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C-H 수소결합을 갖는 유무기 하이브리드 물질에서의 열처리 효과

(Annealing effects of organic inorganic hybrid silica material with C-H hydrogen bonds)

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요 약

SiOC 박막과 같은 유무기 하이브리드 실리카 물질에서의 열처리효과에 의한 결합구조의 변화와 유전상수에 관하여 연구하였다. 유무기 하이브리드 실리카 물질은 BTMSM과 산소의 혼합가스를 이용한 CVD방법에 의하여 증착되었다. 유무기 하이브리드 실리카 물질은 증착조건에 따라 3가지 유형으로 분류되었으며, 유전상수는 MIS 구조에 의하여 조사되었다. XPS 분석에 의하여 C 1s 스펙트라는 O₂/BTMSM=1.5의 유량비를 갖는 박막에서 282.9 eV의 organometallic carbon 반응을 보여주는 피크를 나타내었다. organometallic carbon 반응의 결과는 안정성 있는 크로스 링크 결합구조를 만들어내며, 하이브리드 특성을 갖는 이 박막에서 열처리 후 유전상수는 가장 낮았다.

Abstract

In this paper, It was reported the dielectric constant in organic inorganic hybrid silica material such as SiOC film modeling of bond structure by annealing in organic properties. The organic inorganic hybrid silica material were deposited using bis-trimethylsilyl methane (BTMSM, [(CH₃)₃Si]₂CH₂) and oxygen gas precursor by a plasma chemical vapor deposition (CVD). The organic inorganic hybrid silica material have three types according to the deposition condition. The dielectric constant of the films were performed MIS (Al/Si-O-C film/p-Si) structure. The C 1s spectra in organin inorganic silica materials with the flow rate ratio of O₂/BTMSM=1.5 was organometallic carbon with the peak 282.9 eV by XPS. It means that organometallic carbon component is the cross-link bonding structure with good stability. The dielectric constant was the lowest at annealed films with cross-link bonding structure.

Keywords : SiOC film, low-k materials, C-H bond elongation, C-H bond condensation, chemical shift

I. INSTRUCTION

For multilevel interconnections of ultra large scale integration(ULSI), it is necessary to use a low-k material because they reduce signal propagation delay time, and cross-talk noise between metal layers. Many low-k materials have been researched, and the origin of decreasing the dielectric constant and low-k estimating method in these materials has been

studied[1-5]. Recently, many researchers have focused on the porous materials with $k < 2.0$, and one of the materials is organosilicate films (SiC_xOH, C=CH₃ group, $x \sim 10-25\%$) as a promising material. Organosilicate films are also called carbon-doped oxides or silicon-oxycarbides or carbon-incorporated silicon oxide film or organic-inorganic hybrid type Si-O-C thin films or organic-inorganic hybrid silica materials[6-8]. It was reported to improve of the adhesion of silica to PP(polypropylene) and is attributed to the cross-linking and the cross-linking mechanism involves the methyl group abstraction.

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Organometallic networks are consistent with the cross-linking structures. It was known that the main reason about low dielectric constant of organosilicate films was porosity and low polarizability, but the origin of chemical structures of organosilicate films according to porosity or low polarizability was not clear. Post annealing effect of organosilicate films was also known very important element for the dielectric constant decreases, but chemical structure and reaction mechanism of post annealing effect was not proven^[9~11].

In this paper, organosilicate films measured the dielectric constant using MIS (Al/Si-O-C film/p-Si) structure, and chemical structure of the films with the flow rate ratio of O₂/BTMSM=1.0 were analyzed by XPS. The variation of C 1s electron orbital spectra after post annealing was researched to define the organometallic and organic carbon component which is an important parameter in the bonding structure. It was suggested the reaction mechanism and the bonding structure of organosilicate films with a pore. It was also discussed the correlation between the dielectric constant and the cross-link structure in organosilicate films.

II. EXPERIMENT

Low-k(low dielectric constant) organosilicate films were deposited using a mixture gases of the bis-trimethylsilylmethane (BTMSM, [(CH₃)₃Si]₂CH₂) and oxygen by CVD. The flow rate ratio of O₂/BTMSM(Ar) was varied but total was 20 sccm. The film was deposited at room temperature, and then the annealing process was performed at 500°C for 30 minutes in a vacuum. The BTMSM was vaporized and carried by argon gas at 40°C thermostatic bubbler. High density plasma about 10¹² cm⁻³ was obtained at low pressure with rf power of about 300 W in ICPCVD, and the base pressure of ~ 10⁻⁵ Torr was obtained for each experiment. FTIR(Fourier transform infrared) spectra were obtained in absorbance mode with a FTIR spectrometer (IFS120HR). The chemical structure of

organosilicate films was analyzed by XPS (Microlab350). The thickness of films were measured by FESEM (field-emission scanning electron microscope, S-4700) and ellipsometer (Gaertner L116C). The dielectric constant of the films was obtained by C-V measurements using MIS (Al/Si-O-C film/p-Si) structure.

