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결합력에 의한 가교결합구조의 생성

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Generation of the Cross-link Structure depending on the bonding strength

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ABSTRACT

Organosilicate films are promising porous low-dielectric materials, which can replace the silicon dioxide films. It was researched that organosilicate films have two different chemical shifts according to the increase of the flow rate ratio. There are the red shift due to the electron deficient substitution group, and the blue shift of the electron rich substitution group. Among these chemical shifts, the blue shift from 1000 cm^{-1} to 1250 cm^{-1} was related with the formation of pores. The methylradicals of the electron-rich substitution group terminate easily the Si-O-Si cross-link, and the Si-O-C cage-link near 1057 cm^{-1} is originated from the cross-link breakdown due to much methyl radicals.

Key Words : Si-O-C films, chemical shift, Low-k,

Ⅰ. INTRODUCTION

For semiconductors technology of ultra large scale integration(ULSI), the conventional SiO_2 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, witch replace the conventional SiO_2 films[1, 2].

There are an organic materials such as fluorinated amorphous carbon and hydrogenated amorphous by the chemical vapor deposition (CVD) [3, 4] and an organic-inorganic hybrid type of organosilicate (SiOC) films[5~7]. These low-k materials involve the carbon atom of the tetrahedral bond. The structure of low-k materials with C-H hydrogen bond change the sp^3 carbon bonds in the special conditions of the C-C single bonding. The sp^3 carbon bonds make easily the cross-link structure in low-k materials and improve the adhesion of the films[8, 9]. Recently as promising porous low-k materials, organosilicate

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films containing alkyl groups have a low dielectric constant because of the interaction between the C-H hydrogen bonds and the electro-negative atoms oxygen. 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[6]. 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 [10].

In this study, low-k organosilicate films were deposited on a p-type (100) substrate by using an inductively coupled plasma chemical vapor deposition (ICPCVD) with mixture of BTMSM precursor and oxygen gas for 10 minutes. The detailed deposition conditions in this study have been described in previous story[6]. The bonding structureof the films with a red and blue shift was analyzed by FTIR, respectively. The reason of a red and blue shift in organisilicate films was researched by FTIR, and it was studied the relationship about the porosity and the Si-O-C cage link in the film with a blue shift.

II. EXPERIMENTS

Low-k (low dielectric constant) organosilicate films were deposited using a mixture gas of a BTMSM ($[(CH_3)_3Si]_2CH_2$) and an oxygen by inductively coupled plasma chemical vapor deposition (ICPCVD). The flow rate ratio of BTMSM=10 sccm (square cubic centimeter) was fixed, and the flow rate ratio of oxygen was varied.The film was deposited at room temperature, and then a annealing process was performed at 500℃ for 30 minutes in a vacuum. The detailed deposition condition have been described elsewhere [11]. The characteristic analyses of organosilicate films were performed by Fourier Transform Infrared (FTIR) spectra. FTIR (Fourier transform infrared) spectra were obtained in absorbance mode with a FTIR spectrometer (IFS120HR). The chemical shift of organosilicate films in the range of the flow rate ratio O_2:BTMSM<1.2 was studied.

III. RESULTS AND DISCUSSION

The red and blue shifts are made from different reasons on the basic of a Diels-Alder reaction. A red shift is the broad band in the range from 950 cm^{-1} to 1350 cm^{-1}, but a blue shift is relatively narrow band from 1000 cm^{-1} to 1250 cm^{-1}[6] In addiction, the red and blue shifts were clearly distinguished by the intensity of the FTIR spectra in organosilicate films, in spite of a very few difference of the flow rate ratio. Fig. 1 shows the original FTIR spectra of as-deposited films, witch

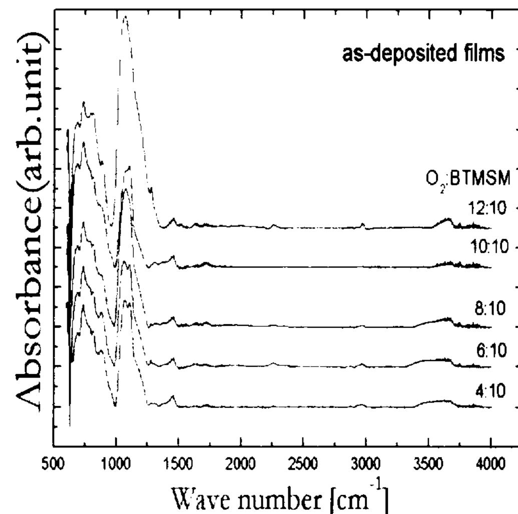

Fig. 1. FTIR spectra of the non-normalizing as-deposited films for the distinction of the chemical shifts.

they were not normalized. As-deposited films with the flow rate ratio O_2/BTMSM≤1.0 show a blue shift, but the film with the flow rate ratio O_2/BTMSM=1.2 shows a red shift. In comparing a red shift with a blue shift, the main peak intensity of as-deposited film with a red shift is very higher than the films with a blue shift. To confirm the chemical shifts, the main bonds of the FTIR spectra are enlarged, and the FTIR spectra were deconvoluted by fitting the data to a number of Gaussian peaks.

