The Characteristics of Dielectric Properties of SiOC(-H) film with the Variation of Dielectric Components on Si-O-C Structure

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Low dielectric constant SiOC(-H) films have been prepared by inductively coupled plasma chemical vapor deposition using bis-trymethylsilyl-methane (BTMSM) and O_2 precursors. The annealing effects on the structural and electrical properties were studied. The results indicate post-annealing could efficiently remove the hydroxyl (-OH) related groups from the as-deposited films and cause the chemical structure re-arrangement, resulting in the more nano-pores being formed in the annealed SiOC(-H) films. The dielectric constant decreased from 2.7 to 2.1, and the refractive index decreased from 1.427 to 1.32.

1. Introduction

As the design rule of integrated circuit (IC) devices approaches 0.1μm and below, resistance-capacitance (RC) delay in the multilevel interconnections has became the determining factor in overall chip performance [1]. This is due to wiring extensions that increase the conductor resistance as well as signal cross-talk. Reducing the dielectric constant(ε) of insulation layer has been regarded as one of the effective way to solve RC delay and cross talk [2]. Silicon dioxide(ε_r =3.9~4.3), which is used as a present inter metal dielectric(IMD) film, is difficult to solve the problem for RC delay and cross-talk [1,3]. Therefore, a new low dielectric material is necessary of the IMD film in order to improve device performance. Recently, many researches have proposed a variety of organic and inorganic materials, such as hydrogensilsequioxane(HSQ) [4], fluorine-doped silicon oxide, and fluorinated amorphous carbon [6], methylsisequioxnae(MSQ) [8] and carbon doped silicon oxide(SiOC) [5,7,10,11], as an alternative to SiO_2. Among these materials, SiOC film has many advantages compared to other low dielectric materials since it has higher thermal and mechanical stability.

The polarization depends on the density of film and dipole moment. Normally, in SiOC film, the dielectric constant is decreased with increasing carbon contents and the density of SiOC film also decreased with increasing carbon contents. The mechanism of decreasing dielectric constant is understood by density of film. However, it is not sufficient to explain the

mechanism of dielectric constant since there is much difference between the decreasing density of film and decreasing dielectric constant. Recently, the bonding length of Si-O-C depends on the carbon contents in SiOC film. It means that the induced dipole moment changes with carbon contents. It is well known that the induced dipole moment depends on the film density and the bonding angle and length.

In this study, we have investigated the relation between bonding angle in Si-O-C film and carbon contents, also studied the changing mechanism of dielectric properties with the dielectric components.

2. Experiment

The SiOC composite films were deposited on p-type Si(100) using BTMSM and oxygen mixture gases by an ICPCVD method. ICPCVD plasma was generated by means of a three turns coil, which was set around a quartz tube and connected to the 13.56MHz rf power supply. A base pressure as 10^{-6} Torr was reached before each deposition. The BTMSM precursor is a nontoxic, colorless liquid with a boiling point of 137°C and a melting point of -41°C at standard atmospheric pressure. It was vaporized and carried by inert argon gas from a thermostatic bubbler(maintained at 40°C) to the reaction chamber. To prevent re-condensation of BTMSM, all of the gas delivery lines were heated and kept at a constant temperature of 40°C. The Oxygen and BTMSM gas flow rates were varied 3 and 17 sccm, respectively. Theses gas were introduced through a mass flow controller (MFC) into the reaction chamber, and the discharge pressure was measured with a Baratron gauge and kept at about 3.0×10^{-1} Torr. To investigate the chemical bond structure of the SiOC(-H) composite films with nano-pore structure we carried out the post-annealing at 400°C for 30 minutes in a vacuum. FT-IR spectroscopy, performed in absorbance mode with a model DA8 Bomem spectrometer, was used to determine the related Si-O-Si bonding angle in the film. The film thickness and refractive index were measured by ellipsometer, at a wavelength of 632.8 nm. The dielectric constant at 1MHz was obtained by a HP4280A C-V meter on the Metal- Insulator-Semiconductor(MIS) structure.

