

A study of the dielectric constant of low-k SiOC film

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As silicon devices keep shrinking in size while the circuits become more complex, they require low dielectric constant materials instead of silicon dioxide. SiOC films as low dielectric constant materials deposited by chemical vapor deposition were analyzed by Fourier transform infrared spectroscopy, ellipsometry and nano-indentation to find the correlation between the dielectric constant and properties according to the flow rates. SiOC film showed a chemical shift according to an increase of the intensity of the Si-O bond in the main bond near 1000 cm^{-1} . Although the variation of the chemical shift was quite small in the FTIR spectra, the hardness and electronic properties such as the dielectric constant showed large differences. The blue shift in the main bond induced an increase in the hardness because of lowering the surface energy and a reduction of the carbon content which decreased the polarity, thickness and dielectric constant. The reduction of the dielectric constant and thickness of the SiOC film was caused by the reduction of ionic polarization owing to the elongation effect by the attractive force between atoms, and made a fine cross linked structure which contributed to a flat surface on substrates.

Keywords: SiOC film, Thickness, Refractive index, Dielectric constant, Hardness.

Introduction

SiOC film is a new low-k material suggested in the semiconductor industry to replace the SiO_2 film as an insulator, because of increasing the line-to-line crosstalk noise and RC delay time of SiO_2 film because of the trend to reduce the scale over the last decades [1-5]. There are many precursors such as tetraethoxysilane (TEOS), dimethyldimethoxysilane (DMDMOS), bistrimethylsilylmethane (BTMSM) and methyltrimethoxysilane (MTMS) for a SiOC film deposited by chemical vapor deposition (CVD). The decrease of the dielectric constant in SiOC film originates from the nano pores formed in the SiOC film by the repulsive force of the alkyl group or low polarization due to the C-H terminal bond [6-8]. Recently, low density SiOC film due to the low polarization has attracted interest because of its good mechanical and thermal stability. However, porous SiOC film has serious problems such as poor hardness and adhesion, in spite of its low dielectric constant. Understanding the reason for lowering the dielectric constant is an important factor to optimize the SiOC film process [9-10]. SiOC film has been deposited using CVD such as ICP (inductive coupled plasma)-CVD and CCP (capacitive coupled plasma)-CVD. SiOC film has different chemical and physical properties according to whether ICP-CVD or CCP-CVD processes are used, because of the different dissociation energies due to the plasma density. The chemical shift in Fourier transform infrared

(FTIR) spectra may easily define the bonding structure of SiOC film and has given useful information about the mechanism of bond formation [11-15].

In this study, SiOC films deposited with various flow ratios prepared with MTMS and oxygen as precursors were analyzed by Fourier transform infrared spectroscopy, ellipsometry and nano-indentation. The dielectric constants of SiOC films were investigated using a C-V measurement system and their refractive indices using ellipsometry to reveal the relationship between the dielectric constant and the polarization.

Experiments

The low-k SiOC films were obtained by inductive coupled plasma chemical vapor deposition (ICP-CVD). The MTMS was vaporized and carried by argon gas at $35\text{ }^\circ\text{C}$ from a thermostatic bubbler. The low-k SiOC films were prepared by various flow rate ratios of MTMS and oxygen mixed precursors. First, the chamber condition was a vacuum with 10^{-5} Torr ($0.00075\sim0.0013\text{ }\mu\text{P}$) by a turbo pump. During the process, each MTMS at various MTMS flow rates $3\sim13\text{ sccm}$ was vaporized at $35\text{ }^\circ\text{C}$ with a thermostatic bubbler carried by argon gas. The base pressure was 3 Torr ($0.0025\text{ }\mu\text{P}$) and the rf power was 800 W in each experiment. The chemical properties of the SiOC films were studied by a Fourier transform infrared spectrometer (FTIR, Galaxy 7020A). The dielectric constant of the polarization was measured from the reflective index (n) by an ellipsometer with a source of 632.8 nm and the capacitance for the dielectric constant was calculated from the C-V (capacitance-voltage) measurements at 1 MHz using an HP4284A on the MIS (Al/SiOC film/Si substrate) structure.

