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Generation of Si-O-C Bond without Si-CH_3 Bond in Hybrid Type SiOC Film

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ABSTRACT

The chemical shift of SiOC film was observed according to the flow rate ratio. SiOC film had the broad main band of 880~1190 cm^{-1} and the sharp Si-CH_3 bond at 1252 cm^{-1}, and the peak position of the main bond in the infrared spectra moved to high frequency according to the increasing of an BTMSM flow rate. So the increment of the alkyl group induced the C-H bond condensation in the film, and shows the blueshift in the infrared spectra. In the case of P5000 system of Applied Materials Corporation, the strong bond of Si-CH3 bond in precursor does not enough to dissociated and ionized, because low plasma energy due to the capactive coupled CVD. Therefore, there was the sharp peak of Si-CH_3 bond at 1252 cm^{-1}.

Key Words : Si-O-C bond; redshift; Si-CH_3 peak; C-H bond elongation

I. INTRODUCTION

In order to reduce signal propagation delay time and cross-talk noise in ultralarge-scale integrated (ULSI) circuits, the development of low dielectric (low-k) constant materials is required instead of silicon dioxide lm[1-3]. There are alternative low-k materials such as hydrogenated amorphous carbon lm (a-C:H), uorinated amorphous carbon lm (a-C:F), uorine-doped silicon dioxide lms (SiOF) and parylene polymer lm. In these materials, SiOC lm using bistrimethylsilylmethane (BTMSM) and an oxygen-mixed precursor possess a lower dielectric constant due to the presence of lighter C and H atoms, as opposed to Si and O atoms. SiOC lm displays a blueshift and redshift in IR absorption spectra, depending on the nature of the bonding structure such as C-H bond elongation or condensation. The distinction between the Si–O–C bond of the redshift and the C–O bond of the blueshift has already been discussed in ref.[4]. The main IR signal involving the Si–CH_3 absorption at 1270 cm-1 accounted for the redshift, while the main signal without the Si–CH_3 absorption at 1270 cm-1 accounted for the blueshift. SiOC film with a blueshift has the organic properties, and that with a redshift has the hybrid or inorganic properties, so there are two kinds of origin of decreasing the dielectric constant in SiOC film. SiOC film with a blueshift decreases the dielectric constant because a silicate network generates pores through the action of steric and electrostatic forces, but that with a redshift decreases the dielectric constant due to the electron deficient effect of C-H bond elongation. Recently, it was reported that the organic-inorganic hybrid type SiOC film as low dielectric constant materials was used for organic gate insulators of OTFTs[5], because SiOC film is a good hybrid type gate insulator for organic TFTs[6,7]. Organic thin film transistors (OTFT) semiconductor has become attractive for application such as flat panel displays, smart cards, identification (ID) tags and electric papers, because the OTFT can be applied to flexible displays and low-cost circuits on plastic [8-14].

In this paper, the SiOC lm deposited using various flow rate ratios of BTMSM ($[(CH_3)_3Si]_2CH_2$) and O_2 mixed precursor were examined by deconvolution of sample spectra using Fourier transform infrared (FTIR) spectroscopy. It was researched the correlation

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between the generation of Si-O-C bonding structure and C-H bond elongation in the SiOC film.

2. EXPERIMENTS

The SiOC films were obtained using the mixed gases of oxygen and bistrimethylsilylmethane by chemical vapor deposition of Applied Materials Corporation (Precision 5000) at Chungbuk Techno-Park Foundation Semiconductor Test Center. The precursor of bistrimethylsilylmethane was purchased from the Applied Materials Corporation. The deposition condition was the substrate temperature at 100°C for 10 sec. The BTMSM was vaporized and carried by argon gas at 35°C from a thermostatic bubbler. SiOC films were prepared by various flow rate ratios, but the total flow was 120 sccm. The base pressure was 3 Torr and the rf power was 300 W in each experiment. The chemical properties were analyzed from Fourier Transform Infrared Spectrometer (FTIR, Galaxy 7020A). The FTIR spectra of samples were deconvoluted.

