

Study on the Formation of SiOC Films and the Appropriate Annealing Temperature

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Abstract—As silicon devices shrink and their density increases, the low dielectric constant materials instead of SiO₂ film is required. SiOC film as low-k films was deposited by the capacitively coupled plasma chemical vapor deposition and then annealed at 300~500 °C to find out the properties of the dependence on the temperature and polarity. This study researched the dielectric constant using by the structure of the metal/SiOC film/p-Si, chemical shift, thickness, refractive index and hardness. The trend of reflective index was inverse proportioned the thickness, but the dielectric constant was proportioned it. The dielectric constant decreased with decreasing the thickness and the increment of the refractive index.

Index Terms— SiOC film, Dielectric Constant, FTIR.

I. INTRODUCTION

IN order to improve the performance of the ultra large scale integration (ULSI), the scaling down have some problems to increase the resistance-capacitance (RC) delay, the signal propagation delay time or cross-talk noise between adjacent interconnect lines. Using low-k (low dielectric constant) materials as inter layer dielectric (ILD) instead of SiO₂ film is one of these problem's solution [1-4]. SiOC film by the chemical vapor deposition (CVD) is promising ILD materials as low-k materials. Lowing dielectric constant is due to the pores or low polarization. However, it is not clearly defined the reason of the reduction of dielectric constant, and new ultra low-k SiOC film need to satisfy properties of electric, chemical, physical, mechanical and thermal requirements. The formation of SiOC film originates from the reaction of the C=O or C-O bonds by the plasma dissociation and recombination with many radicals. There are hybrid properties without polarity between hydrophilic and hydrophobic properties in the carbon based system such SiOC film. [5-8]. The SiOC film produced in CVD system consists of limited substitution of O atoms by the less polarizable C atoms. The C-O group through the phase transition of the C=O group participated in the hydrogen bonding is the reasons of low dielectric constant and the chemical shift [9-13]. The SiOC film

reduces the dielectric constant by the oxidation process owing to the H₂O evaporation. However, the function of carbon after annealing can be the origin of the leakage current. Therefore, it is necessary to find out the relationship between the dielectric constant and thermal stability about the electron effect related to the carbon atom after annealing.

The paper was studied on the leakage current and relationship between the dielectric constant and the refractive index.

II. EXPERIMENTS

The low-k SiOC films were obtained using the mixed gases of oxygen and trimethylsilane (TMS) by capacitively coupled plasma chemical vapor deposition (CCP-CVD). The chemical properties of SiOC film were researched by Fourier Transform Infrared spectrometer (FTIR, Galaxy 7020A). To obtain the dependence on the temperature of currents, SiOC film was annealed at 300, 400 and 500 °C, and the leakage current was measured with increasing the substrate temperature at interval of 10 °C from 20 °C to 150 °C. To comparison with the refractive index and the leakage current, the refractive index was measured by the Ellipsometer with the source of 632.8 nm. The current-voltage characteristics were measured using a HP 4155A semiconductor parameter. The dielectric constant was researched from the C-V (capacitance-voltage) measurement at 1MHz using the HP4284A on the MIS (Al/SiOC film/Si substrate) structure.

III. RESULTS AND DISCUSSION

In SiOC film with low-k by CVD, the gas precursor is dissociated into ions, cations and radicals which are controlled by the bond dissociated energy. These ions, cations and radicals trend toward more stable bonds than before.

Figure 1(a) explains the FTIR spectra of SiOC film. The main bond in the range of 940~1500 cm⁻¹ is Si-O-C bond, and the strong peak of 1250 cm⁻¹ is the Si-CH₃ bond.

