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The Change of Chemical Bonding Structure of Si-O-C Composite Films Deposited by ICPCVD with XPS Analysis

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ICPCVD방법으로 만든 Si-O-C 박막의 XPS 분석에 의한 화학적 결합 구조의 변화

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ABSTRACT

In this paper, we discussed the change of the chemical bonding structure of Si-O-C composite films. Si-O-C composite films with a low dielectric constant were deposited on a p-type Si(100) substrate by an inductively coupled plasma chemical vapor deposition (ICPCVD). Mixture of Bistrimethylsilymethane (BTMSM, H_9C_3-Si-CH_2-Si-C_3H_9) and oxygen gas were used as precursor. The flow rate ratio of O_2:BTMSM(Ar) was 10sccm: 10sccm, and the annealing temperature was 300℃ and 500℃, respectively. The characteristic analysis of Si-O-C films was performed by X-ray photoelectron spectroscopy (XPS). Si-O open link of the films was increased as the Si-CH_3 stretching vibration mode and OH bonds increased during the deposition. Si-O ring link of the films was increased as the Si-CH_3 mode and OH bonds decreased after annealing at 500℃. Because of two OH bonds, H_2O evaporated and oxygen reacted with Si-O open link. Therefore Si-O-C composite films have low dielectric constant.

Key Words : Si-O-C films, chemical shift, Si2p, low-k

Ⅰ. INTRODUCTION

Low dielectric constant(low-k) organic and inorganic material have been extensively studied as an alternative to SiO_2 ($k=3.9\sim4.2$) for interlevel dielectric (ILD) applications[1,2]. Recently, many researchers have proposed various low-k materials, such as a-C:F[3], SiOF[4], methylsilsesquioxane(MSQ) and Si-O-C[5-8]. Among these materials, the hybrid-type film between organic and inorganic materials, Si-O-C composite film is a promising material for low-k applications with stable properties physically. Because Si-O-C composite films have good thermal

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and mechanical stability of inorganic materials and low dielectric constant of organic materials with alkyl groups. In general, the organic materials have poor hardness due to the relative low carbon concentration of Si-O-C composite films[7], but hybrid-type Si-O-C composite films have good adhesion, because of evaporation of hydrogen after annealing[9,10]. The dielectric constant depends on deposition temperature, especially the dielectric constant was lower at room temperature. In case of high deposition temperature, the broad peaks of OH bond decreased or disappeared around 3500cm^{-1} from FTIR analysis. The OH bond evaporated after annealed, in the end, the dielectric constant became small[5].

In this paper, it was studied that the chemical bonding structure of the Si-O-C composite films which were deposited at room temperature and annealed at 300℃ and 500℃ respectively by means of XPS.

II. EXPERIMENTS

The Si-O-C composite films were deposited on the p-type Si(100) substrate by ICPCVD with rf power at 13.56MHz. The precursor mixed with BTMSM and O_2 was used. The flow rate ratio of O_2: BTMSM(Ar) was 10 sccm : 10 sccm. The carrier argon gas was 10 sccm, and O_2 was also 10 sccm. The deposition temperature was room temperature, and the post annealing was done at 300℃ and 500℃ for 30minutes in vacuum. The BTMSM is vaporized and carried by inert argon gas with a thermostatic bubbler. To prevent recondensation of BTMSM, all of the gas delivery lines were heated and kept at a constant temperature of 40℃. High density plasma of about 10^{12}cm^{-3} was obtained at low pressure with rf power of about 300W in ICPCVD, and the working pressure of ~10^{-5} Torr was reached before each experiment. The inductively coupled plasma was generated by means of a three turns coil, which was set around a quartz tube. The film deposition depends on the parameters such as the flow rate of O_2/BTMSM, the rf power and the working pressure. The bonding structure of the Si-O-C composite films was analyzed with a model XPS(X-ray photoelectron spectroscopy) spectrometer(ESCALAB 250). The thickness of film was measured by a SEM (scanning electron microscope : S-4700). Electrical properties such as the dielectric constant and the leakage current density were investigated using a MIS (Al/SI-O-C film/p-Si) structure at floating mode.

III. RESULTS AND DISCUSSION

Fig. 1 is the XPS survey scan spectra of as deposited film, annealed film at 300℃ and annealed film at 500℃, respectively. From Fig. 1, the peak of Si2p electron orbital spectra is near 102 eV, the peak of C1s electron orbital spectra is near 282 eV, and the peak of Si2p electron orbital spectra is near 531 eV.

