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# Thermally Stable Carbon-Doped Silicon Oxide Films Deposited at Room Temperature

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## 1. Introduction

Silicon oxide is widely used for electronic devices such as gate oxides, interlayer dielectrics, and passivation coatings. Low-temperature (<100°C) deposition of the oxide is necessary for manufacturing heat-sensitive devices. Generally, the films deposited at <150°C have poor insulating properties due to hydroxyl (OH) groups contained in the films [1]. In numerous attempts to deposit $SiO_2$ by low-temperature plasma-enhanced chemical vapor deposition (PECVD), a few reports showed acceptable insulating properties of $SiO_2$ deposited using $SiH_4$ at <100°C [2]. Recently, we have succeeded in room-temperature deposition of carbon-doped silicon oxide (SiOCH) films by PECVD using tetraethoxysilane [$Si(OC_2H_5)_4$: TEOS] [3]. During the deposition, low plasma density and low substrate temperature enabled the SiOCH films to incorporate hydrocarbon ($C_mH_n$) groups, resulting in low leakage current of ~$10^{-10}$ A/cm$^2$ at 1 MV/cm [4].

In this contribution, we report thermal stability of the SiOCH films deposited at room temperature. Effects of thermal annealing on structural and electrical properties were investigated.

## 2. Experimental

SiOCH films were deposited on *n*-type Si(100) substrates in a developed remote PECVD system with a radio-frequency (RF) generator (13.56 MHz). Ar of 3.5 sccm was introduced into a plasma chamber where it was dissociated by RF of 50 W. TEOS of 1.0 sccm was introduced into a reactor chamber, downstream the plasma. During the deposition, the substrates were not heated intentionally. Due to plasma heating, the deposition temperature reached a maximum of 30°C. Subsequently, the deposited films were annealed at 200–1000°C in vacuum (~$10^{-3}$ Pa) for 1 h. The film thickness and refractive index of the films were measured by ellipsometry. The chemical bonding structure of the films was investigated by Fourier transform infrared (FT-IR) spectroscopy. Current–voltage (*I*–*V*) measurements were carried out in metal–oxide–semiconductor (MOS) structures with Al top electrodes in $N_2$ ambient.

## 3. Results and Discussion

Figure 1 shows FT-IR spectra of the SiOCH films. The absorbance is normalized by the film thickness. In the spectra of the as-grown film, the largest absorbance band at 1000−1250 cm$^{-1}$ is Si−O−Si stretching. The three peaks at 2800−3000 cm$^{-1}$ are $C-H_n$ stretching and the broad band at about 3400 cm$^{-1}$ is O−H stretching. The $C-H_n$ peaks have a similarity of the shape with $C-H_n$ vibrations in gas phase TEOS molecule [5], indicating that $C_mH_n$ groups are incorporated intact into the SiOCH films. The Si−O−Si network in the films is considered to be terminated by $C_mH_n$ groups like Si−O bonding in TEOS molecule (≡Si−O−$C_2H_5$). The $C-H_n$ peaks are observed even at 400°C. In the film annealed at 600°C, however, they were not easily identified.

Figure 2 shows the integrated absorption intensity of $C-H_n$ and O−H peaks as a function of annealing temperature. The intensity of $C-H_n$ absorption shows remarkable decrease at 400−600°C. On the other hand, The O−H intensity increases rapidly at the annealing temperatures. These results indicate that the $C_mH_n$ groups incorporated into the films at 30°C are thermally stable up to 400°C. The reduction of $C_mH_n$ groups increases OH content in the SiOCH films at high temperatures. It is suggested that decomposition of $C_mH_n$ groups in the films causes formation of OH groups due to moisture absorption.

Figure 3 shows the thickness variation of the SiOCH films and Si−O−Si absorption intensity in the FT-IR spectra. The film thickness of 520 nm remains almost constant below 400°C. Annealing at temperatures above 400°C causes significant film shrinkage. The thickness reduction ratio is about 40% at 600°C (310 nm). The integrated intensity of Si−O−Si increases with annealing temperature. The rapid increase of Si−O−Si intensity at 400−600°C indicates that the thickness reduction is caused by densification of the films.

Figure 4 shows *I*−*V* characteristics of the as-grown and annealed SiOCH films together with that of thermally grown $SiO_2$. The leakage current density of the as-grown SiOCH film is about $7\times10^{-10}$ A/cm$^{-2}$ at an electric field of 1 MV/cm. At low electric fields, the SiOCH shows insulating properties comparable to those of the $SiO_2$. The *I*−*V* characteristics of the film annealed at 200°C are similar with that of the as-grown film. The current density becomes large rapidly in the films annealed at 400−600°C.

