

# 2가지 서로 다른 기능에 의해 생성된 박막의 물리적인 특성의 기원

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## Physical Properties of Thin Films Generated by Two Kinds of Different Function

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### Abstract

SiOC films containing alkyl groups have a low dielectric constant because of the interaction between the C-H hydrogen bonds and the oxygen of high electro-negative atom. The Si-CH<sub>3</sub> in a void is broken by the O<sub>2</sub>, therefore the strength of CH bond in Si-O-O-CH<sub>3</sub> bond increases. The Si-O-O-CH<sub>3</sub> bond is broken by nucleophilic attack due to Si atom, again. The elongation of C-H bond causes the red shift, and the compression of C-H bond causes the blue shift. Among these chemical shifts, the blue shift from 1000 cm<sup>-1</sup> to 1250 cm<sup>-1</sup> was related with the formation of pores. If the oxygen is deficient condition, the methylradicals of the electron-rich substitution group terminate easily the Si-O-Si cross-link, and the pore is originated from the cross-link breakdown due to much methyl radicals of Si-CH<sub>3</sub>. The dielectric constant of the films decreases due to pore generation.

### 1. Introduction

For semiconductors technology of ultra large scale integration (ULSI), the conventional SiO<sub>2</sub> films are not suitable because of the problem of the increase of the line to line coupling capacitance, the cross-talk noise, the power consumption and the signal delay time. Therefore, it is necessary to develop the low dielectric constant (low-k) materials [1~3]. SiOC films are promising

porous low-dielectric materials, which can replace the silicon dioxide films. It was researched that SiOC films have two different chemical shifts according to the increase of the flow rate ratio. Among the various preparation conditions of the films containing alkyl groups, it is known that the flow rate ratio during their deposition is the principal cause of changes in the bonding [4]. The final product of organic materials has different chemical and physical properties according to the amount of methyl radicals due to the flow rate ratio, and then the results reveal the difference between the red and blue shift from the fourier transform infrared (FTIR) spectra analyzer [5]. SiOC films show physical properties of three types due to the chemical shifts. There are the organic properties including a relative much organic species and the inorganic properties including a relative much inorganic species and the hybrid properties between organic properties and inorganic properties [6]. The blue shift are called improper hydrogen bonds in chemistry, however the red shift of the C-H stretching fundamental are traditionally associated with classical hydrogen bonds due to C-H·"E·"EO hydrogen bonding system [7]. Therefore, many researches are still studying on the origin of the red and blue shift in SiOC films. In this paper, organosilicate films were deposited using the various flow rate ratios between O<sub>2</sub> and BTMSM by ICPCVD at room temperature and then annealed at 500 ° in a vacuum. The films were performed the main mode in the ranging from 950

$\text{cm}^{-1}$  to  $1350 \text{ cm}^{-1}$  according to  $\text{O}_2/\text{BTMSM}$  flow rate ratio by FT-IR. The blue shift exclude  $\text{Si}-\text{CH}_3$  peak at  $1270 \text{ cm}^{-1}$ , however the red shift involves the  $\text{Si}-\text{CH}_3$  peak at  $1270 \text{ cm}^{-1}$ . Therefore, we studied about the reason of these chemical shifts by the average bond enthalpy between the atoms, and the effects of the chemical shifts at the film surface by the morphology of the samples using the scanning electron microscope (SEM).

## 2. Experiment

Low-k organosilicate films were deposited on a p-type (100) substrate using a mixture gases of the bis-trimethylsilylmethane (BTMSM,  $[(\text{CH}_3)_3\text{Si}]_2\text{CH}_2$ ) and oxygen by ICPCVD. The flow rate ratio of  $\text{O}_2/\text{BTMSM}$  was varied but total was 20 sccm, and the BTMSM precursor was carried into chamber by the argon gas. The film was deposited at room temperature for 10 minutes, and then the annealing process was performed at  $500^\circ\text{C}$  for 30 minutes in a vacuum. The thickness of films were measured by using FESEM(field-emission scanning electron microscope, S-4700) and ellipsometer (Gaertner L116C). The morphology of the samples due to the chemical shifts was researched by the scanning electron microscope (SEM). The dielectric constant of the films was obtained by C-V measurements using MIS(Al/SI-O-C film/p-Si) structure.

## 3. Result and Discussion

The chemicals shift causes the peculiar interaction of C-H bond, when carbon is surrounded in high electronegative atoms. The blue shift in SiOC films owes to the condensation of C-H bond, and then the SiOC films generate the pores due to the steric hindrance. But the red shift due to the elongation of C-H bond changes the bonding structure from pore structure to the Si-O-C cross-link structure.

Figure 1 shows the reaction between  $\text{C}=\text{O}$  double bond and neighboring condition about the growth of SiOC films according to the deposition condition. The  $\text{C}=\text{O}$  double bond with alkyl group easily makes the pore because of the steric hindrance. On the other hand, the  $\text{C}=\text{O}$  double bond with hydrogen is taken by the nucleophilic attack due to the catalyst of Si atom, and the  $\text{C}=\text{O}$  double bond is easily broken. Therefore, the cross-link structure is made. The carbon due to high electronegative oxygen becomes a proton-carbon. The electron rich atom Si attacks the proton-carbon, and  $\text{C}=\text{O}$  double bonding does not sustain. The C-H bond strength due to the week C-O single bond also becomes weak, and the film is grown the cross-link structure with weak boundary

condition.

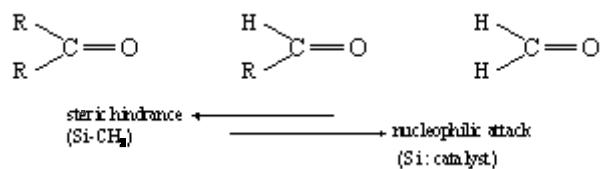


Fig. 1. Various carbonyl compound of  $\text{C}=\text{O}$  double bond according to the deposition condition.

Figure 2 shows the nucleophilic reaction of  $\text{C}=\text{O}$  double bonding due to the metal atom.

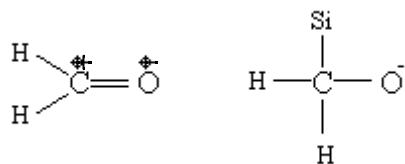


Fig. 2. Cross-link structure by nucleophilic attack.

## 4. Conclusion

Hybrid type SiOC films shows the red and blue shift by FTIR spectra. The blue shift does not contain the  $\text{Si}-\text{CH}_3$  bond in spite of the red shift involves the  $\text{Si}-\text{CH}_3$  bond. The  $\text{Si}-\text{CH}_3$  bond in the void is easily broken by the strong bond enthalpy of  $\text{O}_2$ , and the organo carbon such as C-O bond reunites. Therefore SiOC films with the blue shift show the C-O bond of the range from  $1000 \text{ cm}^{-1}$  to  $1250 \text{ cm}^{-1}$  in the FTIR spectra.

## References

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