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Results and Discussion

Fig. 1(a) displays the FTIR spectra from 600-2400 cm^{-1} of as-deposited SiOC films by inductive coupled plasma chemical vapor deposition (ICP-CVD). These consist of many bonds with the Si-CH₃ bond at 1270 cm^{-1} , the Si-O-C bond near 1000 cm^{-1} and alkyl sites at 650-920 cm^{-1} . Fig. 1(b) is the peak position to find out the chemical shift of the Si-O-C bond from 920-1220 cm^{-1} . It is confirmed that samples 3, 9 and 13 show a blue shift. The Si-O-C bond near 1000 cm^{-1} consists of the left C-O and right Si-O bonds, so the blue shift means an increment of the Si-O bond at the right shoulder in the main bond and the decrement of the carbon content.

Fig. 2(a) is the deconvolution in samples 8 and 9 to find out the blue shift in the main bond from 920-1220 cm^{-1} which consists of the C-O and Si-O bonds. The Si-O bond in sample 9 is larger than that of sample 8. An increment at the right shoulder induces the blue shift in sample 9 owing to the change to a higher wave number observed in FTIR spectra.

Fig. 2(b) is the relative intensity of the main bond in the range from 900-2400 cm^{-1} . Samples 3, 9 and 13 with the blue shift are observed with a reduction of the intensity. The length of Si-O bond is shorter than that of the C-O bond, because of the stronger bonding strength of Si-O than the C-O bond. So the peak position of the Si-O bond is a higher wave number than that of the C-O bond observed in FTIR spectra. The condensation effect of the Si-O bond

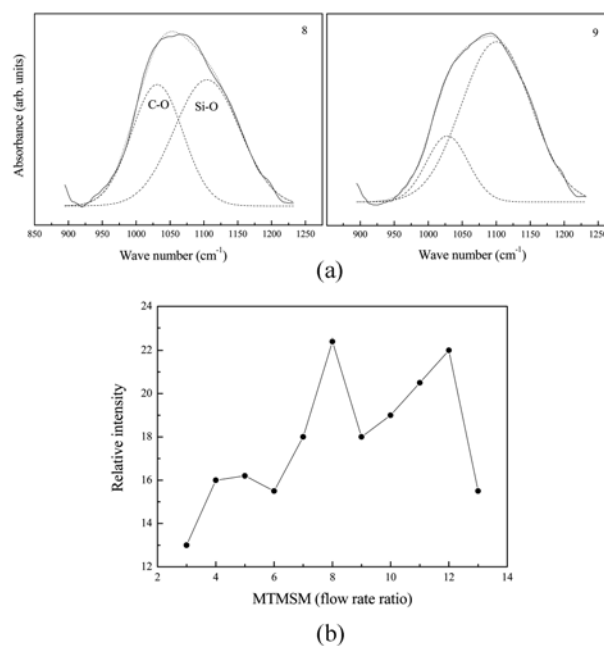


Fig. 2. (a) Deconvoluted FTIR spectra consists of the C-O and Si-O bonds for samples 8 and 9, (b) Relative intensity of the main bond in the range of 900-2400 cm^{-1} .

is related to the intensity of the main bond in the range from 900-2400 cm^{-1} . The main bond with a high content of the Si-O bond shifted to a higher wave number in the FTIR spectra and moreover, decreased the peak intensity.

The MTMS and oxygen mixed precursor which was dissociated by the plasma energy, created the ions, cations and radicals such as Si-O, C-O, Si-CH_n ($n = 1-3$), Si-H, C-H or O-H bonds. The elongation effect between the terminal bond of Si-CH₃ and the oxygen contributes to make a fine cross linked structure. They recombine with other sites in different conditions according to the plasma density, therefore the final materials have various bonding structures such as cross linked breakage owing to the porosity or cross linked structures.

Fig. 3 is the structure with pores by the distance force at the terminal bond of Si-CH₃ with many alkyl groups. The space charge effect in Fig. 3 makes a cavity by the polarity with many ionic radicals and so increases the thickness. Pores enclosed by the alkyl groups also contribute to a decrease in the hardness due to many carbon atoms. However, Fig. 4 indicates the cross linked structure of a SiOC film with the effect of a lowering of the polarization due to ionic forces between the atoms formed by a high plasma density and plasma energy. The Si-CH₃ bond is broken by the oxygen that makes the Si-O, C-OH or C-O bond. The C-O bond is attacked by the nucleophilic attack reaction from a Si atom with many electrons and becomes the bond in O-Si-C. The Si attack reaction and the H₂O evaporation effect between the terminal bonds of O-H contributes to make a fine cross linked structure as shown in Fig. 4. The cross linked structure contributes to make the low surface energy and stability of the final materials. These are the mechanisms

