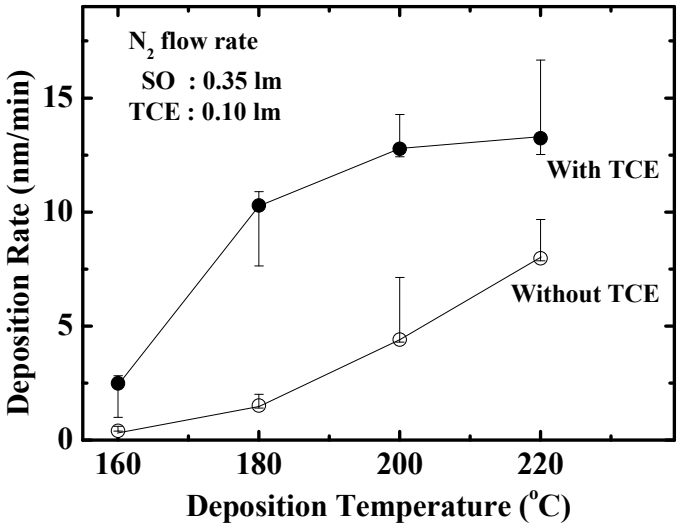

Fig. 3 **BN of JJAP, S. Horita et al.**

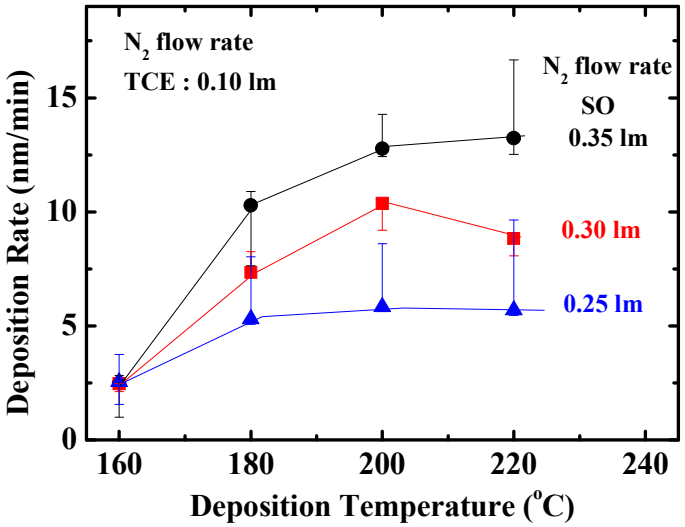

Fig. 4 **BN of JJAP, S. Horita et al.**