The SiOCH films deposited at 30°C showed incorporation of $C_mH_n$ groups and good insulating properties. As the films were annealed at temperatures above 400°C, the $C_mH_n$ content and the film thickness were much decreased. It is considered that annealing at high temperatures dissociates $C_mH_n$ groups from the films, leaving Si−O−Si network. The oxide network then rearranges itself, leading to densification of the film. The reduction of $C_mH_n$ groups increases OH groups. The degradation of insulating properties by high-temperature annealing is considered to be due to this increase of OH in the films. Therefore, the $C_mH_n$ groups in the SiOCH films prevent the incorporation of OH groups and provide the low leakage current.

## 4. Conclusion

We have studied thermal stability of the SiOCH films deposited at 30°C. The as-grown film with high $C_mH_n$ content showed the low leakage current of $7\times10^{-10}$ A/cm$^{-2}$ 1 MV/cm. The $C_mH_n$ groups incorporated in the films are thermally stable up to 400°C. High-temperature annealing above 400°C dissociates the $C_mH_n$ groups from the films, leading to increase of OH groups. This increase of OH groups causes degradation of the insulating properties in the densified films annealed at high temperature.

## References


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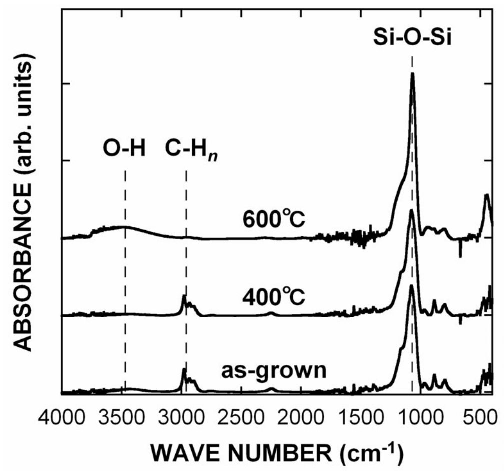


Fig. 1. FT-IR spectra of SiOCH films annealed at 400 and 600°C, which are compared with that of an as-grown film.

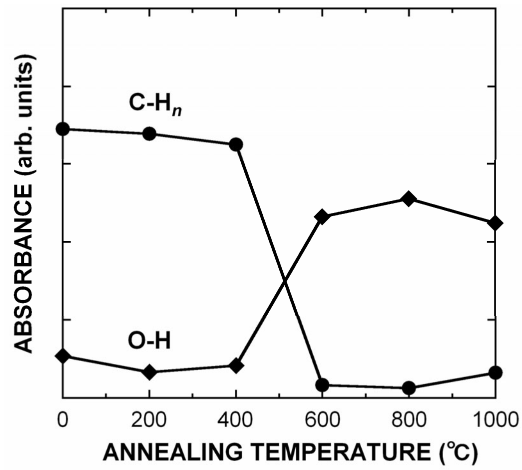


Fig. 2. Integrated absorption intensity of C−$H_n$ and O−H peaks as a function of annealing temperature.

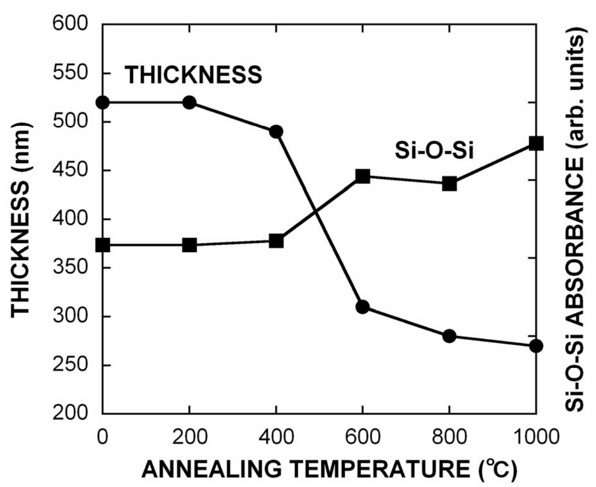


Fig. 3. Film thickness and Si−O−Si absorbance in the FT-IR spectra as a function of annealing temperature.

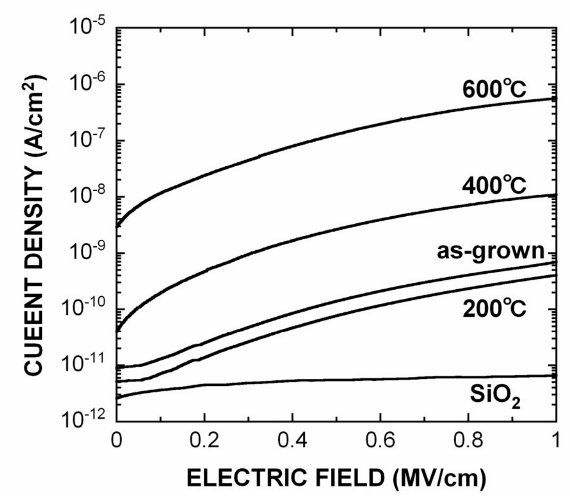


Fig. 4. Current density−electric field curves of an as-grown SiOCH film and films annealed at 400 and 600°C, which are compared with that of thermally grown $SiO_2$.