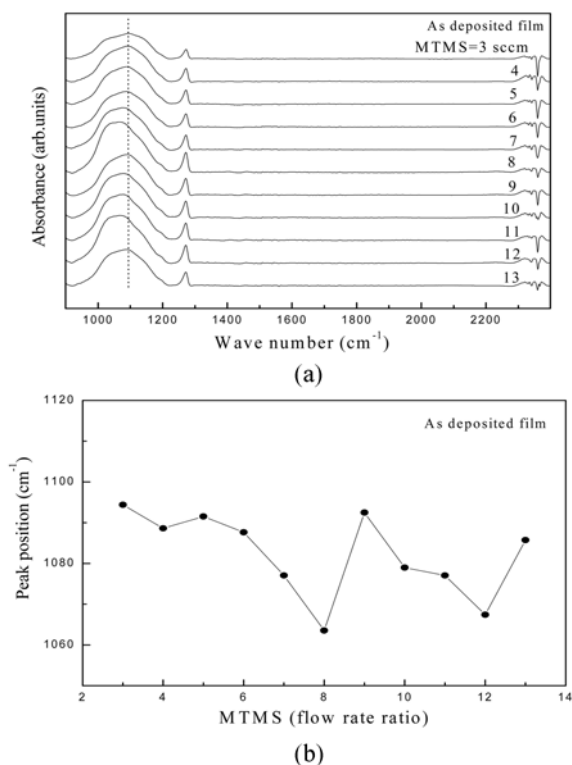


Fig. 1. (a) FTIR spectra of 920-1220 cm^{-1} of as deposited SiOC film with various flow rates, (b) Chemical shift and peak position in the main bond in SiOC film with various flow rates.

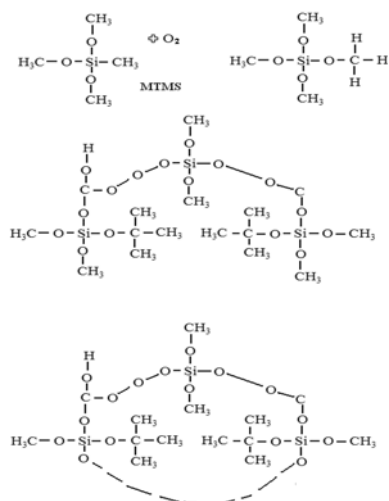


Fig. 3. Bonding structure in a porous SiOC film.

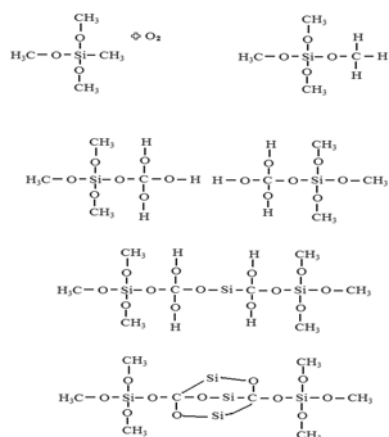


Fig. 4. Cross link bonding structure.

of the Si-O-C cross linked structure to prepare the SiOC low-k thin film.

The Si-O-C main bond of $920\text{--}1220\text{ cm}^{-1}$ consists of the bonds of C-O and Si-O. The increment of carbon is related to the porosity which has the hydrophobic properties as an organic group. However, the Si-O net work is based on the hydrophilic properties with an inorganic group. To make the low dielectric materials suitable for ultra large scale integrated circuits devices, it is necessary to produce non polarization in the insulator because it gives the electric stability for the reduction of the leakage current. Moreover, the low-k candidate materials for semiconductor devices require hardness as a physical-mechanical property.

Fig. 5 shows the thickness of SiOC films with various flow rates. The thickness decreases for samples 9 and 13 with the blue shift as shown in Fig. 1. The blue shift is strongly related to the reduction of the carbon content which causes the cross linked structure. This result disperses the charge of the proton and stabilizes the carbocation. Consequently, the thickness of the film decreases depending on the weak boundary conditions, and makes the final films with a low surface energy because of a lowering of the polarization. However, intensifying the charge of the proton increases the surface