Fig. 2 shows the FTIR spectrum of as-deposited film with a red shift. The deconvoluted FTIR spectrum for the range 950 to 1350 cm^{-1} isdivided into four groups, and there are the first-second bonds of the Si-O-C cross-link, the third bond of the Si-O-Si cross-link and the fourth bond of the Si-CH_3 bond. The peak of a red shift in the total main bond is near 1065 cm^{-1}. Fig. 3 shows the FTIR spectrum of as-deposited film with a blue shift. The deconvoluted FTIR spectrum for the range 1000 to 1250 cm^{-1} is divided into three groups, and there are the first bond of the Si-O-C cage-link near 1057 cm^{-1}, the second bond of the Si-O-C cross-link near 1107 cm^{-1} and the third bond of the Si-O-Si cross-bond near 1150 cm^{-1}. The peak of a blue shift near 1100 cm^{-1} in whole bond is higher than that of a red shift near 1065 cm^{-1}. The reason of a blue shift is the condensation of C-H bond, but a red shift is the reason of the elongation of C-H bond, as shown in the previous other paper.[6] The cage-link near 1057 cm^{-1} is directly related with the porosity, which is originated from the cross-link breakdown due to the electron rich group. Organosilicate films with a low porosity show a small cage-link, therefore a blue shift can be clearly researched because of the small cage-link in a main band by FTIR spectrum of the film. That is the reason that it was hard to know about the existence of a blue shift in organosilicate films. The mode of a blue shift consists of the cross-link and cage-link, therefore the whole mode has two kind of peaks. On the other hand, the mode of a red shift only consists of the cross-link, therefore the whole mode makes the one peak, in spite of broad. If the structure of organosilicate films has a high cage-link due to the increase of a porosity, the

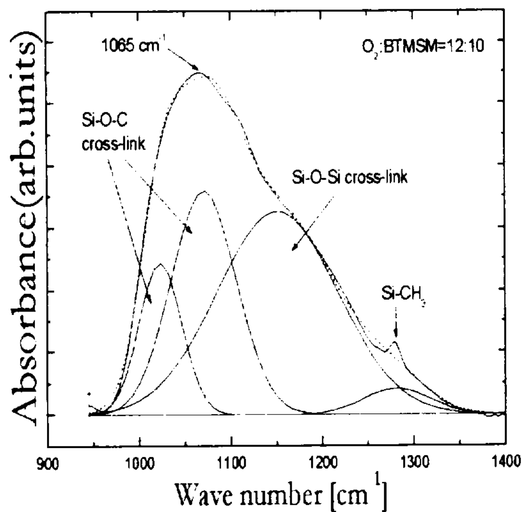

Fig. 2. FTIR spectrum of as-deposited film with a red shift.

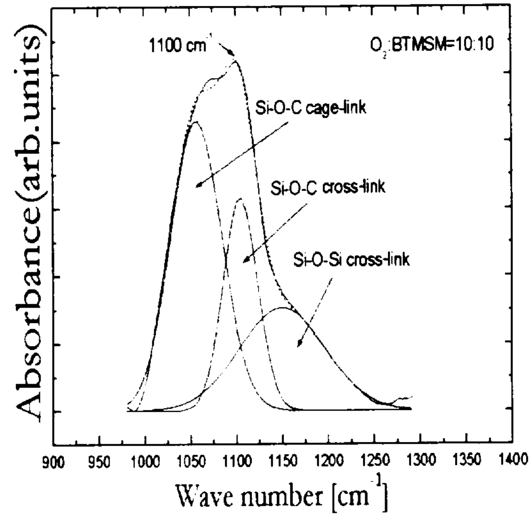

Fig. 3. FTIR spectrum of as-deposited film with a blue shift.

Si-O-C cage-link near 1057 cm^{-1} increases as shown in Fig. 1, therefore the first peak (1057 cm^{-1}) of the films with the flow rate ratio O_2/BTMSM≤0.6 show higher than the second peak (1107 cm^{-1}).Table 1 shows the average bond enthalpy between atoms (Si, C, H, O), and the average bond enthalpy of a single bond is usually weak in comparison with a double bond. The average bond enthalpy reflects the difference between the electro-negativity of the two atoms, therefore the FTIR spectrum of the film with a blue shift can be explained in view of the average bond enthalpy.

Table 1. Average bond enthalpy (kJ/mol)

Si-Si 226	C-H 413
Si-C 301	O-H 463
Si-H 323	O_2 495
C-C 348	C=C 614
C-O 358	C=O 799
Si-O 368	

Fig. 4 shows the relationship between the average bond enthalpy and FTIR spectrum of the film with a blue shift for the presentation about a vibration mode between atoms.