III. RESULT & DISCUSSION

Figure 1 shows the dielectric constant of organosilicate films with various deposited condition by PECVD (plasma-enhanced chemical vapor deposition) and ICPCVD. TMS is tetramethylsilane (Si(CH₃)₄) and Ts parameter is a substrate temperature. These chemical structures of organosilicate films are determined by plasma properties due to radicals, ions and electrons. Specially, it is known that Ts parameter controls ions component, which is related with polarizability. In this paper, the dielectric constant of the films calculates in detail according to the flow rate ratio 1.0<O₂/BTMSM<2.0. However, previous experiment using TMS and O₂ mixed precursor was not done in the range of the flow rate ratio 1.0<O₂/TMS<2.0 as shown in Fig. 1. The dielectric constant of the films is not in proportion to the flow rate ratio O₂/BTMSM. Organic inorganic hybrid silica materials

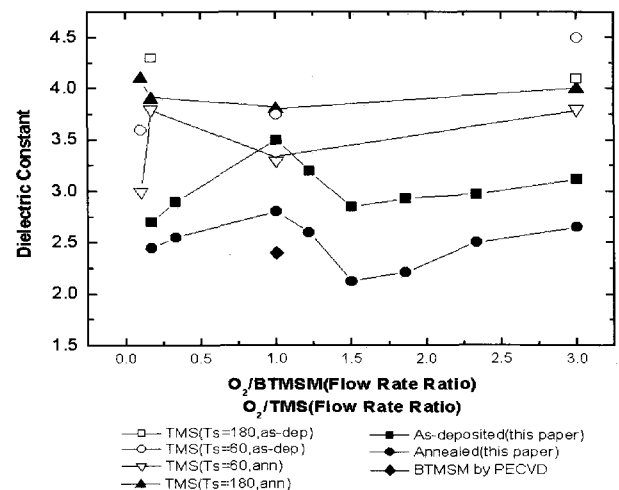


그림 1. 유무기 하이브리드 실리카 물질의 유전상수
 Fig. 1. The dielectric constant of the organic inorganic hybrid silica materials.

are three types such as organic, hybrid, inorganic properties^[1]. It was known that the dielectric constant of this materials is reduced by porosity and ionic polarized potential. The films with organic properties involve the electron releasing group due to the increasing amount of BTMSM, on the other hand, the films with hybrid or inorganic properties have the electron withdrawing group due to the increasing amount of oxygen. In the case of the electron rich such as the electron releasing group, the films are affected attractive and repulsive force by the steric effect, and makes pores. Finally, the bonding structure of the films becomes the cross-link breakage structure. For electron deficient group as hybrid or inorganic properties, the films only have strong attractive force, moreover, the oxygen atoms weakens the strength of C-H hydrogen bonds because of it's high electro-negativity. Therefore the bonding structure of the films sustains the cross-link bonds, although the alkyl group breaks the Si-O cross-link structure. The elongation of the C-H hydrogen bonds affects good adhesion by the low surface energy distribution. The dielectric constant of the films was the lowest at the annealed films with the flow rate ratio $O_2/BTMSM=1.5$.

Figure 2 shows the FTIR spectra of as-deposited film and annealed film with the flow rate ratio

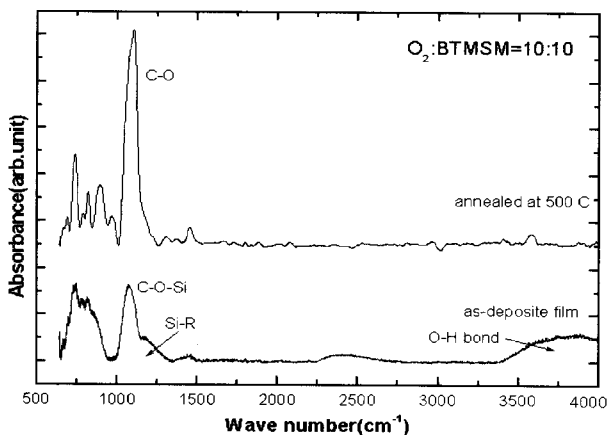


그림 2. $O_2:BTMSM=10$ sccm: 10 sccm의 유량비인 박막의 증착 박막과 열처리된 박막의 FTIR 스펙트럼

Fig. 2. FTIR spectra of as-deposited film and annealed film with the flow rate ratio $O_2:BTMSM=10$ sccm: 10 sccm.

