Thermal Stability of SiOCH Films Deposited by Room-Temperature Plasma-Enhanced Chemical Vapor Deposition Using Tetraethoxysilane

Keisuke Yamaoka, Yuji Yoshizako, Hideaki Kato, Daisuke Tsukiyama,
Yoshikazu Terai and Yasufumi Fujiwara
Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita,
Osaka 565-0871, Japan
Fax: 81-6-6879-7536, e-mail: keisuke.yamaoka@mat.eng.osaka-u.ac.jp

Thermal stability of carbon-doped silicon oxide (SiOCH) films deposited by plasma-enhanced chemical vapor deposition (PECVD) using tetraethoxysilane (TEOS) was investigated. The SiOCH films deposited at room temperature showed a flat surface with root-mean-square roughness less than 1 nm and a leakage current density of 5×10^{-7} A/cm^2 at 0.5 MV/cm. In the temperature dependence of thermal annealing, the film properties of thickness, surface roughness, carbon composition and leakage current hardly changed after the annealing at 400°C for 1 h. When the film was annealed at temperatures above 400°C, the film thickness of 231 nm decreased rapidly to 145 nm. In Fourier transform infrared (FT-IR) measurements, the absorption peaks of hydrocarbon groups which indicate the incorporation of carbon into the films disappeared above 400°C. The annealing dependence of the film thickness and the carbon content originates from a desorption of hydrocarbon groups in the films. The thermal stability of the SiOCH films is discussed with bond stability between hydrocarbon and oxygen in the films.
Key words: silicon oxide, porous silica, PECVD, TEOS

1. INTRODUCTION

As device dimensions shrink, replacement of silicon dioxide (SiO$_2$) dielectrics with low dielectric (low-k) materials is required for interlayer dielectrics of ultra-large-scale integrated (ULSI) circuits. Carbon-doped silicon oxide (SiOCH) thin films deposited by plasma-enhanced chemical vapor deposition (PECVD) are attracting much interest due to their potential as low-k materials. The deposition of SiOCH films by PECVD has been investigated using various organosilicon sources such as trimethylsilane (3MS) [1–3], tetramethylsilane (4MS) [4] and bis-trimethylsilylmethane (BTMSM) [5]. The SiOCH films show a good thermal stability of dielectric constant and leakage current up to 500°C which originates from the incorporation of strong bonds between Si and hydrocarbon (CH$_n$) groups in the films [4,5]. In order to optimize the film properties, however, the SiOCH deposition requires substrate heating or post-annealing treatment in the temperature range of 200–500°C [1–5]. For manufacturing heat-sensitive devices and performing film deposition on polymeric substrates, the deposition technique of SiOCH films at lower temperatures is necessary.

In the PECVD deposition using tetraethoxysilane [Si(OC$_2$H$_5$)$_4$: TEOS], it is well known that hydrocarbon groups are easily-removable due to a weak chemical bonding of O–C$_2$H$_5$ in TEOS [6]. Therefore, TEOS has been widely used for the deposition of carbon-free silicon oxide. In other words, the deposition of SiOCH with the good thermal stability using TEOS has been considered to be difficult. Recently, we have succeeded in the room-temperature deposition of SiOCH films by a developed remote PECVD using TEOS [7]. In the remote PECVD system, the dissociation and

desorption of hydrocarbon groups in TEOS precursors were suppressed by low substrate temperature and low plasma density. The SiOCH films deposited at low RF power showed high carbon content and low film density due to the incorporation of alkyl (C$_n$H$_{2n+1}$) groups [7]. The alkyl groups in the films bind to oxygen atoms of the Si–O–Si network in contrast to Si–CH$_n$ bonds in SiOCH films deposited using other sources. Therefore, the investigation of the thermal stability is necessary for the application of the SiOCH films deposited by TEOS.

In this paper, we report the thermal stability of the SiOCH films deposited by room-temperature PECVD using TEOS. The dependence of the structural and electrical properties on annealing temperature was investigated.

2. EXPERIMENT

SiOCH films were deposited in a home-made remote PECVD system with a radio-frequency (RF) generator (13.56 MHz). A substrate holder in the reactor chamber was far from the plasma chamber (~30 cm) and was electrically grounded. The films were deposited on n-type Si(100) substrates, which were not heated intentionally. Ar of 2.0 sccm and TEOS of 1.0 sccm were introduced into the plasma chamber and the reactor chamber, respectively. During the deposition, total pressure in the chamber was about 20 Pa and applied RF power was 100 W. The substrate temperature increased up to 38°C due to some heating effects by the plasma. Subsequently, the deposited films were annealed at 200–1000°C in a vacuum (~10^{-3} Pa) for 1 h.

