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# 유무기 하이브리드 SiOC 박막의 화학적 이동에 대한 FTIR 스펙트라 분석

( Analysis of FTIR Spectra in Organic Inorganic Hybrid  
Type SiOC Films )

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## 요 약

유무기 하이브리드 SiOC 박막은 차세대 유력한 저유전상수를 갖는 박막이다. SiOC 박막의 결합구조는 FTIR 분석기를 이용하여 화학적 이동이 일어나는 것을 확인하여 분석하였다. 유기화학분야에서의 일반적인 화학적 이동은 red shift에 해당하지만, 하이브리드 타입의 SiOC 박막은 red shift 뿐만 아니라 특이한 경우에 해당하는 blue shift도 관찰되었다. 화학적 이동의 원인은 전기음성도가 큰 원소가 주변에 존재하는 수소결합사이의 상호작용 때문인데, SiOC 박막에서 blue shift는 전자를 많이 포함하는 메틸그룹이 증가함으로 생기는 기공을 만드는 원인을 제공한다. SiOC 박막의 결합구조 역시 2가지 유형의 화학적 이동에 따라서 cross-link 구조와 case-link 구조의 두가지 유형으로 나타난다. 유량비와 증착할 때 주어지는 열에너지에 따라서 두 가지 결합구조를 나타낸다. cross-link 구조와 cross-link breakage 구조는 박막의 유전상수가 낮아지는 원인 서로 다르며 화학적 물리적인 특성 또한 다르게 나타나는 것을 증명하고 있다. Si-O-C cross-link 구조는 red shift의 원인이 된 수소결합에 의한 원자사이의 길이가 길어지는 효과에 의해 표면접착력이 개선되며, 유전상수 역시 감소하였다.

## Abstract

Organic-inorganic hybrid type thin films are the next generation candidates as low-k materials. SiOC films are analyzed the bonding structure by the red and blue chemical shift using the fourier transform infrared spectra. Conventional chemical shift of organic chemistry is 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 is caused by the porosity due to the increase of the electron rich group such as much methyl radicals. The bonding structures of SiOC films are also 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 progressed the adhesion attributed to the C-H bond elongation in the reason of the red shift, and the dielectric constant also decreases.

**Keywords :** high electronegative oxygen, Si-O-Si cross-link, Si-O-C cross-link, Si-O-C cage-link

## I. 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<sup>[1~2]</sup>, because the silicon carbide has proved its ability to be used efficiently under high temperature rather than the SiO<sub>2</sub><sup>[3]</sup>. 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 industry. But the organic materials as low dielectric materials are

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also required to overcome the signal propagation delay and cross talks between wirings<sup>[4]</sup>. In the past decades, relevant low dielectric materials have introduced organic materials such as fluorinated amorphous carbon (a-C:F) films<sup>[5]</sup> and hydrogenated amorphous carbon (a-C:H) films<sup>[6]</sup> 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<sup>[7]</sup>. 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 the red and blue shifts 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<sup>[8]</sup>. 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 researchers<sup>[9]</sup>. The surface of the thin films was progressed the adhesion by the effect of the cross-link bonding structure<sup>[10]</sup>, 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  $\text{O}_2/\text{BTMSM}$  (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  $10^{12} \text{ cm}^{-3}$  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 through 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 shows the characteristic of hybrid type SiOC films, because of too much alkyl groups. The strong CH bonds about  $2900 \text{ cm}^{-1}$  indicate conventional characteristic of organic materials, and the band from  $670 \text{ cm}^{-1}$  to  $950 \text{ cm}^{-1}$  is also related with  $\text{CH}_n$  ( $n=1, 2, 3$ ). There