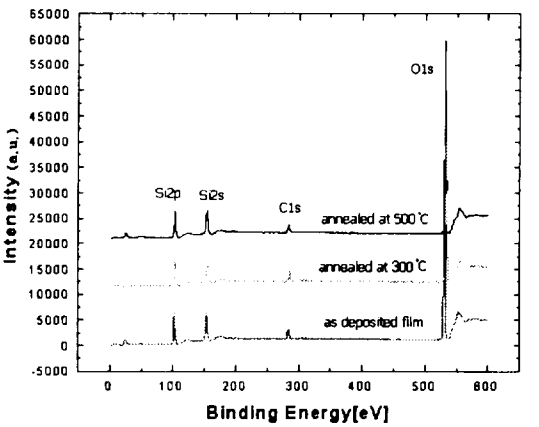
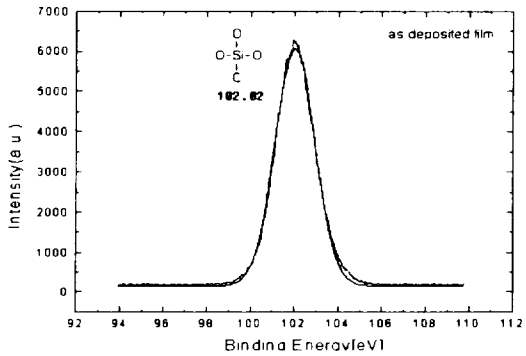
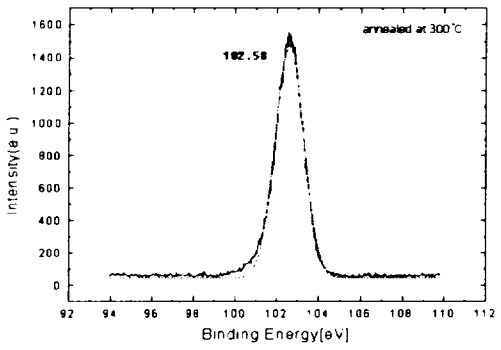


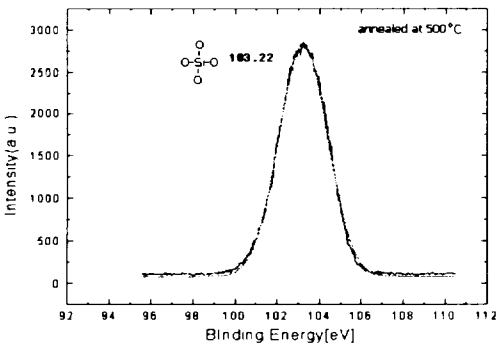
Fig. 1. XPS spectra of Si-O-C films.



(a) As deposited film.



(b) Annealed film at 300°C.



(c) Annealed film at 500°C.

Fig. 2. The Si2p electron orbital spectra by XPS in Si-O-C composite films.

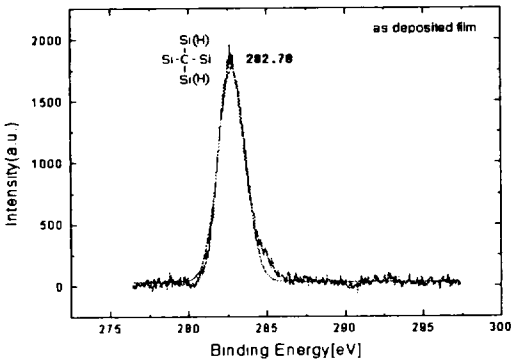
Fig. 2 shows Si2p electron orbital spectra by XPS in Si-O-C composite films. The spectra are generally broad and overlapped due to the complex stoichiometry and the amorphous nature of the film. In order to investigate the analysis of content, electron orbital spectra were deconvoluted. In comparison with as deposited and annealed films, from the electron orbital spectra of Si2p, the main peak of as deposited film is 102.02 eV with Si-O-C open link, and the main peak of an annealed film at 300°C is 102.58 eV with Si-O-C open link, but the main peak of annealed film at 500°C is 103.22 eV with Si-O ring link. Consequently, the Si2p main peak is shifted toward high binding energy as deposition temperature increased. These facts can be confirmed Si-O-C composite films are chemically and thermally stable after annealing.

