
SiOC 박막의 FTIR 스펙트라에 의한 분석결과

이광만* · 오테레사* · 최치규** · 김정식*

Analysis of FTIR Spectra in Organic-Inorganic Hybrid Type SiOC Film

Kwang-Man Lee*, Teresa Oh*, Chi Kyu Choi** and Kyung Sik Kim*

ABSTRACT

SiOC films are porous low-k materials, which have organic-inorganic hybrid type thin films. SiOC films are analyzed the red and blue chemical shift by the fourier transform infraredspectra. Conventional chemical shift of organic compounds is usually a red shift, but hybrid type SiOC films were observed the red and blue shift. The chemical shift originates from the interaction between the C-H bond and high electronegative atoms, and the blue shift in SiOC films causes the porosity due to the increase of the electron rich group such as much methyl radicals. The bonding structures of SiOC films are divided into the Si-O-C cross-link structure and the Si-O-C cage-link structure due to the chemical shifts. The Si-O-C cross-link structure was progressed the adhesion due to the C-H bond elongation from the oxygen by the nano physical interface, and the dielectric constant also decreases because of the increase of the carbon content

Key Words : high electronegative oxygen, Si-O-Si cross-link, Si-O-C cross-link, Si-O-C cage-link

1. INTRODUCTION

In the past forty years, the semiconductor industry is based on the inorganic silicon, silicon dioxide insulators and aluminum metal. However, there has been a research effort in organic electronics to improve the ultra large scale integration (ULSI) devices[1~3], because the silicon carbide has proved its

ability to be used efficiently under high temperature rather than the SiO₂[4]. For semiconductors, two major classes of organic materials are photoresists and insulators. The organic materials as insulators are considered instead of silicon dioxide dielectric typically used on-chip throughout the industryBut the organic materials as low dielectric materials are also required to overcome the signal propagation delay and cross talks between wiring[5]. In the past decades, relevant low dielectric materials have introduced organic

* 제주대학교 전기전자공학부, 첨단기술연구소
Faculty of Electrical & Electronic Engineering, Research
Institute of Advanced Technology, Cheju Nat'l Univ.

** 제주대학교 물리학과
Department of Physics, Cheju Nat'l Univ.

materials such as fluorinated amorphous carbon (a-C:F) films[6] and hydrogenated amorphous carbon (a-C:H) films[7] by the chemical vapor deposition (CVD). These days, an organic-inorganic hybrid type carbon doped silicon oxide (SiOC) films have focus on the promising low dielectric materials[8~10]. It is known that SiOC films have the low dielectric constant due to the porosity and cross-link structure, but the reason of the chemical shift in SiOC films is not well known. The generation of a red and blue shift is key of examination about the reason of the decreasing the dielectric constant, because the chemical shift is directly related with the bonding structure of SiOC films[11]. The conventional chemical shift of organic compound is known the red shift by the elongation of C-H bond, the blue shift at experimental results was reported by some researcher[12~14]. The surface of the thin films was progressed the adhesion by the effect of the cross-link bonding structure[15~16], the red shift originated from the C-H bond elongation and cross-link structure.

In this study, the chemical shift of SiOC films was researched by the fourier transform infrared spectra. SiOC films are classified into three properties according to the chemical shift and the formation of the main mode. SiOC films with Si-O-C cross-link structure were studied the reason of the decrease the dielectric constant.

II. EXPERIMENTS

Low-k organosilicate films were deposited by inductively coupled plasma chemical vapor deposition (ICPCVD) using a mixture of gaseous bistrimethylsilylmethane (BTMSM,

$[(\text{CH}_3)_3\text{Si}]_2\text{CH}_2$) and oxygen. The flow-rate ratio of O_2/BTMSM (Ar) was varied, but total flow was 20 sccm. The films were deposited at room temperature, and then annealed at 500 °C for 30 minutes in a vacuum. The BTMSM was vaporized and carried by argon gas at 40 °C from a thermostatic bubbler. High-density plasma about 10^{12} cm^{-3} was obtained at low pressure with an rf power of 300 W in ICPCVD, and the base pressure was $\sim 10^{-5}$ Torr in each experiment. FTIR spectra were obtained in absorbance mode with a by the fourier transform infrared (FTIR) spectrometer (IFS120HR). FTIR spectroscopy was used to determine the bonding configuration of the films. Film thickness was measured using a field-emission scanning electron microscope (FESEM, S-4700) and an ellipsometer (Gaertner L116C). The dielectric constant of the films was obtained by C-V measurements (hp4280A) using an MIS (Al/Si-O-C film/p-Si) structure.