The C-H bond is easily withdrawn by high electronegative atom oxygen according to the increase of the oxygen gas flow rate ratio. This C-H bond elongation causes the blue shift to change the red shift. First of all, the C-H bond elongation occurs at the first bond (1057 cm^{-1}) and then the first bond moves to low frequency from 1000 cm^{-1} to 950 cm^{-1}, witch is at the lowest frequency of a whole mode. Second, the C-H bond elongation occurs at the third bond (1150 cm^{-1}) due to the inductive effect between oxygen and C-H bond of Si-CH_3 at 1270 cm^{-1}, because the Si-CH_3 bond has very strong bond strength. Therefore, the third bond moves to the highest

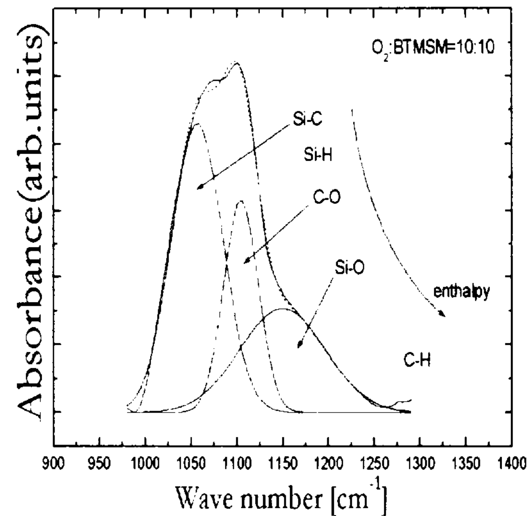

Fig. 4. Relationship between the average bond enthalpy and FTIR spectrum of the film with a blue shift.

frequency from 1250 cm^{-1} to 1350 cm^{-1} in a whole mode. Consequently, the whole mode of a red shift becomes a broad band in the range of 950 cm^{-1} to 1350 cm^{-1}. The main form of a red shift is smooth mode because of the bonding structure of the films with all cross-links such as Si-O-Si cross-link and Si-O-C cross-link, and the peak of main bond moves to a low frequency due to the elongation of C-H bond as shown in Fig. 2.

Ⅳ. CONCLUSION

The surface of a red shift's film becomes low energy distribution due to a weak boundary condition, and the adhesion of the film progresses, and the dielectric constant also decreases because of the high carbon content by the cross-link structure. It is also confirmed that the main mode intensity of the film with a red shift at O_2/BTMSM=1.2 is higher than any other films as shown in Fig. 1.

요 약

반도체의 소자가 소형화됨에 따라서 SiO2 층간 절연막 대신에 더 낮은 유전상수를 갖는 새로운 물질개발이 필요하게 되었다. 저 유전상수 물질로서 SiOC 박막이 최근 많이 연구되어지고 있다. SiOC 박막은 유량의 변화에 따른 매우 다른 물리적 화학적 변화를 나타내는데 따라서 결합구조 역시 발생기원이 매우 다른 것으로 나타났다. 크로스 링크 브레이크 구조는 박막내의 기공을 생성시키는 원인이 되며, 반면에 크로스 링크 구조는 탄소의 함량을 증가시키면서 구성원소들 사이의 약한 경계효과에 의하여 평탄도를 증가시켰다.

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REFERENCE

1) M. A. Tamor, C. H. Wu, 1990, Graphitic network models of diamondlike carbon, J.Appl. Phys. 67(2), pp. 1007-1012.

2) M. A. Tamor, C. H. Wu, R. O Carter and N. E. Lindsay, 1989, Pendant benzene in hydrogenated diamond-link carbon, Appl. Phys. Lett. 55(14),pp. 1388-1390.

3) Kyoung Suk OH,Shou-Yong JING, Chi, Kyu CHOI ,Kwang-Man LEE, Heon-Ju LEE, 2001, Formation and caracteristic of fluorinated amorphous carbon films deposited by CF4/CH4 ICPCVD, Journal of the Korean Physical Society, Vol. 39(2), pp.291-295.

4) Giulia Galli and Richard M. Martin, 1989, Structural and electronic properties of amorphous carbon, Phys. Rev. Lett. 62(5), pp. 555-558.

5) A. Grill and D. A. Neumayer, 2003, Structure of low dielectric constant to extreme low dielectric constant SIOCH films: Fourier transform infrared spectroscopy characterization, J. Appl. Phys. 94, pp. 6697-6707.

6) 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. 42, pp. 6292-6295.

7) 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. 42, pp.1517-1520.

8) P. Masri, 2002, Surface science reports, 48, pp.1-51.

9) H. J. Kim, Q. Shao and Y. H. Kim, 2003, Characterizaion of low-dielectric-constant SiOC thin films deposited by PECVD for interlayer dielectrics of multilevel interconnection, Surface and Coatings Technology, 171, pp. 39-45.

10) X. Li, L. Liu and H. B. Schlegel, 2000, On the physical origin of blue shifted hydrogen bonds, J. AM. CHEM. SOC. 124, pp.9639-9647.