

## Correlation between Hardness and Chemical Shift of SiOC Film by FTIR and XRD Analysis

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### **Abstract**

*SiOC films prepared by the capacitively coupled plasma chemical vapor deposition were analyzed by Fourier Transform Infrared spectroscopy, nanoindentation, capacitance and Xray diffraction patterns to observe the crystallinity and chemical shift of SiOC. The capacitance decreased after annealing process, and the dielectric constant was also decreased by annealing due to the reduction of polarization. In the SiOC annealed at 500 °C, the blue shift in the range of 950~1200 cm<sup>-1</sup> by FTIR analysis showed the peak of 33° in XRD pattern, which indicates the improvement of crystallinity. Moreover, the SiOC with the peak of 33° in XRD pattern increased the hardness. Red shift was due to the weak bonding strength and then decreased the hardness in SiOC film. SiOC film with red shift does not involve the peak of 33° in XRD pattern. In 32,34 and 36 samples with red shifts, the sample 34 was the lowest dielectric constant, because of high quality of amorphous as non-polarity.*

**Keywords:** *SiOC film, Chemical shift, Hardness, FTIR, XRD pattern*

### **1. Introduction**

Recently, amorphous oxide semiconductor has been attracted because of flexible and transparent conductivity. The multi-level interconnect technology has become attractive to the semiconductor industry. A silicon device minimizes and their density increases, it requires that new materials can be replaced the silicon dioxide thin film. It requires a low temperature deposition process while maintaining good material quality and electrical characteristics [1-12]. There have been many studies on the electrical performance and chemical-physical properties of transparent conductive oxide semiconductor (TCOs), such as donor doped ZnO (Zink Oxide), GZO (Gallium Zink Oxide), IZO (Indium Zink Oxide) and In<sub>2</sub>O<sub>3</sub>, which are widely used as transparent electrodes for optoelectronic application, display and solar cell. To realize high performance TCO devices, it is essential not only the formation of high quality metal electrodes but also substrate materials for TCOs [13-20]. However, the growth of TCOs thin films on Si is known to be a difficult task because of the large lattice mismatch between Si and ZnO, and the formation of amorphous SiO<sub>x</sub> layers. To obtain high quality TCO films, Si substrate surface was treated by various methods as passivations. SiOC film instead of SiO<sub>x</sub> is the low dielectric constants as insulator with amorphous structure, which can be replaced the SiO<sub>2</sub> thin film in semiconductor devices. Compared to the conventional SiO<sub>2</sub> film (k=4.0), SiOC film made by chemical vapor deposition (CVD) has been known about 2.0 as the next candidate of low dielectric constant materials [21-30]. Especially, CVD-SiOC film decreased the dielectric constant to reduce the polarization in the films during the deposition and annealing process. The properties of low polarity in SiOC film improved the chemical, physical and mechanical properties. There are many precursors such as tetraethoxysilane (TEOS),

dimethyldimethoxysilane (DMDMOS), bistrimethylsilylmethane (BTMSM) and methyltrimethoxysilane (MTMS) for SiOC film deposited by the chemical vapor deposition (CVD). The decrease of the dielectric constant in SiOC film originates from the nano pores formed in SiOC film by the repulsive force of alkyl group or low polarization due to the C-H terminal bond. Recently, low density SiOC film due to the low polarization has been attracted because of good mechanical and thermal stability. SiOC film with pores has serious problems such as poor hardness and adhesion, in spite of low dielectric constant. Low polarization is essential to low-k materials, which become the amorphous structure to a great degree because of the reduction of the electron density that resulted from the C-H bond elongation effect and the carbon insertion in Si-O network [30-43].

In this study, SiOC films deposited with various flow ratios prepared with BTMSM and oxygen as precursor were analyzed by the Fourier Transform Infrared Spectroscopy and XRD. SiOC films were investigated the dielectric constant using the C-V measurement system to reveal the amorphous structure and the relationship between the dielectric constant and the polarization. To observe the effect of annealing process, SiOC was annealed at from 300 to 500 °C in a vacuum for 30 min, the trend of the hardness and capacitance was researched.

