

The chemical bond structure investigation on the Si-O-C(-H) composite low dielectric constant thin films

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Abstract

Si-O-C-H composite films were deposited using a radio frequency inductively coupled plasma chemical vapor deposition (ICPCVD) system with a bis-trimethylsilylmethane (BTMSM, $H_9C_3-Si-CH_2-Si-C_3H_9$) precursor and oxygen gases. Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) spectra were used to investigate the bonding configurations such as Si-O-Si, Si-O-C and Si-CH₃ bonds in the films. From these result the attachment of the Si-O-Si ring link with CH₃ groups is responsible to form the nano-size void in the film and result in a lower dielectric constant($k = 2.3$).

I. INTRODUCTION

As on-chip device densities are increased and active device dimensions are reduced, signal delays and noise are also increased due to the capacitive coupling and crosstalk between the metal interconnections. Since delays, noise, and power consumption all critically depend on the dielectric constant of the separating insulator, much attention has been focused recently on replacing the standard silicon dioxide with new intermetal dielectric materials which have dielectric constants that are considerably lower than ther-

mal silicon dioxide films($k = 3.9 \sim 4.2$).

Many materials with a low dielectric constant are being investigated as possible candidates required for integration into the present processing schemes[1].

Recently, many researchers have proposed a variety of organic and inorganic materials as an alternative to SiO₂. Organic materials have more significant integration problems than inorganic materials, such as poor adhesion, thermal instability, and low resistance to O₂ plasma. A thin film formed using inorganic materials has good thermal and mechanical stability, as well as better film ad-

hesion during integration processing. However, they generally have higher dielectric constant and more serious moisture absorption than organic materials, and as a result, they require additional liner and capping layers. The hybrid-type film between organic and inorganic materials is promising for low-k (low dielectric constant) material with stable properties[2]. Silicon oxide-based low k material containing alkyl groups has attracted more attention for their higher thermal and mechanical stabilities than many organic materials. The spatial hindrance of alkyl groups will produce abundant nano-voids in film and decrease the dielectric constant[3, 4].

II. EXPERIMENTS

In this study, we investigated the changes of FTIR and XPS spectra of films due to post-annealing and the electrical properties such as the dielectric constant. The Si-O-C(-H) composite films are deposited using radio frequency (13.56MHz) ICPCVD system with a BTMSM and O₂ mixture gases. The RF coil is wound around the quartz tube plasma reactor to couple power inductively to the plasma through a reactor dielectric wall. The high-density plasma is generated without an external magnetic field. The BTMSM is vaporized and carried by inert argon gas with a thermostatic bubbler (maintained at 40 °C)

to the reaction chamber. The flow rate of the argon carrier gas is 3~17 sccm and the O₂ is 17~3 sccm (keep the total flow rate to be 20 sccm) with a pressure of 320 mTorr. At RF power of 300 W discharge conditions, the electron density and electron temperature are measured as $\sim 10^{12}$ cm⁻³ and 1.6 eV, respectively by a fast injection Langmuir probe. The base pressure of $\sim 10^{-5}$ Torr was reached before each experiment. The films are deposited on the 6-in p-type Si(100) wafer at room temperature, and the post annealing is done at 500°C for 30 min in vacuum. Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) are used to determine the Si-O and Si-CH₃ bonding configurations in the films. The film thickness and refractive index are measured by using an ellipsometer. Electrical properties such as dielectric constant are investigated using MIS (Al/Si-O-C(-H) film/p-Si) structure method.

III. RESULTS AND DISCUSSION

Figure 1 shows the FT-IR spectra of as deposited and annealed Si-O-C(-H) composite film, which was deposited at room temperature with an O₂/BTMSM gas flow rate ratio at 3:17 sccm. The spectra are generally broad and overlapped due to the complex stoichiometry and the amorphous nature

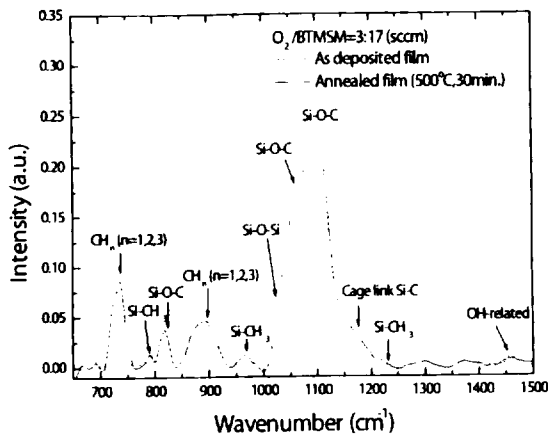


FIG. 1: FTIR spectra of as deposited and annealed Si-O-C-H composite film deposited with O_2 /BTMSM gas flow rate ratio at 3:17 sccm.