3. RESULTS AND DISCUSSION

Fig. 1(a) shows the FTIR spectra in the full range from 600 cm^{-1} to 4000 cm^{-1} of SiOC film with increasing the BTMSM flow rate ratio. There are the CH peak near 2950 cm^{-1}, the conjugated C = O bond of 1500~1750 cm^{-1}, the C = C bond of 1400~1500 cm^{-1}, Si-CH_3 peak near 1252 cm^{-1} and Si-O-C bonds below 1190 cm^{-1}. It is known that the Si-CH_3 peak is very strong bond in organic system. From the Fig. 1(a) of sharp and strong Si-CH_3 peak, it means that the Si-CH_3 group in BTMSM precursor does not dissociated sufficiently.

The sharp and weak Si-CH_3 peak in SiOC film origins from the recombination due to the sufficient dissociation of alkyl group in precursor, when is used the inductive coupled plasma CVD[4]. Therefore, the sharp and strong Si-CH_3 peak formation excluded from the main bond near 1000 cm^{-1} is the characteristic properties made in the capactive coupled plasma chemical vapor deposition (CCP-CVD). In the ICP-CVD system, SiOC film is generally divided into the blue and red shifts by FTIR spectra, and classified into three types by chemical properties: organic, hybrid and inorganic[4]. In the case of this CCP-CVD system, the main band near 1000 cm^{-1} does not possess the Si-CH_3 peak near 1252 cm^{-1}, and the C-H bond near 2950 cm^{-1} display. It is a common characteristic in SiOC film with organic properties. Fig. 1(b) shows the FTIR spectra of the low range of 750~1450 cm^{-1}. The samples were named BT20, BT30, BT40 and BT50 with increasing the BTMSM flow rate ratios, respectively. The peak intensity of bonds increased according to the increasing of the BTMSM flow rate ratio. However, the sample with the flow rate ratio of BT20 was distinguished from other samples because of low content of BTMSM precursor. The BT20 sample is almost like as SiO_2 film.

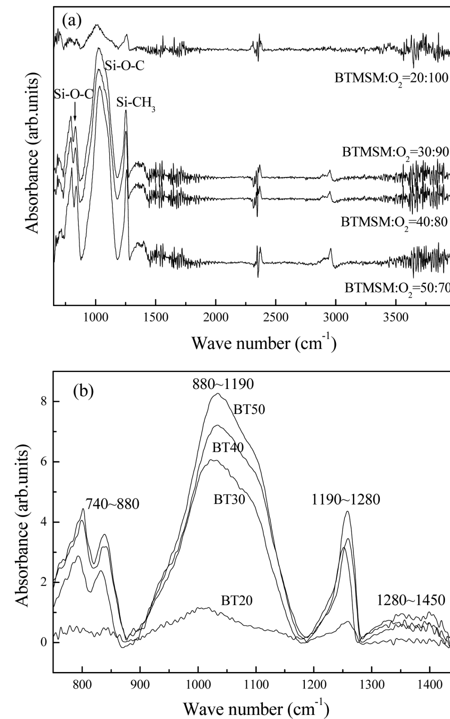

Fig. 1. FTIR spectra of SiOC film in (a) the full range from 600 to 4000 cm^{-1}, (b) the low range of 750~1450 cm^{-1}.

Fig. 2 shows the tendency of the chemical shift of the bond peaks. Fig. 2(a) displays the main bond in the range of 880~1190 cm^{-1}. The peak position of the main bond changed to high frequency according to

the increasing of the flow rate ratio of BTMSM precursor. The main bond was made by the elongation effect between alkyl group and oxygen, and the blue shift occurred due to the effect of the C-H bond condensation. Fig. 2(b) shows the Si-O-C bond in the range of 740~880 cm^{-1}. The bond near 794 cm^{-1} is the C-O related bond and the bond near 832 cm^{-1} is the Si-O related bond[5].

In view of the Si-O-C bond formation in the range of 740~880 cm^{-1}, the sample BT20 is very difference with others. The samples without BT20 shift higher frequency because of the effect of C-H bond condensation.

