

Supercritical Fluid Deposition of SiO₂ Thin Films: Growth Characteristics and Film Properties

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Supercritical fluid deposition (SCFD) of SiO₂ thin film using supercritical fluid CO₂ (SCF CO₂) was investigated. Tetraethyl orthosilicate (TEOS) and O₂ were used as precursor and reactant, respectively. Growth characteristics of SCFD SiO₂ were investigated as a function of key growth parameters including the concentration of precursors, deposition time, and temperature. The activation energy of SCFD SiO₂ was lower than the reported value of chemical vapor deposition of SiO₂, indicating the solvation effects of SCF CO₂ on the reaction of TEOS and O₂. By controlling precursor concentrations, excellent gap filling of SCFD SiO₂ was achieved even inside of anodic aluminum oxide with less than 50 nm hole diameter. Leakage current of SCFD SiO₂ films increased with increasing oxygen concentration, which was attributed to the decrease of the film density. Higher O₂ concentration led to rapid reaction of SCFD SiO₂, resulting in the low density SiO₂ formation with high leakage current. (© 2011 The Electrochemical Society. [DOI: 10.1149/2.031202jes] All rights reserved.

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Supercritical fluid deposition (SCFD) is an attractive deposition method for nanoscale device fabrication. Supercritical fluids are advantageous as solvents for their high diffusivity, high solubility, low viscosity, and low surface tension, resulting in excellent gap filling by SCFD.¹ Among various supercritical fluids, CO₂ has been widely studied for SCFD due to its relative low critical temperature, 31.2°C, and pressure, 7.38 MPa.² CO₂ is also non-toxic and easily removable after processing. For these reasons, SCFD processes for Cu and Ru have been investigated for depositing barrier and seed layers in Cu interconnect technology.^{3–7} Furthermore, low temperature SCFD processes below 200°C of various oxides such as Al₂O₃, ZrO₂, MnO₂, RuO₂, and HfO₂ have been reported.^{8–10} Additionally, various film properties including conformality have been studied for SCFD of HfO₂, ZrO₂, and TiO₂.¹¹

SiO₂ is one of the mostly widely used materials in the fabrication of Si devices. With downscaling of Si devices, complicated 3D structures are being extensively studied. Thus, the ability to deposit SiO₂ with high gap filling and good electrical properties is required more than ever. In this regard, SCFD is an attractive alternative to conventional deposition processes such as chemical vapor deposition (CVD) and physical vapor deposition (PVD). Although several reports are available for SCFD SiO₂, those are all on the fabrication of nanostructures using SCFD SiO₂ together with nanotemplate.¹²⁻¹⁶ No detailed study is available yet on the growth characteristics and thin film properties of SCFD SiO₂. We investigated SCFD of SiO₂ using metal-organic precursors and O₂ as a reactant. By varying deposition conditions, the growth characteristics and film properties were studied with a focus on applications for insulating layers such as shallow trench isolation for nanoscale semiconductor devices. In particular, the effects of reactant on the electrical properties were studied systematically.

Experimental

A flow type supercritical fluid deposition chamber was used (Fig. 1). The chamber is compatible with high-pressure processes, being made of stainless steel. The SCFD system is composed of a high-pressure pump with a cooler, a canister for precursors, and a deposition chamber. A resistive heater is located inside the deposition chamber are 10.2 mL and 290 mL, respectively. After condensation of CO₂ in the cooler at 2° C, the CO₂ was pressurized by a high-pressure plunger pump before entering the canister and the deposition chamber. The pressures in the deposition chamber and canister were

separately controlled by back-pressure regulators equipped on a vent line as shown in Figure 1.