For the deposition process, OH group were made from the attaching oxygen with CH_3 orginic group. Alkyl groups, which is made from deposition, can be made nano-void in the film and alkyl groups decreased after annealing. In the end, Si-O-C composite films became chemically and thermally stable.

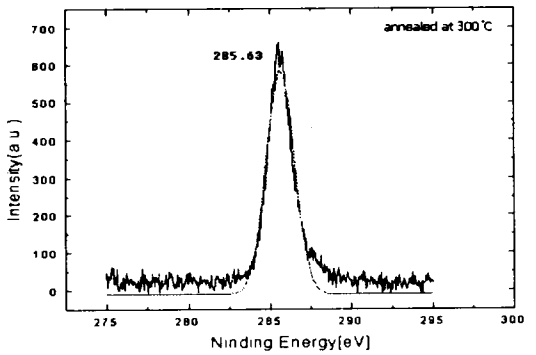
Fig. 3 shows C1s electron orbital spectra by XPS in Si-O-C composite films. For electron orbital spectra of C1s, the main peak of as deposited film 282.78 eV, but the main peak of annealed film at 500°C moves 284 eV. For electron orbital spectra of O1s, the main peak of as deposited and annealed films have almost no change.

For the analysis of FTIR spectra, as deposited film has main peak near 1071.8 cm^{-1} with Si-O-C open link, the main peak of annealed film moved toward 1104 $cm^{-1}$with Si-O ring link of stable cross linking bond. It confirms that concentration of $Si-CH_3$ bonds decreased after annealing. $Si-CH_3$ bonding structure is almost stable annealed at 500°C.

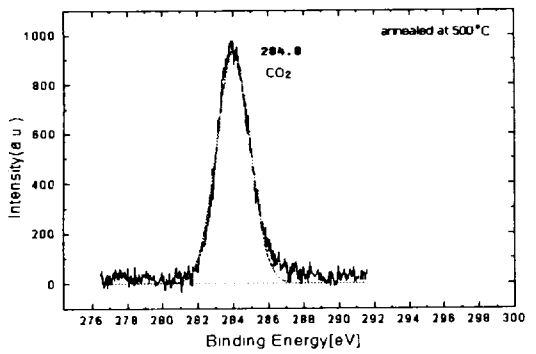
Fig. 4(a) shows that Si-O-C open links are made from the chemical reaction between BTMSM and oxygen during the deposition, and Fig. 4(b) shows that H_2O and Si-O ring link are made from two of



(a) As deposited film.



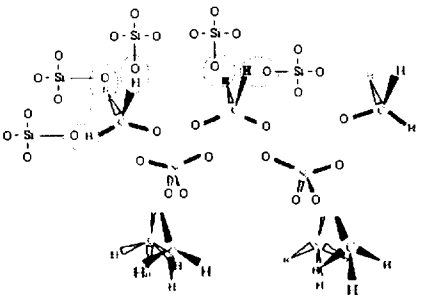
(b) Annealed film at 300°C.



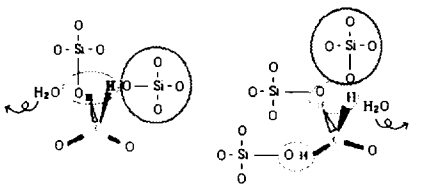
(c) Annealed film at 500°C.

Fig. 3. The C1s electron orbital spectra by XPS of Si-O-C composite films.

OH bonds. In the end, Si-O-C composite films changed to the stable bonding structure with Si-O



(a)



(b)

Fig. 4. The formation of Si-O ring link from OH groups.

ring link during the annealing process, and void can be formed in the films. The formed nano-void of the Si-O-C composite film can result in low dielectric constant behavior.

Ⅳ. CONCLUSION

Chemical analysis on the bonding structure consisting of Si-O-C open links and Si-O ring links, was performed by X-ray photoelectron spectroscopy (XPS). From XPS analysis, it was verified that as deposited film has Si-O-C open links and the open link was exchanged by Si-O ring links from Si2p electron orbital spectra after annealing. The film has Si-O ring link is more stable than the one does have Si-O-C open link chemically. From the results, we verified that hybrid type Si-O-C composite films have thermal and mechanical stability after annealing.

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