The film thickness and refractive index of the films were measured by ellipsometry. The surface morphology of the samples was studied with atomic force microscopy (AFM). The film composition and

496

*Thermal Stability of SiOCH Films Deposited by Room-Temperature
Plasma-Enhanced Chemical Vapor Deposition Using Tetraethoxysilane*

chemical bonding structure were investigated by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy. Current–voltage (I–V) measurements were carried out using metal–oxide–semiconductor (MOS) structures with Al top electrodes in N_2 ambient.

3. RESULTS AND DISUCUSSION

SiOCH films were deposited by decomposition of TEOS molecules with Ar plasma [7]. The film thickness measured by ellipsometry was 231 nm. Figure 1 (a) shows an AFM image of the film, which has a smooth surface with a root-mean-square (RMS) roughness of about 0.3 nm. XPS and FT-IR measurements of the SiOCH films showed that the films contained carbon due to incorporation of CH_n groups. The composition of the film was estimated roughly at $SiO_{1.59}C_{0.64}$:H from the XPS spectra [7].

To study thermal stability of the SiOCH films, the films were annealed at 200–1000°C in a vacuum. Figure 2 shows thickness variation of the SiOCH films annealed at various temperatures. The thickness remains almost unchanged after annealing at 400°C. Annealing at temperatures above 400°C reduces the film thickness drastically. The thickness of the film annealed at 800°C is decreased to 145 nm, corresponding to the reduction ratio of about 40%. This obvious decrease of the thickness would involve structural changes of the films such as surface morphology and film composition.

The surface morphology of the films hardly changed after annealing at 200 and 400°C. Figure 1 (b) shows an AFM image of the film annealed at 600°C, which has a flat surface with RMS roughness of about 0.3 nm. The SiOCH films keep flat surface in spite of the appreciable change of the film thickness by high-temperature annealing.

FT-IR spectra of the as-grown SiOCH film and the

Fig. 2. Film thickness of SiOCH films as a function of annealing temperature.

films annealed at 400 and 600°C are shown in Fig. 3. The absorbance is normalized by the film thickness. The peak centered at about 1070 cm^{-1} is corresponding to Si–O–Si and Si–O–C stretching [8]. The term "Si–O–Si stretching" is used throughout this paper to refer this peak in the spectra. In the spectra of the as-grown film, the absorptions at about 2950 cm^{-1} are observed. The absorptions correspond to CH_n stretching [8]. The inset shows the detailed spectra of the as-grown film at about 2950 cm^{-1}. As seen in the inset, the absorption peaks at 2935 and 2976 cm^{-1} are observed clearly. These absorption peaks are attributed to CH_2 and CH_3 stretching of ethoxy (O–C_2H_5) groups in TEOS molecules [8,9]. The broad band centered at about 3400 cm^{-1} is due to O–H stretching and indicates incorporation of silanol (Si–OH) groups into the films [9]. The CH_n peaks are observed up to 400°C, however, they are absent in the films annealed at 600°C. The film annealed at 600°C shows two dominant peaks of O–H and Si–O–Si stretching. Figure 4 shows the integrated absorbance of Si–O–Si, CH_n and O–H peaks

Fig. 1. AFM images of SiOCH films (a) as-grown and (b) annealed at 600°C.
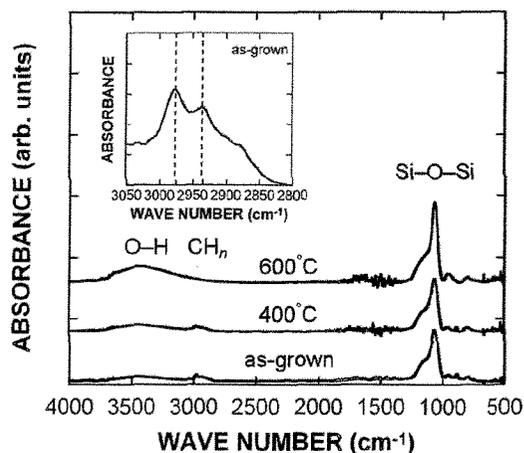
Fig. 3. FT-IR spectra of SiOCH films annealed at 400 and 600°C. The absorbance is normalized with film thickness. The inset is the detailed spectra of the as-grown film.
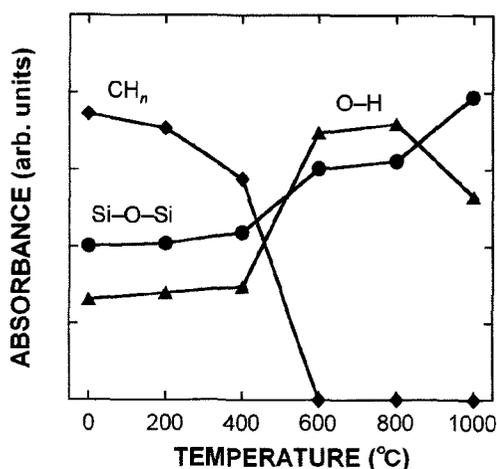
Fig. 4. Integrated absorbance of Si-O-Si, CH_n, O-H peaks as a function of annealing temperature.