Tetraethyl orthosilicate (TEOS) and O_2 (99.999%) were used as a precursor and a reactant, respectively. The volume of TEOS was measured by a micropipette and a precisely measured amount of TEOS was put into the canister in a glove box. The concentration of TEOS (C_{TEOS}) in the canister, defined by the moles of TEOS per canister volume, was varied from 13.3 mmol/L to 133.1 mmol/L. After sealing of the canister and the deposition chamber, residual air in the entire SCFD system was flushed by low pressure CO_2 for 5 min. The volume of TEOS loaded was roughly measured by the glass window of the canister, and significant loss of TEOS was not observed during the flushing. After flushing, O2 was added into the deposition chamber at room temperature, isolated from the canister by closing the separation valve (V5). The amount of O₂ in the main chamber was controlled by O₂ pressure from 1 MPa to 5 MPa. The concentration of O_2 reactant (C_{O_2}) was approximately calculated by Peng-Robinson equation of state using O2 pressure and the volume of the deposition chamber,¹⁷ which was varied from 450 mmol/L to 1250 mmol/L. The CO₂ was separately added into each of the canister and the deposition chamber to form SCF CO₂. The pressures of the canister and the deposition chamber were set to be 16 MPa and 15 MPa, respectively, in order to flow the TEOS dissolved in SCF CO₂ by a pressure difference. After each set pressure was reached, the CO₂ was only supplied to the canister. By opening the canister valves (V3 and V4) and the separation valve (V5), the precursor dissolved in SCF CO₂ was flown into the deposition chamber for a certain deposition time. The temperature of the canister and feed lines inside the dash line of Figure 1 was maintained at 50°C. The Si(001) substrates were cleaned by dipping in buffered oxide etchant (6:1) for 10 s followed by deionized (DI) water rinsing and N₂ blowing.

The morphology of the films was analyzed by field emission scanning electron microscopy (FE-SEM). The microstructure and density SiO₂ films were analyzed by synchrotron radiation X-ray diffraction (XRD) and X-ray reflectivity (XRR), respectively, at the Pohang acceleration laboratory, 3C2 beam line. Ellipsometry was used to analyze the SiO₂ thickness by using laser energy between 1.5 eV and 5 eV at an angle of 70° .

To investigate the insulating properties of the SCFD SiO₂ film, metal-oxide-semiconductor (MOS) structures were fabricated. The SiO₂ films were deposited with a constant $C_{TEOS} = 133.1$ mmol/L at $T_s = 200^{\circ}$ C for 60 min. At $C_{O_2} = 450$ mmol/L and 1250 mmol/L, the thicknesses of SiO₂ films were 42 nm and 138 nm, respectively. For comparison, SiO₂ was also deposited by plasma enhanced CVD (PE-CVD) using SiH₄ and O₂ plasma, which is a typical SiO₂ deposition process for conventional device fabrication. After deposition of SiO₂ on a p-type Si substrate, 40 nm-thick Ru gates were defined by

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Figure 1. Schematic drawing of SCFD system. The temperature of dashed-area was kept as 50° C.

sputtering with a shadow mask. For studying the gap filling properties of SCFD SiO₂, porous anodic aluminum oxide (AAO) was used as a nanosize via hole. AAO was fabricated on an Al thin film-coated Si substrate, and the barrier layer at the bottom of AAO was removed by reactive ion etching. The diameter and depth of AAO holes were 50 nm and 200 nm, respectively. Further detail process of AAO pattern fabrication can be found elsewhere.¹⁸

Results and Discussion

Deposition Characteristics. --- The growth characteristics of SCFD SiO2 with changing TEOS concentration and deposition time were investigated. Figures 2a and 2b show the thickness of SCFD SiO₂ with increasing deposition time at different TEOS concentrations (CTEOS = 13.3 mmol/L and 133.1 mmol) under a constant O_2 concentration $(C_{O_2} = 450 \text{ mmol/L})$. At $C_{TEOS} = 13.3 \text{ mmol/L}$, the thickness of SCFD SiO₂ rapidly increases up to 14 nm at 20 min, and then saturates as shown in Figure 2a. At high TEOS concentration (CTEOS = 133.1 mmol/L), a larger saturation thickness of around 200 nm was observed at over 100 min of deposition time. For both cases, the thickness saturation is attributed to the consumption of the precursor molecules. Figure 2c shows the film thickness of SCFD SiO₂ as a function of C_{O_2} at $C_{TEOS}=133.1$ mmol/L at $T_s=200^\circ C$ for 20 min of deposition time. Deposition only occurred with the presence of oxygen, indicating the necessity of oxygen in the deposition reaction. The thicknesses of SiO₂ films almost linearly increase with increasing C_{O_2}