Fig. 2(c) shows the $Si-CH_3$ bond in the range of 1190~1280 cm^{-1}. The peak position of the $Si-CH_3$ bond changed to high frequency according to the

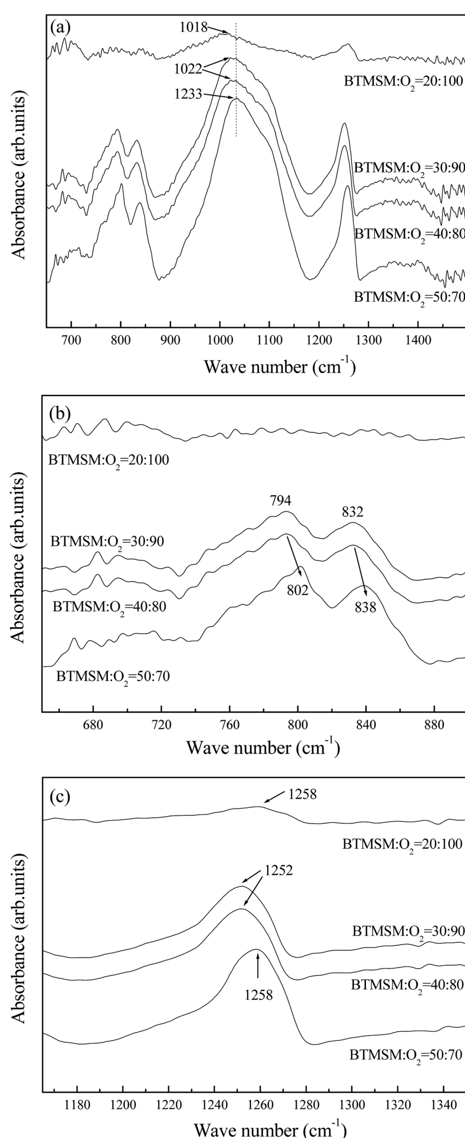

Fig. 2. FTIR spectra of the low range of 750~1450 cm^{-1}, (a) chemical shift in the range of 880~1190 cm^{-1}, (b) chemical shift in the range of 740~880 cm^{-1}, (c) chemical shift in the range of 1190~1280 cm^{-1}.

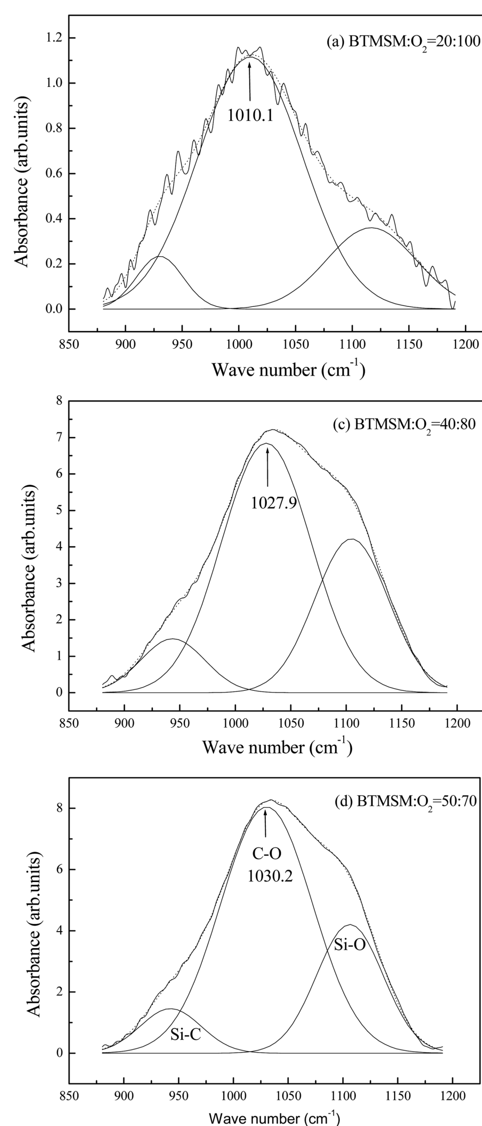

Fig. 3. Deconvoluted FTIR spectra of the main bond in the range of 880~1190 cm^{-1}, (a) $BTMSM:O_2 = 20:100$ (BT20), (b) $BTMSM:O_2 = 30:90$ (BT30), (c) BTMSM: $O_2 = 40:80$ (BT40), (d) $BTMSM:O_2 = 50:70$ (BT50).

increasing of the flow rate ratio of BTMSM precursor, but the $Si-CH_3$ bond of the sample with the flow rate ratio of BT20 was the same position as the sample with the flow rare ratio of BT50.