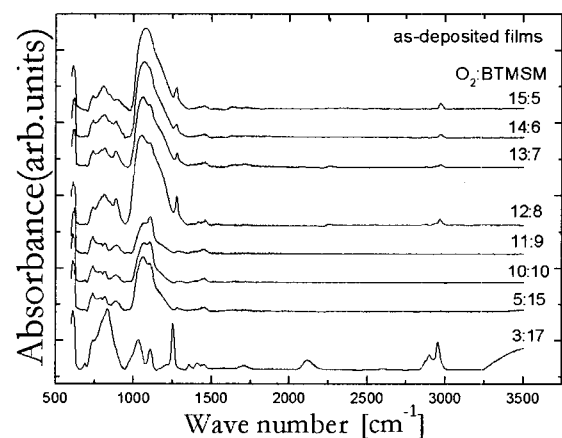


그림 1. SiOC 박막의 FTIR 스펙트라.  
Fig. 1. FTIR spectra of as-deposited SiOC films.

another films without  $O_2:BTMSM=3:17$  (sccm) could come under hybrid type SiOC films, which the FTIR spectra of the samples feature by low frequency.

C-O mode is band from the peak at  $950\text{ cm}^{-1}$  to the peak at  $1250\text{ cm}^{-1}$ . Si-O-C asymmetric stretching vibration mode is broad band from the peak at  $950\text{ cm}^{-1}$  to the peak at  $1350\text{ cm}^{-1}$ , and the broad vibration mode around  $3500\text{ cm}^{-1}$  is the characteristic for that of a hydrogen-bond. The sharp signal at  $1270\text{ cm}^{-1}$  is Si-CH<sub>3</sub> bonds. There are CH<sub>3</sub> bending mode at  $1450\text{ cm}^{-1}$ , C-H stretching mode at  $2900\text{ cm}^{-1}$ , respectively<sup>[8]</sup>. But the formations from  $700\text{ cm}^{-1}$  to  $950\text{ cm}^{-1}$  in the hybrid type SiOC films are distinguished from that of the film with  $O_2:BTMSM=3:17$  (sccm). In view of the main mode near  $1000\text{ cm}^{-1}$ , the intensity of the film with  $O_2:BTMSM=11:9$  (sccm) is the smallest height, but that of the film with  $O_2:BTMSM=12:8$  (sccm) is the largest height, in spite of, the difference of the flow rate ratio is very little. 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 occurs the red shift at the film with  $O_2:BTMSM=11:9$  (sccm).

Fig. 2 shows clearly the FTIR spectra from  $700\text{ cm}^{-1}$  to  $1400\text{ cm}^{-1}$  in hybrid type SiOC films. Hybrid type SiOC films are classified into three properties according to the flow rate ratio; organic, hybrid and

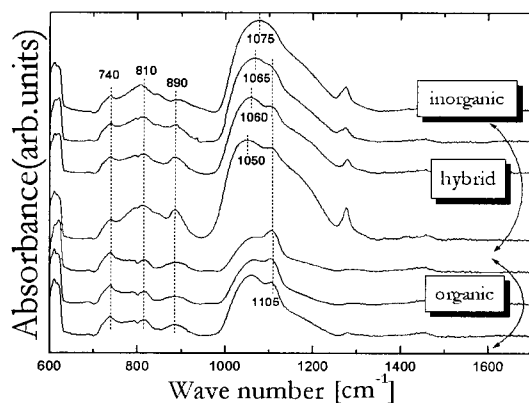


그림 2. 하이브리드 SiOC 박막에 대한  $700\text{ cm}^{-1}$  부터  $1400\text{ cm}^{-1}$  영역의 FTIR 스펙트라.

Fig. 2. FTIR spectra from  $700\text{ cm}^{-1}$  to  $1400\text{ cm}^{-1}$  in hybrid type SiOC films.

inorganic properties. There are the Si-O-C bond with sharp signal at  $1270\text{ cm}^{-1}$ , and the C-O bond without signal at  $1270\text{ cm}^{-1}$ . SiOC films with organic properties have two peaks in the range of C-O bond from  $950\text{ cm}^{-1}$  to  $1250\text{ cm}^{-1}$ . SiOC films with hybrid properties also have two peaks in the range of Si-O-C bond from  $950\text{ cm}^{-1}$  to  $1350\text{ cm}^{-1}$ , but SiOC films with inorganic properties have one peak in the range of Si-O-C bond from  $950\text{ cm}^{-1}$  to  $1350\text{ cm}^{-1}$ .