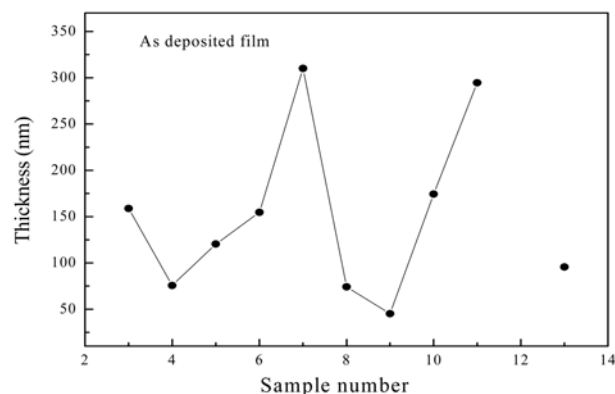


Fig. 5. Thickness of SiOC films with various flow rates.

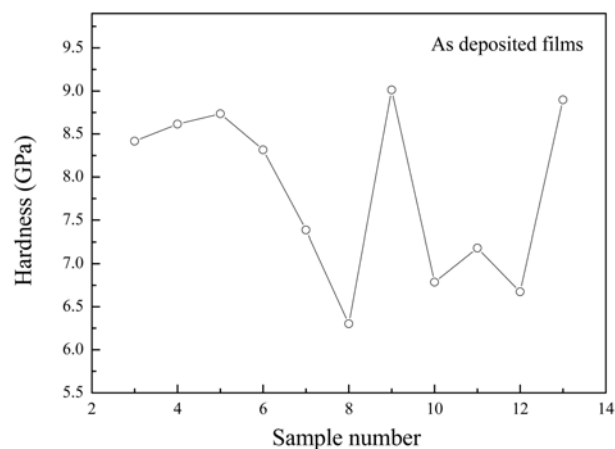


Fig. 6. Hardness of SiOC films with various flow rates.

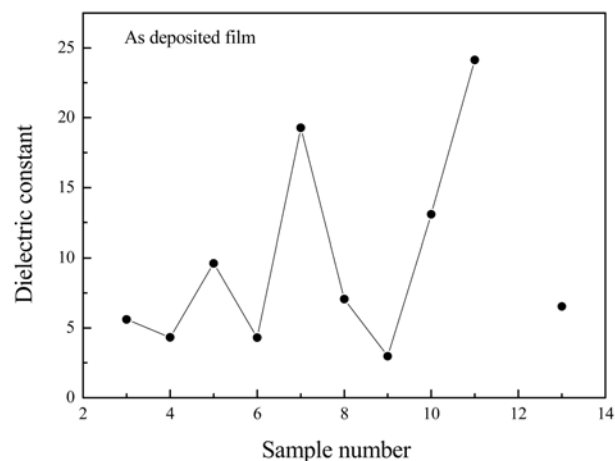


Fig. 7. Dielectric constant of SiOC films with various flow rates.

energy of the film, and leads to an increase of the thickness of the film such as for samples 7 and 11.

Fig. 6 shows the hardness of SiOC films with various flow rates. The hardness increases for samples 5, 9 and 13 which shows the blue shift as shown in Fig. 1(b). The blue shift depends on an increase of the C-O bond content which supports the hardness, because the Si-O bonding strength is stronger than the Si-C bond in the SiOC films.

Fig. 7 shows the dielectric constant of SiOC films which

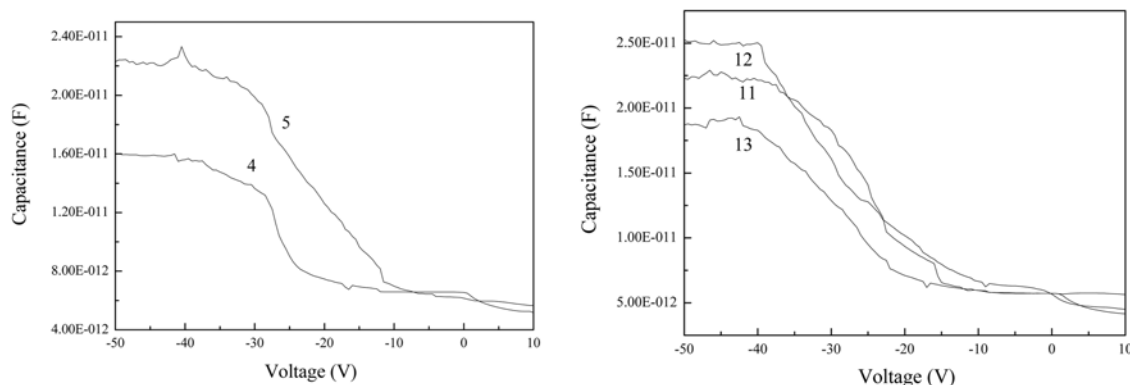


Fig. 8. Contribution of ionic polarization of SiOC film with various dielectric constants, (a) Capacitance of samples 4 and 5, (b) Capacitance of samples 11, 12 and 13.