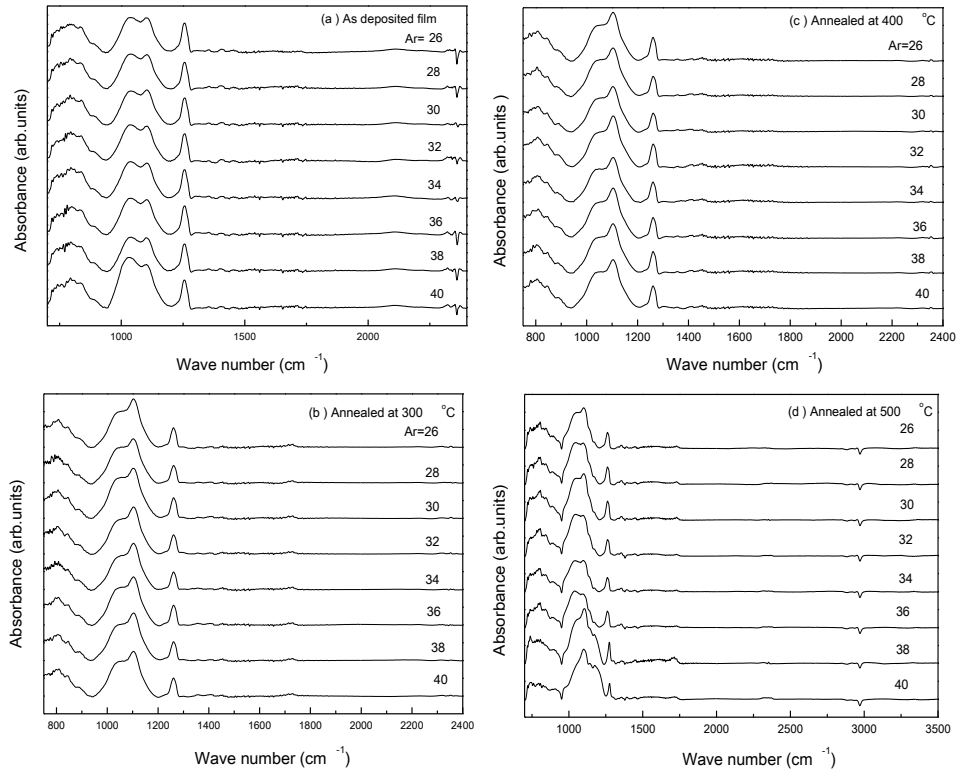
## 2. Experiment Method

The SiOC films were obtained using the mixed gases of oxygen and bistrimethyl silylmethane (BTMSM) by capacitively coupled plasma chemical vapor deposition (CCP-CVD). The precursor of bistrimethyl silylmethane was purchased from the Applied Materials Corporation. The deposition condition was the substrate temperature at 100 °C for 10 sec. The BTMSM was vaporized and carried by argon gas at 35 °C from a thermostatic bubbler. The carbon doped silicon oxide films were prepared by various flow rate ratios of BTMSM precursors, but the oxygen gas flow rate was 60 sccm. Then the samples were named 26~40 owing to the BTMSM flow rates. The base pressure was 3 Torr and the rf power was 450 W in each experiment. The films were processed at annealing temperature at 300~500 °C for 30 minute at various BTMSM flow rate ratios. To research the surface's properties of SiOC film, SiOC film was researched by Fourier Transform Infrared spectrometer (FTIR, Galaxy 7020A). For the analysis of electric properties, the aluminum was evaporated using the mask pattern on the surface of the specimen, where the sputter-deposited aluminum with an area of  $(0.1/2)^2 \times \pi$  cm was used on the top electrode. Electrical leakage currents for the films were measured by the semiconductor parameter analyzer at 1MHz using MIS (metal/insulator/Si, Al/SiOC films/p-Si) structure. The structural characteristic of SiOC film was investigated by X-ray diffractometer (XDS 2000) at Chungbuk national university. To research the surface properties of SiOC film with various flow rates, the spectra of SiOC film were obtained by using a Fourier Transform Infrared spectrometer (FTIR, Galaxy 7020A), and the hardness was measured nano-indentation.