Figure 3 shows an Arrhenius plot for growth rate ranging from $T_s = 100^{\circ}$ C to 250°C. For all the growth temperatures, the growth time was constant as 20 min with $C_{TEOS} = 133.1 \text{ mmol/L}$ and $C_{O_2} = 1250 \text{ mmol/L}$. Apparent activation energy of SiO₂ deposition by SCFD is 15.85 kcal/mol (0.68 eV) from linear fit of the plots. This activation energy is smaller than the reported value of CVD SiO₂ process (54.97 kcal/mol) using the same set of precursor and reactant (TEOS and O₂) as the current SCFD process.¹⁹ This value is comparable with that of ozone based CVD using TEOS as a precursor (13.15 kcal/mol).¹⁹ Smaller activation energy values of SCFD than those of CVD were reported previously for other oxides, which was attributed to the high solvation power of the SCF solvent accelerating the removal of ligands from the precursor molecules.⁸⁻¹⁰ This high solvation power of SCF was explained by a model using clustering of solvent molecules around one solute molecule.^{20,21}

TEOS is one of the well-known precursors for CVD of SiO₂ thin films. Since TEOS is an alkoxide, SiO₂ thin films can be deposited through a thermal decomposition processes without any oxidant at high temperature. However, to lower the deposition temperature, reactants such as oxygen, ozone, or oxygen plasma are required. According to previous reports, the reaction of CVD SiO₂ using TEOS and O₂ occurs through the dissociative adsorption of TEOS molecules



Figure 2. Thickness vs. deposition time graphs of SCFD SiO₂ by using C_{TEOS} = (a) 13.3 mmol/L and (b) 133.1 mmol/L with constant C_{O_2} = 450 mmol/L at T_s = 200°C. (c) Thickness vs. O₂ concentration with constant C_{TEOS} = 133.1 mmol/L at T_s = 200°C.

on the surface, according to

 $*Si-OH-+Si(OC_2H_5)_4\rightarrow *Si-O-SiO(OC_2H_5)_3+C_2H_6,$

where the star (*) denotes surface atoms.^{22–24} Although oxygen is not directly involved in the reaction, it assists the clean removal of ligands.^{22–24} In fact, the required temperature for SiO₂ CVD using TEOS with O₂ should be higher than the deposition temperature used in the current experiment. Thus, it is likely that the SiO₂ SCFD occurs through the decomposition of TEOS, facilitated by ligand removal



Figure 3. Arrhenius plots of thickness vs. deposition temperature of SCFD SiO₂ deposited for 20 min with $C_{TEOS} = 133.1$ mmol/L and $C_{O_2} = 1250$ mmol/L.

which is assisted by oxygen whose reactivity is promoted by SCF CO_2 .

Gap filling property.— As one of the advantages of SCFD is excellent gap filling inside nanosize structures without seams, the current SiO₂ SCFD process was tested on photo-lithographically patterned, low aspect ratio Si trenches with less than 200 nm width. Figure 4 shows an SEM cross sectional image of an SCFD SiO₂ film on Si trenches, deposited at $C_{TEOS} = 133.1 \text{ mmol/L}$ and $C_{O_2} = 450 \text{ mmol/L}$ for 120 min. The SiO₂ film uniformly covers the entire surface. Furthermore, the film completely fills sub-100 nm-size trench patterns without any seams.

The gap filling ability of SCFD SiO₂ for nanoscale vias was also investigated using an AAO template with nanoscale holes (diameter and depth of 50 nm and 200 nm, respectively). Figure 5a shows a cross sectional SEM image of AAO after SCFD SiO₂ using the same deposition conditions as that used for the trenches above. Here the SiO₂ film deposited only on the top 30% of the holes, unlike that of the trench deposition. To improve the gap filling the O₂ concentration was increased. Figure 5b shows that complete gap filling was achieved at C_{O2} = 1250 mmol/L.

In a previous report on metal SCFD, the gap filling properties could be changed by changing deposition conditions, such as deposition temperature and the amount of precursors.²⁵ The effect of the amount of precursor on gap filling was attributed to the difference in the



Figure 4. The SEM image of Si trench coated by SCFD SiO₂ films.



Figure 5. The SEM images of SCFD SiO₂ films by using $C_{O_2} = (a)$ 450 mmol/L and (b) 1250 mmol/L on AAO patterns.

amount of precursors reaching a specific portion of the nanostructure caused by geometrical factors. As described above, the existence of O_2 is critical in the low temperature deposition of SiO₂ during SCFD process. Therefore, limited gap filling of SCFD SiO₂ in AAO can be attributed to the deficiency of O_2 reactant inside AAO holes. These results indicate that higher O_2 concentration is essential for good gap filling of SiO₂ SCFD.