$O_2:BTMSM=10$ sccm: 10 sccm

The C-O mode is broad from the peak at 1000 cm^{-1} to the peak at 1250 cm^{-1} . The Si-O-C asymmetric stretching vibration mode is broad from the peak at 1000 cm^{-1} to the peak at 1350 cm^{-1} , and the broad peak mode about the 3500 cm^{-1} is OH bond. In generally, the Si-CH₃ peak is very strong bonds and sharp peak at 1270 cm^{-1} , but in this case, the Si-CH₃ peak is broad. The Si-O-C cross link structure and the C-O cross link breakdown structure were validated by FTIR spectra. The elongation of C-H hydrogen bonds moves to low wave number such as the red shift in its vibration frequency, but the condensation of C-H hydrogen bonds changes high wave number such as the blue shift by FTIR spectra. The bonding structure was usually settled by the deposition condition, and the annealing process.

Figure 3 shows the main peak from 1000 cm^{-1} to 1350 cm^{-1} . It is confirmed that the red shift is the Si-O-C cross link structure, and the blue shift is the C-O cross link breakdown structure, because of the elongation or condensation of C-H hydrogen bonds. C-O peak is made by steric effect such as cross link breakdown and separated from Si-CH₃ peak. The film with the flow rate ratio $O_2/BTMSM$ has organic properties by annealing processes. This film has the lowest porosity and the highest dielectric constant in organic properties. The cross link structure and the cross link breakdown structure are certainly

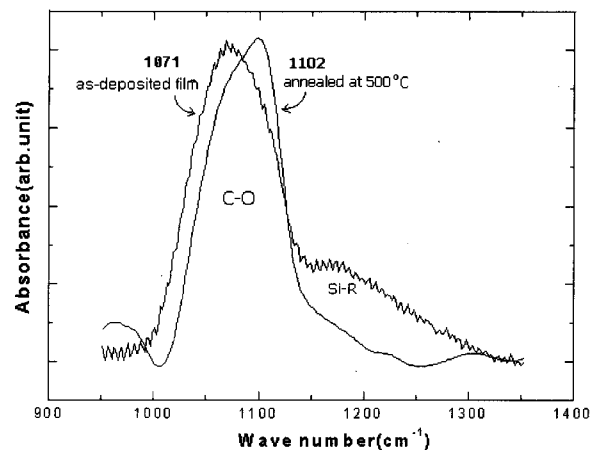


그림 3. 화학적 이동

Fig. 3. The chemical shift.

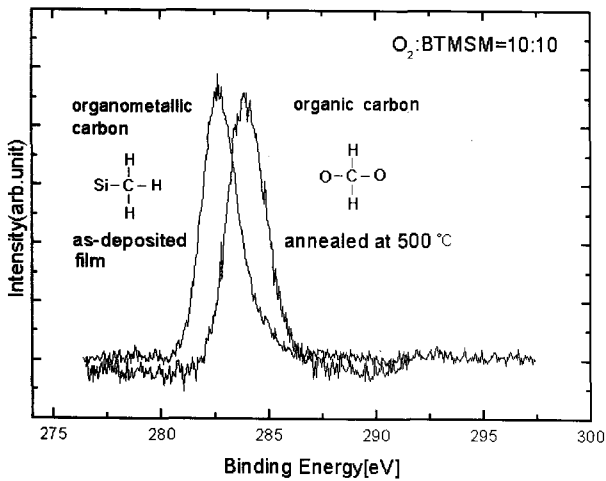


그림 4. C 1s 전자궤도 스펙트라
Fig. 4. C 1s electron orbital spectra.

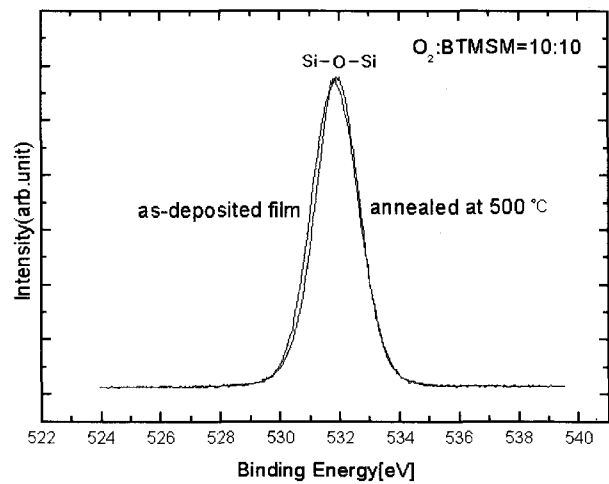


그림 5. O 1s 전자궤도 스펙트라
Fig. 5. O 1s electron orbital spectra.

confirmed by XPS spectra.

Figure 4 shows the C 1s electron-orbital spectra of the films. The peak of 282.9 eV is the peak of organometallic carbon, which has a properties of ionic polarization. On the other hand, the peak of 284.1 eV is the peak of non-polar organic carbon.