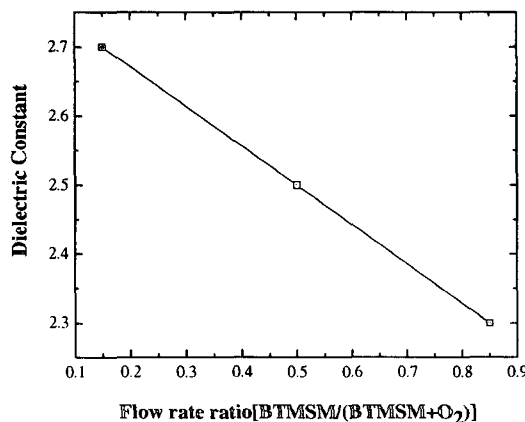


Fig.1. The dielectric constant of SiOC(-H) films as the fucntion of flow rate ratio

3. Results and Disscussion

Figure 1 shows the dielectric constant of the film as a function of BTMSM/O_2 flow rate ratio. The dielectric constant decreases as BTMSM/ O_2 flow rate ratio increases; the lowest relative dielectric constant of annealed film with BTMSM/O_2 flow rate of 17/3 (sccm), is obtained as approximately 2.1. This result means that the alkyl group ($-CH_3$) in source gas increased as the carbon contents increased. Usually, the carbon atom is connected with two or three hydrogen atoms so that the inclusion of carbon atom may break the -Si-O- chain and decrease the film density. However, the dielectric constant depends on the film density and polarizability. For better understanding, it is important to remind the relation between polarizability and dielectric constant. The total polarization is composed of three modes of polarizability :

$$\alpha_{tot} = \alpha_{electronic} + \alpha_{ionic} + \alpha_{permanent\ dipole\ orientation}$$

The electronic polarizability is due to the displacement of negative charges of electronic clouds with respect to the positive charges of ionic atom under electric field conditions. The ionic polarizability results from the rearrangement of the nuclei in response to the electric field. The permanent dipole orientation polarizability results from the redistribution of charge when a group of atoms with a net permanent dipole moment reorients itself in space in response to an electric field. There is no contribution of the ionic polarizability on the dielectric constant in high frequency region(>10^{14}Hz), so that the electronic polarizability can be infer from the dielectric constant at high frequency region($\varepsilon_{electronic} \approx n^2$, n : refractive index).