of the film. It is known that there are $Si-CH_3$ (790 cm^{-1} , 980 cm^{-1} , 1240 cm^{-1}), $Si-O-Si(C)$ ($1000\sim 1200\text{ cm}^{-1}$), $CH_n(n=1,2,3)$ (740 cm^{-1} , 900 cm^{-1}), and OH-related ($1420\sim 1500\text{ cm}^{-1}$) bonds[3, 5-7]. After annealing, the $Si-CH_3$ bond-related peak intensity and position has almost no change, but the broad peak about $1000\sim 1200\text{ cm}^{-1}$ have obvious changes. This FTIR was taken one month after the films were deposited. We obtained the same spectra right after the films are prepared as shown in Fig.1. From these results, we know that a small amount of the un-reacted $Si-CH_3$ bond exist in the film, and O-H bond is formed during the deposition process because the peak of O-H bond in the annealed film is the same spectra of as deposited film.

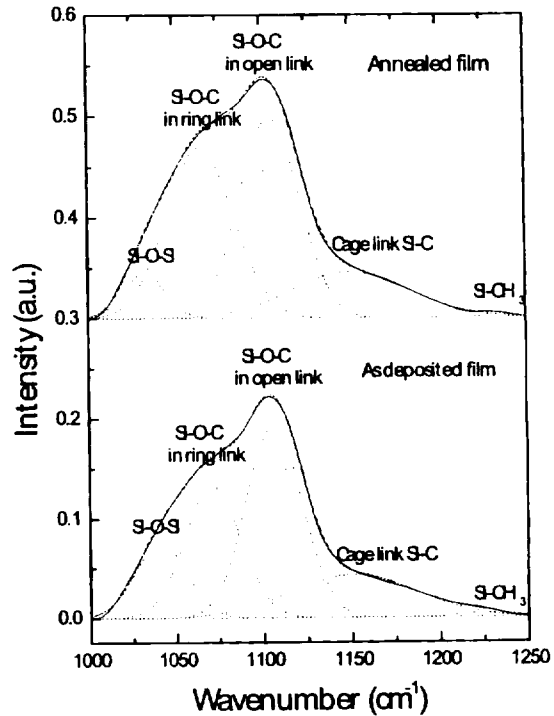


FIG. 2: The deconvoluted spectra of Si-O-C bonding mode in the wavenumber range from 1000 cm^{-1} to 1250 of the same sample as in Fig. 1.

In order to investigate the Si-O-C bonding mode in the film, the deconvoluted spectra in the range from 1000 cm^{-1} to 1250 cm^{-1} is shown in Fig.2 and the peak is resolved by Gaussian fitting. From Fig.1, we know that the bonding mode near 1040 cm^{-1} is for the Si-O-Si asymmetric stretching mode, and bonding modes near 1065 cm^{-1} and 1105 cm^{-1} are for Si-O-C asymmetric stretching mode in a ring link and open link respectively[8]. The broad bonding mode

1150 cm^{-1} is for the Si-O cage-like stretching mode[9]. The peak near 1240 cm^{-1} is best identified as for the Si-CH₃ bonding mode.

Compared with the relative intensity of bonding modes related in this range, the annealed samples show very little change in the intensity for Si-CH₃ bond (1230 cm^{-1}), and the Si-C cage like bond (1153 cm^{-1}), but the intensity of Si-O-C bond (1103 cm^{-1}) in Si-O-Si open link and Si-O-Si bond (1040 cm^{-1}) decrease, and those of Si-O-C bond in Si-O-Si ring link increases simultaneously. For the other samples which have different O₂/BTMSM gas flow rate ratio, similar changes have also been found. This result means that for the Si-O-C-H composite film, the annealing at 500°C for 30 minutes in vacuum would induce the re-arrangement of chemical bonds in the film. Some of the Si-O-Si open links will change into ring links in which the CH₃ organic groups have been attached. Because there is a force between the CH₃ group and other part of Si-O-Si links, the space of the voids can be formed. In case of links, the void can be filled easily by other open links. Therefore, we then infer the formation of the Si-O-C ring links by attaching CH₃ groups to the Si-O-Si ring links is good for forming the nano-size void in the film. As previously mentioned, the void formed in film can result in low dielectric constant.