The bonds from  $700\text{ cm}^{-1}$  to  $950\text{ cm}^{-1}$  consist of Si-C bond at  $740\text{ cm}^{-1}$ , C-O bond at  $810\text{ cm}^{-1}$  and Si-O bond at  $890\text{ cm}^{-1}$ . SiOC films with inorganic properties are stronger Si-C ( $740\text{ cm}^{-1}$ ) bond than any other peaks, and SiOC films with hybrid properties are stronger Si-O ( $890\text{ cm}^{-1}$ ) bond than any other peaks, and SiOC films with organic properties are stronger C-O ( $810\text{ cm}^{-1}$ ) bond than any other peaks. The main modes near  $1000\text{ cm}^{-1}$  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  $950\text{ cm}^{-1}$  to  $1250\text{ cm}^{-1}$  in SiOC films with organic properties.

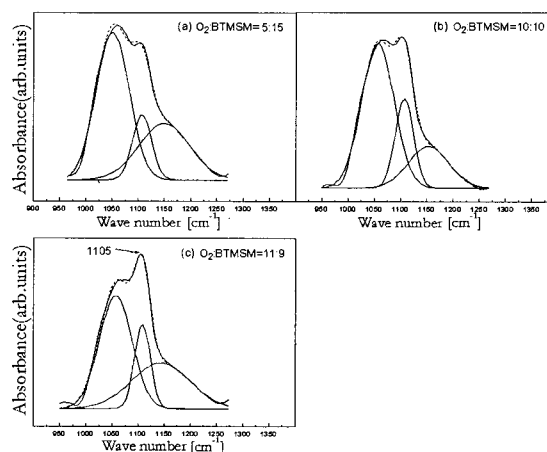


그림 3. 유기물특성의 SiOC 박막에서  $950\text{ cm}^{-1}$  부터  $1250\text{ cm}^{-1}$  영역의 C-O 결합모드에 대한 FTIR 스펙트라, (a)  $O_2:BTMSM=5:15$ 인 박막, (b)  $O_2:BTMSM=10:10$ 인 박막, (c)  $O_2:BTMSM=11:9$ 인 박막.

Fig. 3. The deconvoluted spectra of C-O bonding mode in the wave number range from  $950\text{ cm}^{-1}$  to  $1250\text{ cm}^{-1}$  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  $\text{cm}^{-1}$ ~1250  $\text{cm}^{-1}$ ) moves to high frequency at 1105  $\text{cm}^{-1}$ , it is called by the blue shift.

Fig. 4 and 5 show the deconvoluted FTIR spectra in the range from 950  $\text{cm}^{-1}$  to 1350  $\text{cm}^{-1}$  with the various  $\text{O}_2$ /BTMSM flow rate ratio. They show that two peaks change to one peak according to the increase the oxygen.

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-CH<sub>3</sub> at 1270  $\text{cm}^{-1}$ . Therefore, there are two peaks because of two kinds of cross-link in the Si-O-C mode. The changing to high

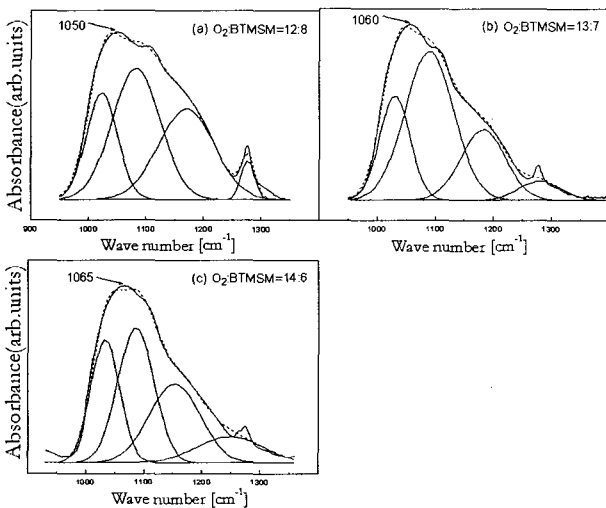


그림 4. 하이브리드특성의 SiOC 박막에서 950  $\text{cm}^{-1}$  부터 1350  $\text{cm}^{-1}$  영역의 Si-C-O 결합모드에 대한 디컨볼루티드 FTIR 스펙트라, (a)  $\text{O}_2$ :BTMSM=12:8인 박막, (b)  $\text{O}_2$ : BTMSM=13:7인 박막, (c)  $\text{O}_2$ : BTMSM=14:6인 박막.