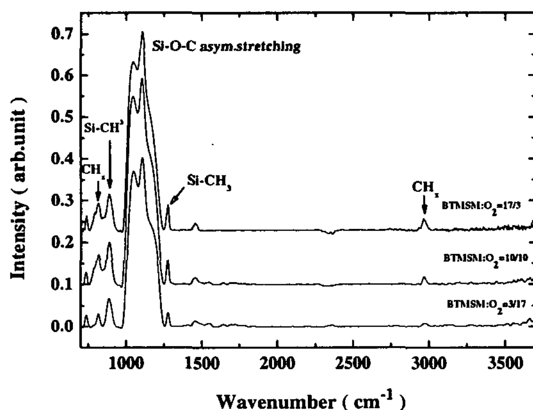


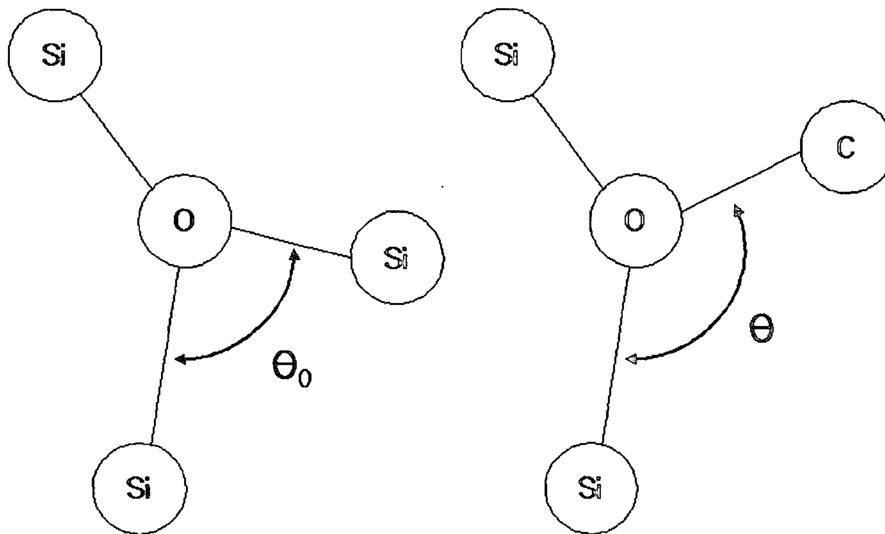
Fig.2 The FT-IR spectra of as deposited SiOC(-H) composite films

Table 1. The bonding angle and carbon contents

Flow rate ratio	0.85	0.5	0.15
Si-O-Si(C) Wavenumber(cm^{-1})	1042.87	1028.18	1026.13
Bonding angle(°)	149.6	144.4	143.6
Relative Carbon Contents(%)	44.6	23.0	19.6

Figure 2 shows the FT-IR spectra for film deposited with BTMSM/O_2 flow rate ratio of 17/3, 10/10, 3/17. It is known that there are Si-CH_3 (883 cm^{-1}), Si-O-Si(C) (1000 ~1250 cm^{-1}), CH_n(n=1,2,3) (740 cm^{-1}). In the range from 1000 cm^{-1} to 1250 cm^{-1} [10,11], the bonding

mode near 1030 cm^{-1} is the Si-O-Si asymmetric stretching mode, and the bonding modes near 1104 cm^{-1} and 1180 cm^{-1} are due to Si-O-C asymmetric stretching mode in an open link and Si-C cage-link, respectively. The broad bonding mode at 1171 cm^{-1} and at 1267 cm^{-1} of the as-deposited sample with an BTMSM/ O_2 flow rate of 17/3 are due to the Si-C cage-link stretching and Si-CH_3 bonding modes [11], respectively. In the sample with an O_2/BTMSM flow rate increase, the peak of Si-O-C asymmetric stretching mode in an open link is shifted to a higher wave number (blue-shift) [10]. This wavenumber shifts in IR spectra are related to the change of bonding characteristics, such as bonding angle and bond length. From these results, we can infer that the repulsive power between the oxygen atom and carbon atom increased as carbon contents increased. The bonding angle of Si-O-C increase as indicated in the following diagram:



A variation of bonding angle(θ) can be drived by the using equation (1) and the table 1 shows the arrangement on its experimental results [10,11].

$$\bar{\nu} = \bar{\nu}_0 \sin(\frac{\theta}{2}) \quad (1)$$

Where, $\bar{\nu}$ is experimentally obtained for $\bar{\nu}_0$=1080cm^{-1} in thermal oxide(SiO_2). When the flow rate of BTMSM is increased, the carbon contents increased as in the Table 1 and the bonding angle was extended and the wavenumber was extended also. Figure 3 shows that the bonding angle of deposited films versus carbon contents. This trend indicated that the increasing of carbon contents, the extension