III. RESULTS AND DISCUSSION

Fig. 1 shows the primary FTIR spectra of as-deposited samples in SiOC films, which the samples were deposited according to the flow rate ratio of $\text{O}_2:\text{BTMSM}$. The sample with the flow rate ratio of $\text{O}_2:\text{BTMSM}=3:17$ (sccm) does not show the characteristic of hybrid type SiOC films, because of too much alkyl groups. The strong CH bonds about 2900 cm^{-1} indicate conventional characteristic of organic materials, and the band from 670 cm^{-1} to 950 cm^{-1} is also related with CH_n ($n=1, 2, 3$). There another films without $\text{O}_2:\text{BTMSM}=3:17$ (sccm) could come under hybrid type SiOC films, which the FTIR

spectra of the samples feature by low frequency.

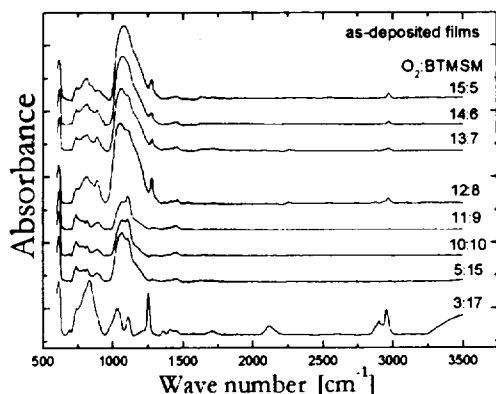


Fig. 1. FTIR spectra of as-deposited SiOC films.

C-O mode is band from the peak at 950 cm⁻¹ to the peak at 1250 cm⁻¹. Si-O-C asymmetric stretching vibration mode is broad band from the peak at 950 cm⁻¹ to the peak at 1350 cm⁻¹, and the broad vibration mode around 3500 cm⁻¹ is the characteristic for that of a hydrogen-bond. The sharp signal at 1270 cm⁻¹ is Si-CH₃ bonds. There are CH₃ bending mode at 1450 cm⁻¹, C-H stretching mode at 2900 cm⁻¹, respectively [8, 11]. But the formations from 700 cm⁻¹ to 950 cm⁻¹ in the hybrid type SiOC films are distinguished from that of the film with O₂:BTMSM=3:17 (sccm). In view of the main mode near 1000 cm⁻¹, the intensity of the film with O₂:BTMSM=11:9 (sccm) is the smallest height, but that of the film with O₂:BTMSM=12:8 (sccm) is the largest height, in spite of few difference of the flow rate ratio. These results show an abrupt variation of the chemicals shift and the C-O bond does not sustain this condition, which it has low density of methyl radicals and increase high electronegative oxygen. In the end, the elongation of C-H bond by oxygen causes the red shift at the film with

O₂:BTMSM=11:9 (sccm).

Fig. 2 shows clearly the FTIR spectra from 700 cm⁻¹ to 1400 cm⁻¹ in hybrid type SiOC films. Hybrid type SiOC films are classified into three properties according to the flow rate ratio; organic, hybrid and inorganic properties. There are the Si-O-C bond with sharp signal at 1270 cm⁻¹, and the C-O bond without signal at 1270 cm⁻¹. SiOC films with organic properties have two peaks in the range of C-O bond from 950 cm⁻¹ to 1250 cm⁻¹. SiOC films with hybrid properties also have two peaks in the range of Si-O-C bond from 950 cm⁻¹ to 1350 cm⁻¹, but SiOC films with inorganic properties have one peak in the range of Si-O-C bond from 950 cm⁻¹ to 1350 cm⁻¹.

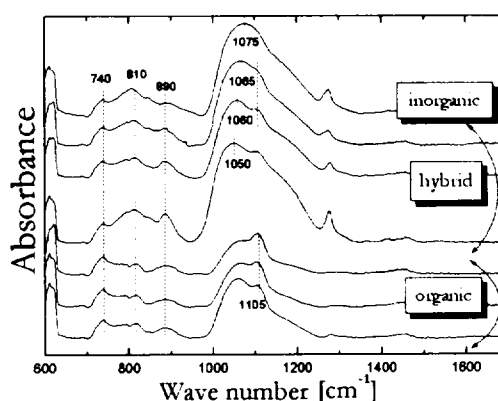


Fig. 2. FTIR spectra from 700 cm⁻¹ to 1400 cm⁻¹ in hybrid type SiOC films.