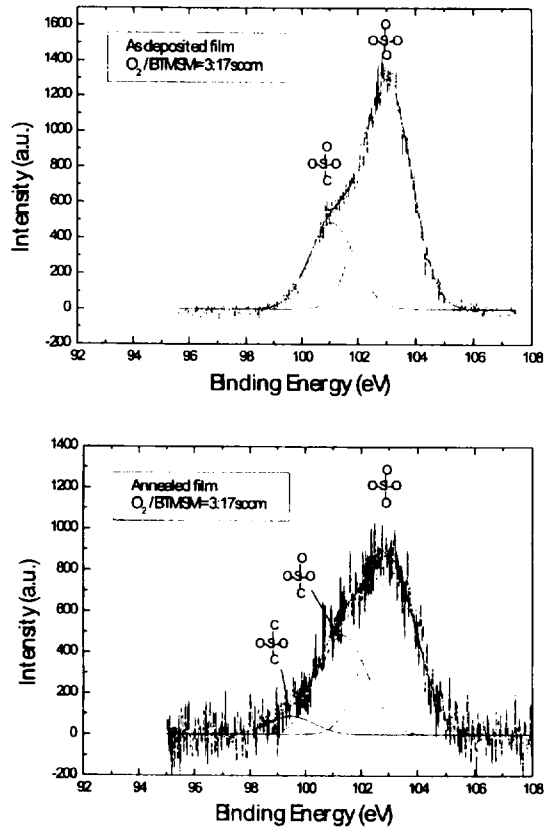


FIG. 3: The Si2p XPS spectra of as-deposited sample and annealed sample at 500 °C for 30 min in vacuum.

To confirm the O-Si-O, Si-C, C-H and C-O bonds in the film, the XPS narrow scan spectrum of the C 1s, Si 2p, and O 1s peak is deconvoluted by fitting the data with a number of Gaussian peaks. The O 1s electron orbital spectra consist of two peaks, which can be assigned as O-Si bond (532.6 eV) and O-C bond (530.6 eV)[10]. After annealing, the relative intensity of C-O bond is a little bit higher than that of as-deposited film

(from 25.6% to 29.9%), which means that there are many more Si-O-C bonds formed during the annealing process. The Si 2p electron orbital spectra of as-deposited film consists of two peaks, which can be assigned as the Si-O₄ bond (103.0 eV) and the C-Si-O₃ bond (101.0 eV). In the annealed sample, it consists of three peaks: the Si-O₄ bond (103.1 eV), the C-Si-O₃ bond(101.3 eV) and the C₂-Si-O₂ bond(99.4 eV)[11, 12], as shown in Fig.3. The C 1s electron orbital spectra of as-deposited film consists of one broad peak with the FWHM as 3.2 eV, and the spectrum of annealed film consists of two peaks with FWHM about 1.6 eV and 1.9 eV, which one is a C-O/H bond (284.2 eV) and the other is a Si-C bond (282.2 eV). These results also show that there are many more C atoms integrated into the Si-O link and formed the Si-O-C link.

We have obtained the dielectric constants of the as-deposited sample and annealed sample using the MIS (Al/Si-O-C-H film/p-Si) method. The calculated dielectric constant for the as-deposited film is approximately 2.7, and after 500°C for 30 min annealing at vacuum ambient, it decreased to 2.3. It means

that the rearrangement of the bond configuration formed in a void with a preexisting atomic scale nanoporosity in the film, which the CH₃ groups in the annealed sample have much different bonding configurations from the as deposited sample[3, 5].

IV. CONCLUSIONS

We performed the FTIR and XPS spectra studies on the Si-O-C-H composite films deposited with a BTMSM precursor and oxygen gas by a radio frequency (13.56MHz) ICPCVD system. The annealing treatment at 500°C for 30 min causes the more Si-O-C ring links, which has CH₃ groups attached, to be formed in the film. From the aloof force that exists between the organic groups, we infer the formation of Si-O-Si ring link with CH₃ groups attached is responsible for forming the nano-size void in the film which can result in a low dielectric constant.

Acknowledgements

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저유전 상수를 갖는 Si-O-C(-H) 초박막의 결합구조

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요 약

액체상태의 BTMSM과 산소 가스를 원재료로 하여, rf 인가전압을 이용한 ICPCVD 방법으로 Si-O-C-H 박막을 형성하였다. FTIR과 XPS 스펙트럼을 이용하여 박막 내의 Si-O-Si, Si-O-C 그리고 Si-CH₃ bond 등을 조사하였다. 형성한 박막을 열처리하여 FTIR과 XPS 스펙트럼의 변화를 비교하여 박막내의 Si-O-Si와 CH₃ group이 nano-size의 void 형성에 기여하는 것으로 추론한다. 유전율을 계산한 결과 열처리 후에 2.3의 값을 얻을 수 있었다.