Electrical Property.— In order to study insulating properties of SCFD SiO₂ films, MOS capacitors with SCFD SiO₂ as the dielectric were prepared as described in the experimental procedure section. Figure 6 shows the leakage current results for SCFD SiO₂ films deposited at different C_{O2} together with PE-CVD SiO₂ prepared for comparison. The results show that the leakage current density is critically dependent on C_{O2}. At E = -1 MV/cm, the leakage current density was 1.11 $\times 10^{-5}$ A/cm² at C_{O2} = 450 mmol/L and increases to around 1.13 $\times 10^{-4}$ A/cm² at C_{O2} = 1250 mmol/L. For comparison, the leakage current density of PE-CVD SiO₂ was 6.46 $\times 10^{-3}$ A/cm⁻² at the same electric field.

Figure 7 shows synchrotron radiation XRR curves of SiO₂ films. The curves have different critical angles, and the angle increases with decreasing O₂ concentration, indicating the formation of a denser SiO₂ film at lower O₂ concentration. The film densities obtained from the critical angles were 2.100 g/cm³ and 2.041 g/cm³ for SiO₂ films deposited at C_{O2} = 450 mmol/L and 1250 mmol/L, respectively. Compared to the density of bulk fused silica, 2.2 g/cm³, the density of SCFD SiO₂ prepared at C_{O2} = 450 mmol/L is very close to the bulk value. Generally, it is accepted that the denser SiO₂ films have lower leakage current and higher breakdown voltage.^{26,27}



Figure 6. I-V characteristics of SCFD SiO₂ films. SiO₂ deposited by SCFD using $C_{O_2} = (\Box)$ 450 mmol/L, (Δ) 1250 mmol/L, and (\bigcirc) PE-CVD. The thicknesses for four different SiO₂ films by $C_{O_2} = 450$ mmol/L, 1250 mmol/L, and PE-CVD are 42 nm, 138 nm, and 55 nm, respectively.



Figure 7. The SR-XRR curves of SCFD SiO₂ films deposited by using C_{O_2} = (solid) 450 mmol/L and (dot) 1250 mmol/L.

According to the reaction mechanism described above, SiO2 SCFD occurs through: (1) TEOS molecule adsorption on the surface, (2) ligand removal by O₂, and (3) re-adsorption of TEOS on the newly generated SiO₂ surface. Since the diffusivities of TEOS and O₂ dissolved in SCF CO2 are very high, TEOS molecules rapidly occupy the newly generated surface sites. The reaction rate is therefore mainly determined by ligand removal reaction. Thus, when the amount of O₂ increases, the reaction rate increases, resulting in the formation of a low-density film. For instance, CVD using catalytic reaction (Cat-CVD) usually produces lower density films than high temperature CVD since Cat-CVD has a higher reaction rate than normal CVD.²⁸ Therefore, the increase in O₂ concentration leads to the increase in reaction rate, resulting in the formation of low-density films with high leakage current. Our SCFD SiO₂ results demonstrate the effects of O₂ on both the growth characteristics and the electrical properties. In order to apply SCFD SiO₂ to nanoscale insulators, precise optimization of O₂ concentration is necessary between high C_{O2} for better gap filling and low C_{O2} for low leakage. However, since the amount of oxygen reaching far inside the nano-vias will be smaller than that on a planar surface, the actual leakage current density of the oxide film deposited inside the vias is expected to be higher than the value shown in Fig. 6.

Conclusions

SiO₂ SCFD process was investigated by using TEOS and O₂ as a precursor and reactant, respectively. The thickness of SCFD SiO₂ saturated with increasing deposition time due to the consumption of precursors. The activation energy of SCFD SiO₂ turned out to be low, 15.85 kcal/mol, compared to the reported value for CVD SiO₂, indicating the solvation effects of SCF CO₂. Complete gap filling of SCFD SiO₂ was achieved on nanometer scale trenches, although it was limited in the case of nano-sized vias. The gap filling of vias was significantly improved by increasing C_{O2}, which is attributable to the increase in the number of oxygen molecules reaching inside the vias. The leakage current density of the SCFD SiO₂ films was less than conventional PE-CVD SiO₂. However, the leakage current values were critically dependant on C_{O2}. XRR density analysis showed that the high leakage current is attributable to low film density.

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