The bonds from 700 cm⁻¹ to 950 cm⁻¹ consist of Si-C bond at 740 cm⁻¹, C-O bond at 810 cm⁻¹ and Si-O bond at 890 cm⁻¹. SiOC films with inorganic properties are stronger Si-C (740 cm⁻¹) bond than any other peaks, and SiOC films with hybrid properties are stronger Si-O (890 cm⁻¹) bond than any other peaks, and SiOC films with organic properties are stronger C-O (810 cm⁻¹) bond than any

other peaks.

The main modes near 1000 cm^{-1} are deconvoluted by fitting the data with a number of Gaussian peaks as shown in Fig. 3, 4 and 5.

Fig. 3 shows the deconvoluted FTIR spectra in the range from 950 cm^{-1} to 1250 cm^{-1} in SiOC films with inorganic properties.

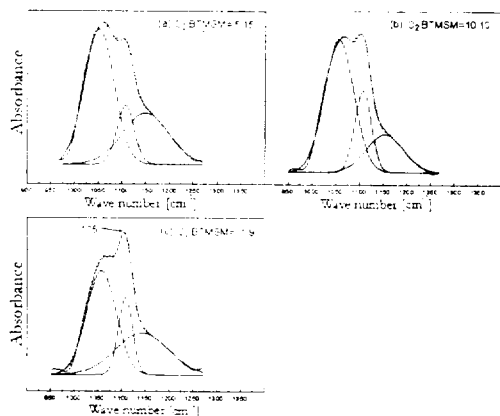


Fig. 3. The deconvoluted spectra of C-O bonding mode in the wave number range from 950 cm^{-1} to 1250 cm^{-1} in SiOC films with organic properties, (a) the sample with O_2 :BTMSM=5:15, (b) the sample with O_2 :BTMSM=10:10, (c) the sample with O_2 :BTMSM=11:9.

There is the first Si-O-C cage-link, the second Si-O-C cross-link and the third Si-O-Si cross-link. The first Si-O-C cage-link is related with the porosity in the films, which the pore is made from steric hindrance of methyl radicals. Therefore, the size of the first peak becomes small due to the decrease of the BTMSM flow rate. The second Si-O-C cross-link in the sample increases relatively, and the peak of the main mode ($950\text{ cm}^{-1}\sim 1250\text{ cm}^{-1}$) moves to high frequency at 1105 cm^{-1} , it is called by a blue

shift.

Fig. 4 and 5 show the deconvoluted FTIR spectra in the range from 950 cm^{-1} to 1350 cm^{-1} with the various O_2 /BTMSM flow rate ratio. They show that two peaks change to one peak according to the increase the oxygen.

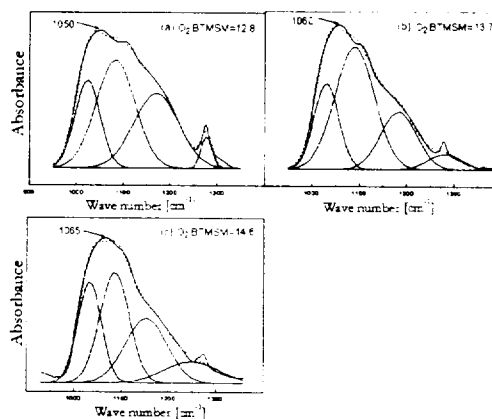


Fig. 4. The deconvoluted spectra of Si-O-C bonding mode in the wave number range from 950 cm^{-1} to 1350 cm^{-1} in SiOC films with hybrid properties, (a) the sample with O_2 :BTMSM=12:8, (b) the sample with O_2 :BTMSM=13:7, (c) the sample with O_2 :BTMSM=14:6.

Fig. 4 shows the Si-O-C main mode of SiOC films with hybrid properties, which Si-O-C main mode consists of the first and second Si-O-C cross-link and third Si-O-Si cross-link and Si-CH₃ at 1270 cm^{-1} . Therefore, there are two peaks because of two kinks of cross-link in the Si-O-C mode. The changing to high frequency of the main peak causes the superior Si-O-Si cross-link than the Si-O-C cross-link as a function of the increase of oxygen flow rate. These results show the conventional red shift, which it is explained by the elongation of C-H bond, because of the inductive effect between

high electronegative atom oxygen and the C-H bond of Si-CH₃ (1270 cm⁻¹) according to the increase of oxygen flow rate.

Fig. 4(a) shows the peak of the lowest frequency of the main mode in SiOC films with hybrid properties. This result shows the relative high content of the Si-O-C cross-link in the samples, and then the carbon content should be also higher than any other sample in SiOC films with hybrid properties.