the MIS (Al/SiOC film/Si substrate) structure from the C-V measurement system. The dielectric constant decreases for samples 4, 9 and 13 having a low thickness and the blue shift. The lowest dielectric constant is 2.9 for sample 9. It is inferred that the dielectric constant directly decreases depending on the thickness. The C-O bond attacked by a Si atom can easily make a Si-O-C cross-linked structure with a low surface energy because of the electron deficient group owing to the weak π bond.

Fig. 8 displays the capacitance of samples 4 and 12 with a low dielectric constant. The capacitance is closely related to the dielectric constant using a MIS structure, and the capacitances of samples 4 and 13 are also lower than that of any other samples. The dielectric constant is related to the polarity which consists of dipole, ionic and electronic polarization. The dielectric constant of SiOC films is generally made up of ionic and electronic polarization without a dipole moment because of it is a low dielectric constant material which is an insulator.

Conclusions

SiOC films were prepared with various flow rates by inductive coupled plasma chemical vapor deposition. The blue shift in the main bond was strongly related to the reduction of the dielectric constant and thickness. The dielectric constant decreased from a sample with a low thickness by lowering the polarization. The blue shift was caused by increasing the intensity of the Si-O bond at the right shoulder in the main bond which contributes to a reduction of the carbon content. The decrease of the carbon content induced the increase of the hardness and a cross linked structure in the final film. Increasing the thickness was due to the formation of nano pores by the steric hindrance at the terminal bond, therefore its hardness

was decreased because of these voids. The pores resulted from the space charge effect were made by the increment of ionic polarization such as by the alkyl groups which therefore increased the thickness by producing the voids.

References

1. Y.L. Hsu, Y.K. Fang, Y.T. Chiang, T.H. Chou and F.C.N Hong, *Jpn. J. Appl. Phys.* 46 (2007) 530-535.
2. Z.Q. Fang, B. Claflin, D.C. Look and G. C. Farlow, *Journal of Electronic Materials*, 36 (2007) 307-311.
3. M.S. Kim, J.H. Kim and E.K. Kim, *Journal of the Korean Physical Society*, 48 (2006) 1552-1555.
4. P. de Rouffignac, Z. Li and R.G. Gordon, *Electrochemical and Solid State Letters*, 7, (2004) G360-G368.
5. Z.X. Yang, N.R. Ha, M.S. Jang, K.H. Hwang and J.K. Lee, *J. Ceram. Proc. Res.*, 10[3] (2009) 266-268.
6. J. Heo, H.J. Kim, J.H. Han and J.W. Shon, *Thin Solid Films*, 515 (2007) 5035-5039.
7. K.W. Nam, S.H. Park and J.S. Kim, *J. Ceram. Proc. Res.*, 10[4] (2009) 497-501.
8. J. Widodo, W. Lu, S.G. Mhaisalkar, L.C. Hsia, P.Y. Tan, L. Shen and K.Y. Zeng, *Thin Solid Films*, 462-463 (2004) 213-218.
9. M.K. Mazumder, R. Moriyama, D. watanabe, C. Kimura, H. Aoki and T. Sugino, *Jpn. J. Appl. Phys.*, 46 (2007) 2006-2010.
10. P. Jakob and B.N.J. Persson, *Journal of Chemical Physics*, 109 (1998) 8641-8651.
11. M. Damayanti, J. Widodo, T. Sritharan, S.G. Mhaisalkar, W. Lu, Z.H. Gan, K.Y. Zeng and L.C. Hsia, *Materials Science and Engineering B*, 121 (2005) 193-194.
12. T. Oh, *IEEE Trans. Nanotechnology*, 5 (2006) 23-29.
13. R. Navamathavan and C.K. Choi, *Journal of the Korean Physical Society*, 48 (2006) 1675-1679.
14. T. Oh, *Jpn. J. Appl. Phys.* 44 (2005) 4103-4107.
15. A. Grill and D.A. Neumayer, *J. Appl. Phys.* 94 (2003) 6697-6707.