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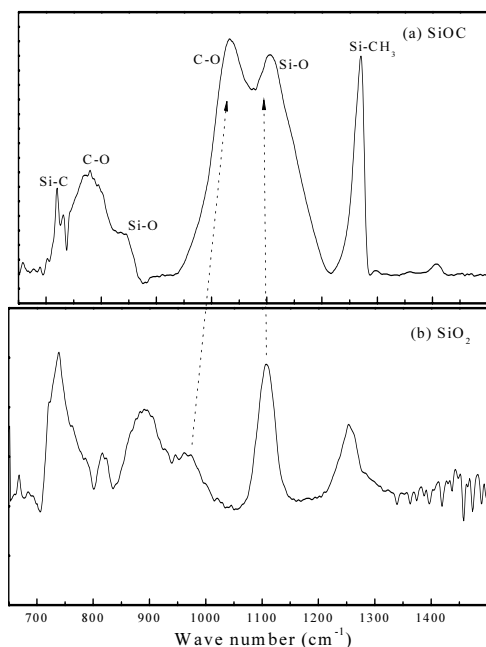


Fig. 1. Comparison of SiO₂ and SiOC films using TMS precursor with the range of 650~1500 by using FTIR spectra (a) SiOC film, (b) SiO₂ film.

The low range of 700~880 cm⁻¹ is related with the union of Si-O, Si-C and C-O bonds, which define the chemical properties of SiOC film. In the narrow band of FTIR spectra under 900 cm⁻¹, the band of 700~880 cm⁻¹ consists of Si-C, C-O and Si-O bonds. The intensity of these peaks changes as a function of chemical properties of SiOC film. To understand the formation of the bonding structure in SiOC film, it compared with the FTIR spectra of the SiO₂ film as shown in Fig. 1(b). The SiO₂ film with inorganic properties involves the Si-CH₃ bond of 1250 cm⁻¹, Si-O near 1100 cm⁻¹ and Si-O-C related bond under 1050 cm⁻¹ which shows the strong bond at 740 cm⁻¹ and small bond with 820 cm⁻¹. In comparison with the strong bond at 740 cm⁻¹ in the SiO₂ film, SiOC film has the strong peak near 750 cm⁻¹ but the intensity decreases. However, in the range of 700~880 cm⁻¹, the middle C-O bond at 780 cm⁻¹ in SiOC film becomes very strong and broad bond. Moreover, the Si-CH₃ bond of 1250 cm⁻¹ is also very strong and the Si-O-C bond of 940~1200 cm⁻¹ is split two peaks in SiOC film. These characteristic means that the SiOC film becomes organic-inorganic properties owing to the infiltration of carbon atom in Si-O net work mechanism. Finally, the FTIR spectra under 900 cm⁻¹ shortens in spite of the increment of Si-O-C bond observed in FTIR spectra in the range of 940~1200 cm⁻¹.

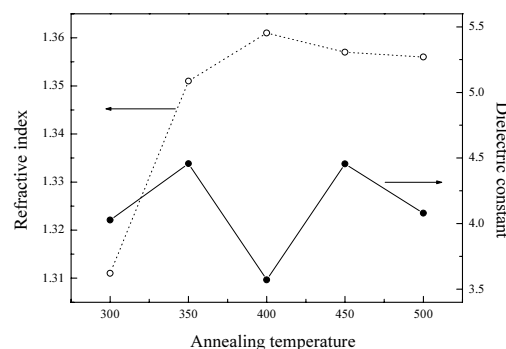


Fig. 2. SiOC film according to the annealing temperature, (a) Refractive index, (b) Dielectric constant.

Figure 2(a) indicates the dielectric constant of SiOC film using the MIS (metal/SiOC film/p-Si) structure. The dielectric constant changes owing to the annealing temperature. SiOC film annealed at 400 °C is the lowest dielectric constant.