Fig. 5 shows the deconvoluted spectra of Si-O-C bonding mode in the wave number range from 975 cm⁻¹ to 1350 cm⁻¹ in SiOC films with inorganic properties.

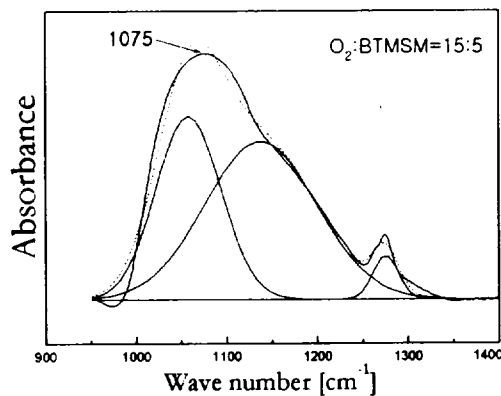
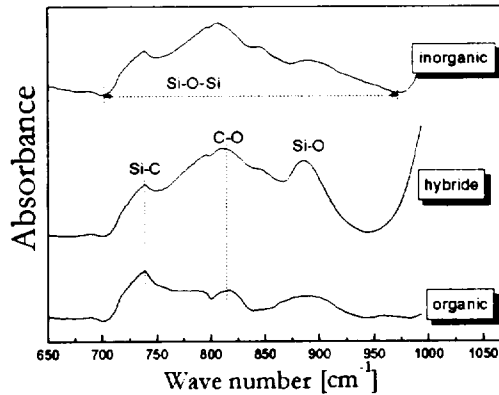


Fig. 5. The deconvoluted spectra of Si-O-C bonding mode in the wave number range from 975 cm⁻¹ to 1350 cm⁻¹ in SiOC films with inorganic properties.

There are the first Si-O-C cross-link and the second Si-O-Si cross-link and the peak of Si-CH₃ at 1270 cm⁻¹. The main mode of SiOC films with inorganic properties consists of mostly Si-O-Si cross-link, because of weak Si-O-C cross-link, therefore, the main mode is not also divided into two peaks. The deconvolute spectra also show larger Si-O-Si cross-link than any other bond in the sample. Consequently, the Si-O-C modes of SiOC

films need to be distinguished by the bonding structure from the results of the deconvolute spectra as shown in Fig. 4 and 5.

Figure 6 shows the FTIR spectra of SiOC films in the wave number range from 700



cm⁻¹ to 975 cm⁻¹.

Fig. 6. FTIR spectra of SiOC films in the wave number range from 700 cm⁻¹ to 975 cm⁻¹.

The band from 700 cm⁻¹ to 975 cm⁻¹ consists of Si-C, C-O and Si-C bond. The organic properties have a strong bond of Si-C peak, because the carbon need to made pores in the films. The hybrid properties have a strong Si-O bond, because oxygen need to made the cross-link bonding structure. The FTIR spectrum of SiOC films with inorganic properties is the broad band from 700 cm⁻¹ to 975 cm⁻¹, in spite of others is the band from 700 cm⁻¹ to 950 cm⁻¹. Therefore, The band from 700 cm⁻¹ to 975 cm⁻¹ need to be classified as Si-O-Si bond in SiOC films with inorganic properties due to the increase of the Si-O-Si cross-link as shown in Fig. 5. The lowest dielectric constant of SiOC films is 2.1 at the annealed sample of hybrid properties with O₂:BTMSM=12:8 (sccm). Si-O-C cross-link structure of hybrid properties is the bonding structures of ideal

low-dielectric materials because of high carbon content, good adhesion and good flatness.

IV. CONCLUSION

SiOC films using the CVD method are divided into three properties, which these properties change mostly according to the flow rate ratio during the deposition. The properties of SiOC films were researched by the analysis of the red and blue shifts in FTIR spectra. The red and blue shifts originate from the interaction between the high electronegative atoms and the C-H bonds. The red shift makes the Si-O-C cross-link structure in SiOC films by the elongation between oxygen and C-H bond. Si-O-C cross-link structure of hybrid properties improves the adhesion of the films due to weak boundary condition. SiOC films with hybrid properties were also obtained the lowest dielectric constant.