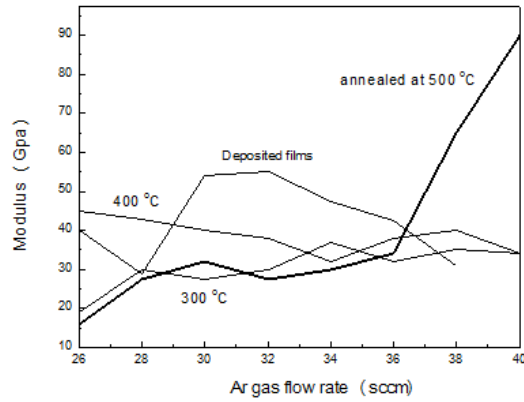
## 3. Results and Discussion

The analysis by Fourier Transform Infrared spectrometer is useful to define the structure due to the bonding strength in carbon based materials. Characteristic of SiOC film was defined by the decreasing of polarization between OH and CH groups as different polarity. Therefore, the non-polar properties of SiOC film were easily observed by FTIR. Figure 1 is the FTIR spectra of SiOC film with Ar gas flow rate of

26 sccm to 40 sccm. There is the Si-CH<sub>3</sub> at 1260 cm<sup>-1</sup>, the main bond of 950~1200 cm<sup>-1</sup> and the Si-O-C bond below 950 cm<sup>-1</sup>. The main bond of 950~1200 cm<sup>-1</sup> consists of two bonds such as left shoulder Si-C and right shoulder Si-O bonding. The bond of Si-O-C at 950~1200 cm<sup>-1</sup> in Figure 1 showed the chemical shift with increasing the Ar (BTMSM) flow rate ratios depending on polarity such as alkyl or hydroxyl group. The shoulder Si-O bond increased with increasing annealing temperature at 300 and 400 °C, but 32, 34 and 36 samples as SiOC annealed at 500 °C were observed the decreased Si-O bonds. Moreover, the intensity of Si-CH<sub>3</sub> at 1260 cm<sup>-1</sup> was decreased with increasing the right shoulder Si-O. High electro-negative oxygen atoms attack the Si-CH<sub>3</sub> at 1260 cm<sup>-1</sup> and then weaken the bonding strength of Si-CH<sub>3</sub> as well as the right shoulder Si-O bond. Annealed SiOC at 500 °C in Figure 1 (d) is the chemical shift in the main bond of 950~1200 cm<sup>-1</sup>. Increment of left shoulder Si-C induces the red shift in FTIR analysis and changing to low wave number. The elongation effect of bonding length between atoms and terminal groups was shown in the red shift and improved an amorphous structure in SiOC film.