Fig. 4. The deconvoluted spectra of Si-O-C bonding mode in the wave number range from 950  $\text{cm}^{-1}$  to 1350  $\text{cm}^{-1}$  in SiOC films with hybrid properties, (a) the sample with  $\text{O}_2$ :BTMSM=12:8, (b) the sample with  $\text{O}_2$ : BTMSM=13:7, (c) the sample with  $\text{O}_2$ : BTMSM=14:6.

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-CH<sub>3</sub> (1270  $\text{cm}^{-1}$ ) 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  $\text{cm}^{-1}$  to 1350  $\text{cm}^{-1}$  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-CH<sub>3</sub> at 1270  $\text{cm}^{-1}$ . 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 must

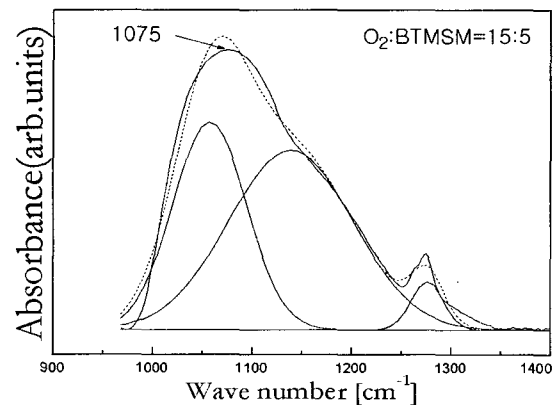


그림 5. 무기물특성의 SiOC 박막에서 950  $\text{cm}^{-1}$  부터 1350  $\text{cm}^{-1}$  영역의 Si-C-O 결합모드에 대한 FTIR 스펙트라.

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

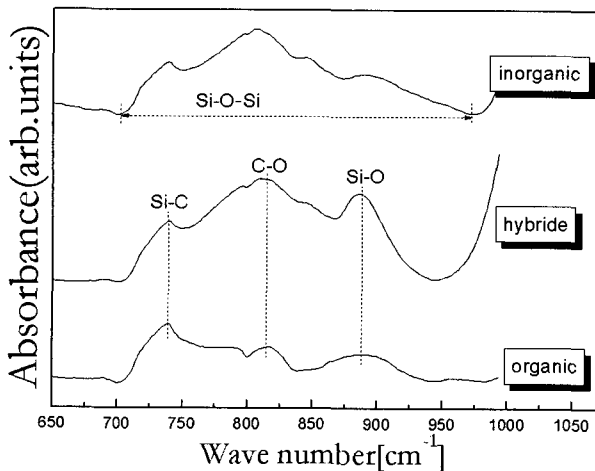


그림 6. 700  $\text{cm}^{-1}$  부터 975  $\text{cm}^{-1}$  영역에서의 SiOC 박막의 FTIR 스펙트럼.

Fig. 6. FTIR spectra of SiOC films in the wave number range from 700  $\text{cm}^{-1}$  to 975  $\text{cm}^{-1}$ .

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  $\text{cm}^{-1}$  to 975  $\text{cm}^{-1}$ .

The band from 700  $\text{cm}^{-1}$  to 975  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  to 975  $\text{cm}^{-1}$ , in spite of others is the band from 700  $\text{cm}^{-1}$  to 950  $\text{cm}^{-1}$ . Therefore, The band from 700  $\text{cm}^{-1}$  to 975  $\text{cm}^{-1}$  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  $\text{O}_2:\text{BTMSM}=12:8$  (sccm). Si-O-C cross-link structure of hybrid properties is the bonding structures of ideal low-dielectric materials because of 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.

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