The as-deposited film has the peak of organometallic carbon and the annealed film has the peak of organic carbon. It means that annealed film of organic carbon peak is the same result by the FTIR spectra as the steric effect of cross link breakdown.

Figure 5 shows the O 1s electron orbital spectra of as-deposited film and annealed film. O 1s spectra of as-deposited film does not move after annealing process. It mean that the H₂O evaporation is just induced to recombine C-H-O hydrogen bonds, and

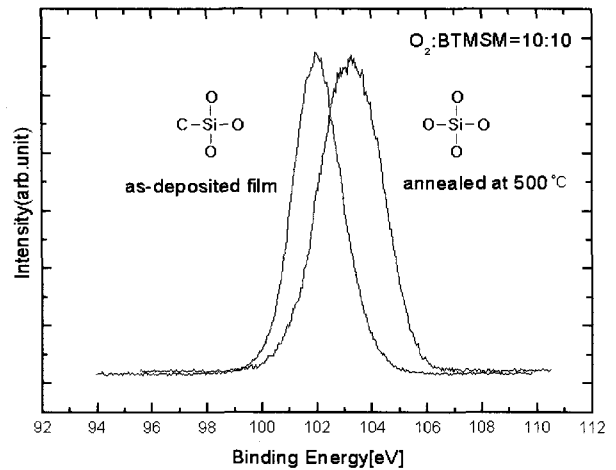


그림 6. Si 2p 전자궤도 스펙트라
Fig. 6. Si 2p electron orbital spectra.

has no relation with oxygen in Si-O cross link bonds.

Figure 6 shows the Si 2p electron orbital spectra

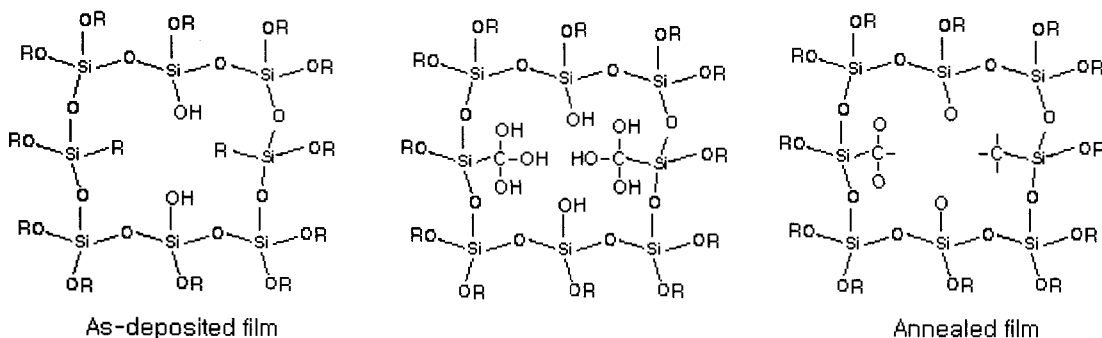


그림 7. O₂/BTMSM=10 sccm:10 sccm의 박막에서 열처리 효과에 따른 결합구조의 변화
Fig. 7. The variation of bonding structure by annealing effect at the film with O₂/BTMSM=10 sccm:10 sccm.

of the films. The Si 2p electron orbital spectra of as-deposited film shifts from 101.9 eV to 103.2 eV after annealing process. In the C-H-O hydrogen bond, two OH bonds reunite each other and make a H₂O and oxygen during the annealing process. The H₂O evaporates and oxygen attaches to silicon, therefore the adhesion of the films improves due to increasing the O-Si bonds. Consequently, the relative carbon concentration increases after annealing in the bonding structure with the C-H-O hydrogen bond, and the dielectric constant of the films decreases by annealing process.

Figure 7 shows the bonding structure by the annealing effect of organic inorganic hybrid silica materials from XPS spectra of the figure 4, 5 and 6. The Si-O cross link breaks by R(alkyl group) group but the bonding structure becomes cross-link breakdown or cross-link according to the relative amount of R group during the deposition. OH group evaporates by annealing in the C-H-O bonds, but the carbon is locked in the films. From these results, it is confirmed that the increasing of relative carbon content decreased the dielectric constant of the films.

IV. CONCLUSION

The dielectric constant of organic inorganic hybrid silica materials did not vary linearly with increasing the O₂/BTMSM flow rate ratio. The bonding structure of organosilicate films was classified by organic carbon or organometallic carbon from XPS spectra. The films with the flow rate ratio of O₂/BTMSM=1.0 showed the organometallic carbon reaction, and the chemical shift was observed after annealing process. The elongation effect of C-H hydrogen bonds due to the electron withdrawing group made the film with the cross link structure. The dielectric constant was the lowest at annealed films of hybrid properties with cross-linking structure.

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