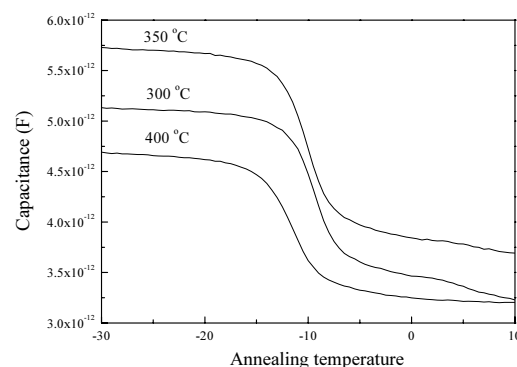


Fig. 3. Capacitance of SiOC film according to the annealing temperature.

Figure 2(b) shows the refractive index of SiOC film at various annealing temperature. The trend of refractive index of 300 °C, 350 °C and 400 °C increases, but that of 450 °C and 500 °C decreases. SiOC film annealed at 400 °C is the highest refractive index.

Figure 3 presents the capacitance according to various annealing temperature in SiOC film. The dielectric constant measured using the MIS structure directly depends on the capacitance or thickness. The capacitance is the lowest at sample annealed at 400 °C, and the dielectric constant is also the lowest at this sample as shown in the Fig. 2(a).

Figure 4 is the thickness of annealed SiOC film. The thickness decreases with increasing the annealing temperatures. The effect of annealing process can be obtained from the research about the variation due to the oxidation. The OH bonds disappear after annealing

at high temperature. Two OH bonds in R-OH, Si-OH, CH or OH bonds react with each others and H₂O evaporates.

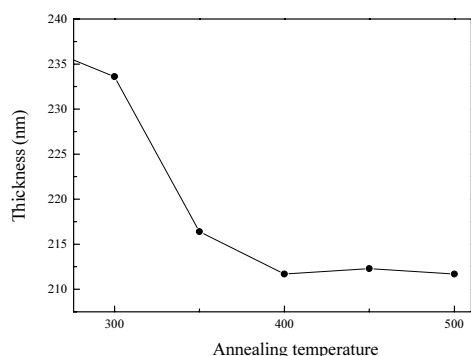
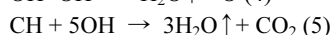
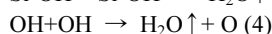
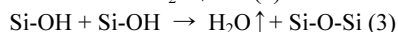
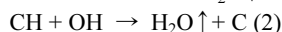
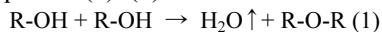


Fig. 4. Thickness of SiOC film according to the annealing temperature.

These sites generate the R-O-R or Si-O-Si cross-link form the oxidation reaction as given by the following equation (1)~(5).



In view of the progress of reaction, the reaction of the equation of (1) and (2) occurs at lower temperature than that of the equation of (3)~(4), because the bond dissociated energy of CH bond or R-O-R group is lower than that of OH or Si-OH bonds. That is, there are many carbon or alkyl group obtained by the low annealing temperature. The alkyl group or carbon has many electrons, and can be the source of the leakage current. On the other hand, the high annealing temperature generates the Si-O-Si bonds or oxygen atoms as given by the equation of (3) and (4). The Si-O-Si bond with few carbons make the fine cross link structure without the space effect in the film and finally decreases the thickness. Therefore, it is necessary to do the high annealing process for low-k SiOC film.

IV. CONCLUSIONS

The SiOC film was prepared with the mixed precursor of TMS and oxygen by the capacitively coupled plasma chemical vapor deposition. The lowest dielectric constant was obtained at the annealed film at 400 °C and the leakage current at this film was also decreased with increasing the substrate temperature. The thickness decreased in accordance with the increasing of the annealing temperature. But the refractive index increased with increasing the annealing temperature.

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Teresa Oh obtained M.S. and Ph.D. majoring in Electronic Engineering and Communication Engineering at Jeju National University, South Korea, in 1996 and 2000 respectively. She has been a professor in Department of Semiconductor Engineering at Cheongju University since 2005. She worked as a researching professor in Department of Ceramic Eng. at Changwon National University in 2005. Aug., Her research field includes dielectric materials, organic TFT or materials for solar cell.