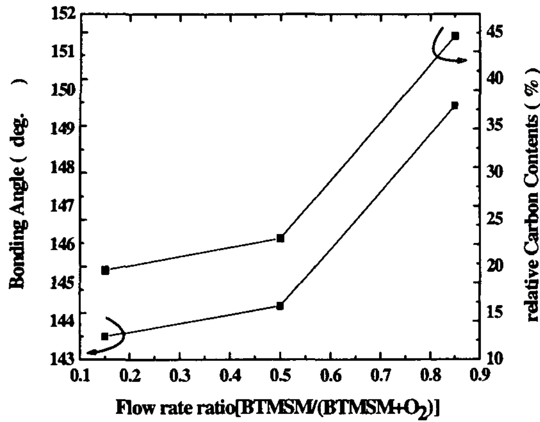


Fig. 3. The bonding angle vs. relative carbon contens

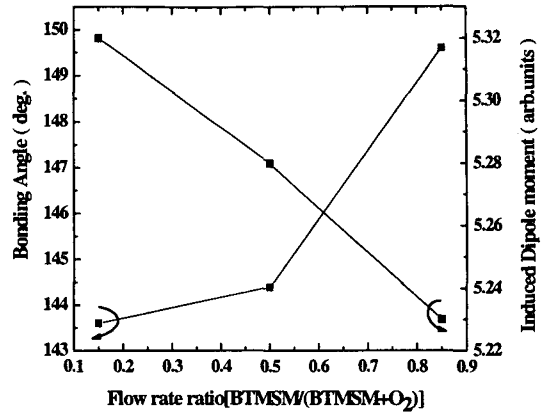


Fig.4. The bonding angle vs dipole moment

of bonding angle between Si-O and O-C bonds. Figure 4 indicated the variation of dipole moment by the variation of the bonding angle using the equation (2).

$$\mu_{elec} = \mu_{Si-O} + \mu_{O-C} \qquad (2)$$

Where , μ_{elec} is the total induced dipole moment and $\mu_{Si-O} + \mu_{O-C}$ is the sum of the vector dipole moment in the Si-O and O-C bonds. When the boning angle extended so that the dipole moment was decreased, it is indicated that the contribution of dipolar polarizability was decreased because the dipole moment decreased with the variation of bonding angle. The dielectric constant was based upon the variation of electronic polarizability, Figure 5 shows the electronic dielectric constant by the square of refractive index at high frequency region(>10^{14}Hz). The minimum electronic dielectric constant is 2.07 and the maximum electronic dielectric constant is 2.19

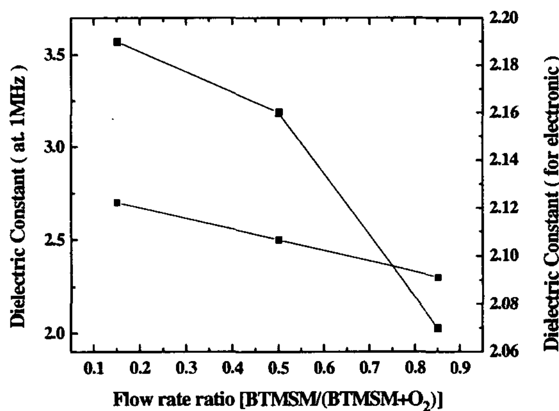


Fig.5. The electronic dielectric constant vs. total dielectric constant

from refractive index ($\varepsilon_{ele} \approx n^2$). That is to say, the reduced electronic polarizability contribution had large influence on reducing the overall dielectric constant because that the electronic dielectric constant took a large part nearly 90% of total dielectric constant.

4. Conclusions

The SiOC composite films were deposited with a BTMSM precursor and oxygen gas by a radio frequency (13.56MHz) ICPCVD system, with various O_2/BTMSM flow rate ratios. The electronic, ionic, and dipolar contributions to the dielectric constants of the SiOC films were separately investigated. The electronic contribution is larger than other polarization (ionic, dipolar polarization). Reaction between bonding species just like Si-CH_x(alkyl group) and Si-O make lower the dielectric constant than silicon dioxide films [9]. However, the reduced electronic contribution had large influence on reducing the overall dielectric constant. This reason is that the low dielectric constant of SiOC films mainly results from reduction of the electronic contribution, which can be explained by the decrease of the Si-O bonding network in the film.

Acknowledgments

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