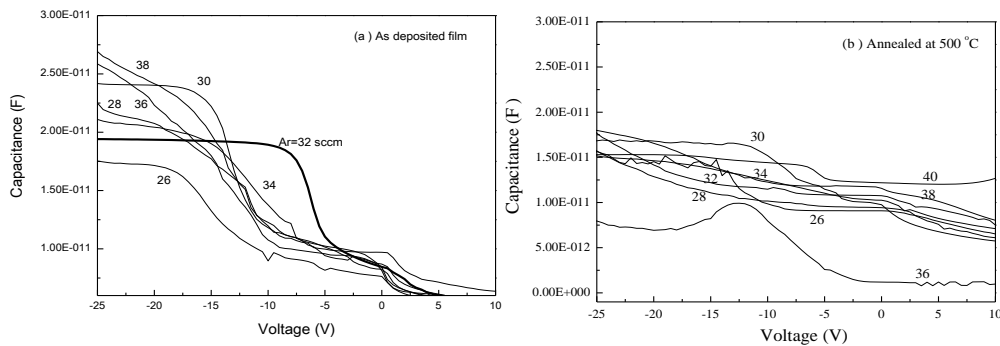
**Figure 1. Fourier Transform Infrared Spectroscopy of SiOC Film with various Ar Gas Flow Rates, (a) SiOC as Deposited Films, (b) Annealed at 300 °C, (c) Annealed at 400 °C, (d) Annealed at 500 °C**



**Figure 2. Modulus of SiOC film with various Ar gas flow rates and annealing temperatures**

On the other hand, the increment of right shoulder Si-O bonding induced the low grade amorphous SiOC due to the effect of polarity, which enhances the crystallinity in the thin films.

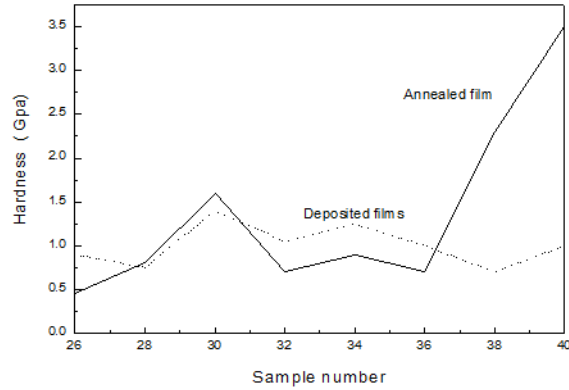
Figure 2 is the modulus of SiOC film deposited with various Ar gas flow rates and annealing temperatures. As deposited samples of 30, 32 and 34 showed the increasing of modulus, but the modulus decreased after annealing process because of increasing the degree of amorphism and decreasing of the thickness after annealing. The lowest modulus was the sample 30 at annealed at 300 °C, sample 34 at annealed at 400 °C and sample 32 at annealed 500 °C. The effects of polar decrease due to the nucleophilic chemical reaction between oxygen atoms and alkyl site in the precursor at samples of 30, 32 and 34 can be observed by the capacitance change after annealing process as shown in Figure 3.



**Figure 3. Capacitance of SiOC films, (a) as-deposited films, (b) annealed films at 500 °C**

Figure 3 is the capacitance of SiOC film. The capacitance of annealed films decreased in comparison with the as-deposited films. Especially, the saturation mode of the 32 sample as the lowest polarity in the C-V curve showed closer at voltage than other samples. The

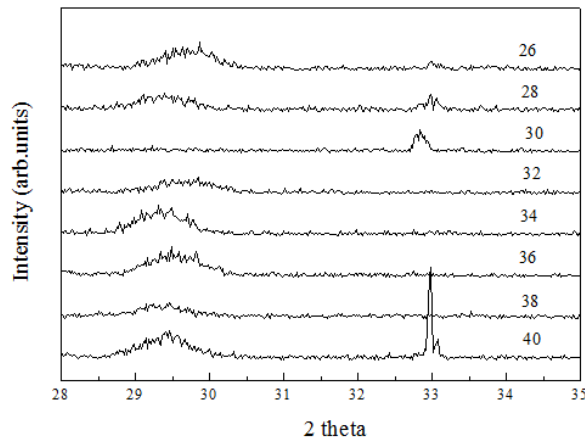
dielectric constant was calculate by the equation of  $\epsilon = \frac{Cd}{A}$  , where C, d and A is the capacitance, thickness and areas. Therefore, the decrease of capacitance and thickness