The samples of BT30, BT40 were made from the nucleophilic reaction between hydroxyl and alkyl group, and the generation due to the CH group and oxygen atoms. Therefore, the samples of BT30, BT40 showed the difference of peak position $Si-CH_3$ bond as shown in Fig. 2(c).

Fig. 3 shows the deconvoluted FTIR spectra of the main bond in the range of 880~1190 cm^{-1}. The main bond consisted of Si-C, C-O and Si-O related bonds, and the C-O related bond occupies most of the main bond. The peak position of the C-O related bond changed to higher with increasing the BTMSM flow rate ratios, and is the highest 1030.2 cm^{-1} at the sample BT50 (BTMSM:O_2 = 50:70) as shown in Fig. 3(d). In view of Si-C bond, the content of Si-C bond decreases in spite of the increase of the BTMSM flow rate ratio. This means that the dissociation of $Si-CH_3$ groups induced the recombination with the oxygen. Finally, the C-O bond or Si-O bonds were generated. The effect of C-H bond condensation due to the increase of the BTMSM flow rate ratios causes the peak position of C-O bond to change high frequency.

4. CONCLUSION

The SiOC films were obtained using the mixed gases of oxygen and bistrimethylsilylmethane by chemical vapor deposition. The peak positions of SiOC film in the ranges of 880~1190 cm^{-1} and 740~880 cm^{-1} moved to low frequency according to the increase of oxygen content. The increase of alkyl group induced the condensation effect of C-H bond, and the C-O bond peak near 1020 cm^{-1} shifted to higher frequency. The Si-O bond near 1100 cm^{-1} increased in spite of the increase of the amount of alkyl group. On the other hand, the Si-C bond content also increased according to the increase of oxygen flow rate ratio.

REFERENCE

1. T. C. Chang, P. T. Liu, Y. S. Mor, S. M. Sze, Y. L. Yang, M. S. Feng, F. M. Pan, B. T. Dai and C. Y. Chang, J. Electrochem. Soc., 146 (1999) 3802.
2. T. Oh, “Generation of SiOC films by the Thermal Induction,” Jpn. J. Appl. Phys. 44 (2005) 1409.
3. P. W. May, S. Hohn, W. N. Wang and N. A. Fox, Appl. Phys. Lett. 72 (1998) 2182.
4. T. Oh, K. M. Lee, K. S. Kim and C. K. Choi, Jpn. J. Appl. Phys. 43 (2004) 6354.
5. T. Oh, IEEE transactions on Nanotechnology, 5 (2006) 23.
6. J. Jang and S. H. Han, Current Appl. Phys. 6S1 (2006) e17.
7. W. J. Huang, B. Q. Li and J. M. Zuo, Surface Science, 12 (2005) 157.
8. Ioannis Kymissis, C. D. Dimitrakopoulos and Sampath Purushothaman, IEEE TRANSACTIONS ON ELECTRON DEVICES, 48 (2001) 1060.
9. D. J. Gundlach, Y. Y. Lin, T. N. Jackson, S. F. Nelson and D. G. Schlom, IEEE ELECTRON DEVICE LETTERS, 18 (1997) 87.
10. S. F. Nelson, Y.-Y. Lin, D. J. Gundlach and T. N. Jackson, Applied Physics Letters, 72(15) (1998) 1854.
11. J. Endo, T. Matsumoto and J. Kido, Jpn. J. Appl. Phys. 41 (2002) L358.
12. Max Shtein, Jonathan Mapel, Jay B. Benziger and Stephen R. Forrest, Applied Physics Letters, 81(2) (2002) 268.
13. D. Knipp, R. A. Street, J. Non-crystalline Solids, 338-340 (2004) 595.
14. Nathalie Vets, Mario Smet and Wim Dehaen, Tetrahedron Letters, 45 (2004) 7287.

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