REFERENCE

- 1) M. A. Tamor, C. H. Wu, R. O. Carter and N. E. Lindsay, 1989, Pendant benzene in hydrogenated diamond-link carbon, *Appl. Phys. Lett.* Vol. 55(14), pp. 1388-1390.
- 2) H. J. Kim, Q. Shao and Y. H. Kim, 2003, Characterization of low-dielectric-constant SiOC thin films deposited by PECVD for interlayer dielectrics of multilevel interconnection, *Surface and Coatings Technology*, Vol. 171, pp. 39-45.
- 3) T. C. Chang, P. T. Liu, Y. S. Mor, S. M. Sze, Y. L. Yang, M. S. Feng, F. M. Pan, B. T. Dai, C. Y. Chang, 1999, The Novel Improvement of Low Dielectric Constant Methylsilsequioxane by N_2O Plasma Treatment, *Journal of The electrochemical Society*, Vol. 146, No. 10, pp.3802-3806.
- 4) P. Masri, 2002, Silicon carbide and silicon carbide-based structures: The physics of epitaxy, *Surface science reports*, Vol. 48, pp. 1-5.
- 5) A. Grill and D. A. Neumayer, 2003, Structure of low dielectric constant to extreme low dielectric constant SiOC films: Fourier transform infrared spectroscopy characterization, *J. Appl. Phys.* Vol. 94, pp. 6697-6707.
- 6) Kyoung Suk OH, Shou-Yong JING, Chi, Kyu CHOI, Kwang-Man LEE, Heon-Ju LEE, 2001, Formation and characteristic of fluorinated amorphous carbon films deposited by CF_4/CH_4 ICPCVD, *Journal of the Korean Physical Society*, Vol. 39, No. 2, pp. 291-295.
- 7) Giulia Galli and Richard M. Martin, 1989, Structural and electronic properties of amorphous carbon, *Phys. Rev. Lett.* Vol. 62, No. 5, pp. 555-558.
- 8) Jin Yong Kim, Moo Sung Hwang, Yoon-Hae Kim, and Hyeong Joon Kim, Young Lee, 2001, Origin of low dielectric constant of carbon-incorporated silicon oxide film deposited by plasma enhanced chemical vapor deposition, *J. Appl. Phys.* Vol. 90, pp. 2469-2473.
- 9) Y-H Kim, S-K Lee and H-J Kim, 2000, Low-k Si-O-C-H composite films prepared by plasma-enhanced chemical vapor deposition using bis-trimethylsilylmethane precursor, *J. Vac. Sci. Technol. A* Vol. 18, No. 4, pp. 1216-1219.
- 10) Teresa Oh, Kwang-Man Lee, Sung-Teak Ko, Kyung Sik Kim, Khi-Jung Ahn and

-
- Chi Kyu Choi, 2003, Bonding Structure of the Cross-link in Organosilicate Films Using O₂/BTMSM Precursors, Jpn. J. Appl. Phys. Vol. 42, pp.1517-1520.
- 11) Teresa Oh, Heung-Soo Kim, Sung-Bo Oh and Mi-Sook Won, 2003, The Chemical Shift According To The flow Rate Ratio O₂/BTMSM by FTIR and XPS, Jpn. J. Appl. Phys. Vol. 42, pp. 6292-6295.
- 12) X. Li, L. Liu and H. B. Schlegel, 2000, On the physical origin of blue shifted hydrogen bonds, J. AM. CHEM. SOC. Vol. 124, pp. 9639-9647.
- 13) Sofie N. Delanoye, Wouter A. Herrebut and Benjamin J. Van der Veken, 2002, Improper or classical hydrogen bonding? A comparative cryosolutions infrared study of the complexes of HCCIF₂, HCCl₂F and HCCl₃ with dimethyl ether, J. Am. Chem. Soc. Vol. 124, pp. 7490-7498.
- 14) Carina E. Cannizzaro and K. N. Houk, 2002, Magnitudes and chemical consequences of R₃N⁺-C-H...O=C hydrogen bonding, J. AM. CHEM. SOC. Vol. 124, pp. 7168-7169.
- 15) Tomoyuki Ono, Yoshiyuki Suda, Masamichi Akazawa, Yosuke Sakai and Kaoru Suzuki, 2002, Effects of oxygen and substrate temperature on properties of amorphous carbon films fabricated by plasma assisted pulsed laser deposition method, Jpn. J. Appl. Phys. Vol. 41, pp. 4651-465.
- 16) Jong-Ho YUN, Eun-Seok CHOI, Choel-Min JANG and Choon-Soo LEE, 2002, Effect of post-treatments on atomic layer deposition of TiN thin films using tetrakis (dimethylamido) titanium and ammonia, Jpn. J. Appl. Phys. Vol. 41, pp. L418-L421.