Fig. 5. Current density–electric field curves of an as-grown SiOCH film and a film annealed at 400°C.

as a function of annealing temperature. The CH_n absorption slightly decreases up to 400°C. The intensity of CH_n peaks decreases significantly at 600°C and no absorption is observed at temperatures above 600°C. On the other hand, the O-H intensity is roughly constant up to 400°C and increases drastically at 600°C. It is noticeable that O-H contained in the films annealed at 1000°C is less than that of the films annealed at 600 and 800°C. The intensity of Si-O-Si stretching also increases with annealing temperature and is up to about two times higher for the film annealed at 1000°C compared with the as-grown film. These results indicate that high-temperature annealing of the SiOCH films removes CH_n groups from them, resulting in formation of OH groups and Si-O-Si network. The increase of Si-O-Si absorbance at 1000°C implies that formation of Si-O-Si bonds is also caused by elimination of Si-OH bonds [10].

Figure 5 shows *I–V* characteristics of the as-grown film and the film annealed at 400°C. The leakage current density of the as-grown film is about 5×10^{-7} A/cm^2 at 0.5 MV/cm. The film annealed at 400°C has almost the same leakage current density ($J = 8 \times 10^{-7}$ A/cm^2 at 0.5 MV/cm). This leakage current is comparable to that of SiOCH films deposited from other sources [5].

As described before, the SiOCH films deposited at room temperature showed high carbon content and low leakage current. When the films were annealed at temperatures below 400°C, the film thickness and leakage current did not change though the carbon content slightly decreased. These results indicate that the SiOCH films can be used as interlayer insulators in the devices which need the low-temperature processes. In silicon oxide films deposited at low temperature using organosilicon sources, thermally unstable CH_n groups are incorporated into the films [11]. The unstable CH_n groups are easily desorbed by annealing at low temperature. The desorption corresponds to the slight decrease of carbon content below 400°C in our films. While, alkyl groups tightly bonded to oxygen atoms in Si-O-Si network are stable up to 400°C. Therefore, the film thickness and the leakage current are considered
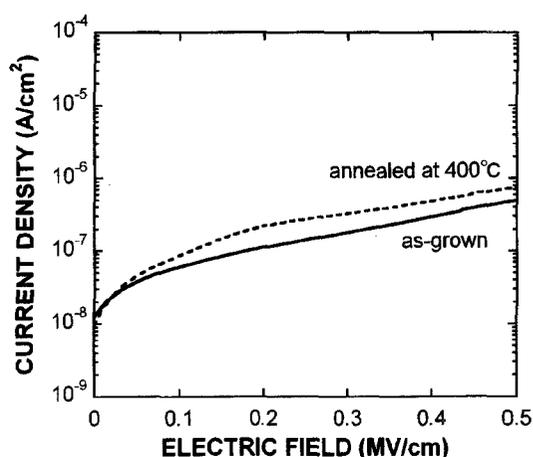
to be stable up to 400°C.

As the films were annealed at temperatures above 400°C, the film thickness and the carbon content were much decreased. On the other hand, the absorption intensity of O-H and Si-O-Si bonds increased. The structural changes are understood by the thermal dissociation of hydrocarbon groups in the films. According to the kinetic scheme of TEOS decomposition by O_2 plasma [12], TEOS precursors can be formed by electron impact dissociation, e.g.,

$$e + Si(OC_2H_5)_n(OH)_{4-n}$$
$$\rightarrow Si(OC_2H_5)_{n-1}(OH)_{4-n+1} + C_2H_4 + e, \quad n = 1-4, \quad (1)$$
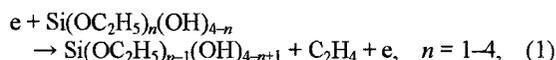
or by O-atom reactions with TEOS and its precursors, e.g.,

$$O + Si(OC_2H_5)_n(OH)_{4-n}$$
$$\rightarrow Si(OC_2H_5)_{n-1}(OH)_{4-n+1} + C_2H_4O, \quad n = 1-4. \quad (2)$$
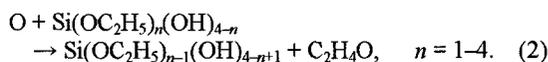
In both reactions, hydrocarbon groups are removed from the precursors and are replaced by OH groups, because the bond energy of C-O (3.7 eV) is smaller than that of Si-O (4.7 eV) and C-H (4.2 eV) [8]. These reactions lead a supposition that thermal decomposition of hydrocarbon groups takes place easily. We consider that the thermal dissociation of hydrocarbon groups induces the reduction of carbon content at temperatures above 400°C. In SiOCH films deposited with other sources, it is reported that the dissociation of hydrocarbon groups by annealing causes the shrinkage of the film thickness [13,14]. In our films, the annealing temperature dependence of film thickness corresponds to that of CH_n absorbance. Therefore, the decrease of thickness shown in Fig. 2 is due to the desorption of hydrocarbon groups. When the thermal desorption of hydrocarbon groups take places, dangling bonds of oxygen are formed inside the films. The dangling bonds may recombine with the residual hydrogen in the films during the rearrangement of Si-O-H networks, resulting in the increase of O-H absorption in FT-IR spectra. In further studies, direct observation of the dissociation species will be necessary.

498

*Thermal Stability of SiOCH Films Deposited by Room-Temperature
Plasma-Enhanced Chemical Vapor Deposition Using Tetraethoxysilane*

5. CONCLUSION

Thermal stability of the SiOCH films deposited by room-temperature PECVD using TEOS was investigated. The as-grown film with high carbon composition showed the flat surface and low leakage current of 5×10^{-7} A/cm^2 at 0.5 MV/cm. The thickness and leakage current of the films did not change up to 400°C due to the stable bonds between alkyl groups and oxygen atoms in Si–O–Si network. The remarkable decrease of the film thickness and carbon content at temperatures above 400°C was induced by the decomposition of the alkyl groups in the films.

ACKNOWLEDGEMENTS

REFERENCES

[1] M.R. Wang, Rusli, M.B. Yu, N. Babu, C.Y. Li, K. Rakesh, *Thin Solid Films*, **462/463**, 219–222 (2004).

[2] R. S. Brusa, M. Spagolla, G. P. Karwasz, A. Zecca, G. Ottaviani, F. Corni, M. Bacchetta and E. Carollo, *J. Appl. Phys.*, **95**, 2348–2354 (2004).

[3] P. Gonon, A. Sylvestre, H. Meynen and L. Van Cotthem, *J. Electrochem. Soc.*, **150**, F47–F52 (2003).

[4] A. Nara and H. Itoh, *Jpn. J. Appl. Phys.*, **36**, 1477–1480 (1997).

[5] Y.-H. Kim, S.-K. Lee and H. J. Kim, *J. Vac. Sci. Technol. A*, **18**, 1216–1219 (2000).

[6] M. A. Lieberman and A. J. Lichtenberg, "Principles of Plasma Discharges and Materials Processing", Wiley-Interscience, New York (1994) pp. 518–521.

[7] K. Yamaoka, Y. Yoshizako, H. Kato, D. Tsukiyama, Y. Terai and Y. Fujiwara, *Physica B* (in press).

[8] S. P. Mukherjee and P. E. Evans, *Thin Solid Films*, **14**, 105–118 (1972).

[9] S. C. Deshmukh and E. S. Aydil, *J. Vac. Sci. Technol. A*, **13**, 2355–2367 (1995).

[10] N. Hirashita, S. Tokitoh and H. Uchida, *Jpn. J. Appl. Phys.*, **32**, 1787–1793 (1993).

[11] S.-K. JangJian, C.-P. Liu, Y.-L. Wang, W.-S. Hwang and W.-T. Tseng, *Thin Solid Films*, **469/470**, 460–465 (2004).

[12] P. J. Stout and M. J. Kushner, *J. Vac. Sci. Technol. A*, **11**, 2562–2571 (1993).

[13] C.-C. Chiang, I-H. Ko, M.-C. Chen, Z.-C. Wu, Y.-C. Lu, S.-M. Jang and M.-S. Liang, *J. Electrochem. Soc.*, **151**, G704–G708 (2004).

[14] H. Lu, H. Cui, I. Bhat, S. Murarka, W. Lanford, W.-J. Hsia and W. Li, *J. Vac. Sci. Technol. B*, **20**, 828–833 (2002).