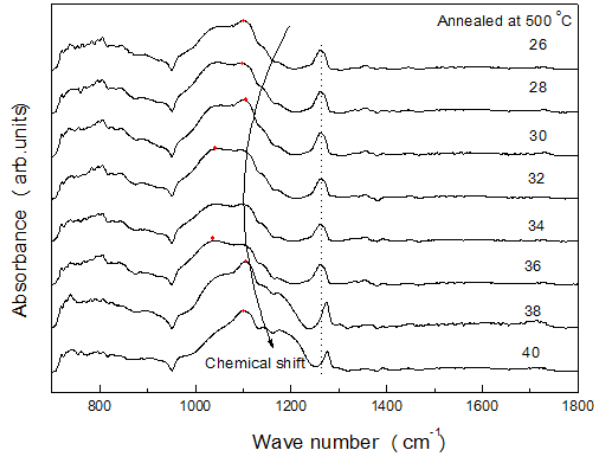
**Figure 4. Hardness of SiOC Film as a Function of Ar Gas Flow Rates**

as the results of annealing induces the dielectric constant. It could be confirmed that the low polarity of SiOC film was due to the effect of annealing as well as the nucleophilic reaction during the deposition. Moreover, the reduction of thickness and capacitance enhanced the amorphous in SiOC film.

Figure 4 is the hardness of SiOC with various Ar gas flow rates and annealing at 500 °C. Sample 32 was low hardness, because of increase of amorphism and decrease of crystallinity. The high degree of amorphism and the low dielectric constant is closely related to low polarity. The degree of amorphism of SiOC and crystallinity was shown in Figure 5.



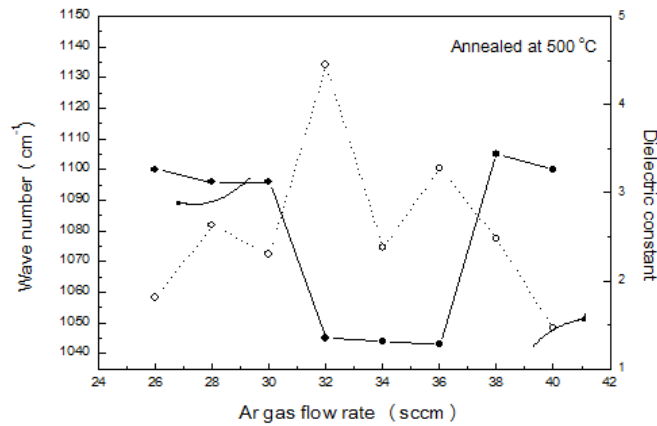
**Figure 5. XRD Patterns of SiOC Film after Annealing at 500 °C**



**Figure 6. Red Shift of 30, 32 and 34 Samples and the others with Blue Shift**

Figure 5 is the XRD patterns of SiOC film. There are weak peaks with  $29^{\circ}\sim 30^{\circ}$  and  $33^{\circ}$ , which was related to the degree of amorphous structure. Peak of  $33^{\circ}$  as increasing the crystallinity existed in SiOC films with polarity such as samples of Ar=26, 28, 30 and 40 sccm. These results indicate that the bonding structure of SiOC film is various types according to the Ar and oxygen mixed gas flow rates. Polar sites could increase the crystallinity and increased the hardness as shown in Figure 4.

The blue shift was due to the polar sites such as alkyl or hydroxyl group, and these sites enhanced the crystallinity in SiOC formation. Oxygen vacancy in oxide semiconductor controlled the electrical characteristic in TFT, and improved the high mobility performance of devices. On the contrary, SiOC film with non-polarity of Ar=32, 34 and 36 sccm decreased the hardness and became an amorphous structure. Hardness of SiOC film due to the red shift decreased because of weak bonding structure between atoms as shown in Figure 1(d).



**Figure 7. Dielectric Constant and Chemical Shift of Main Bond with 950~1200 cm<sup>-1</sup> as a Function of Gas Flow Rates**

Figure 6 indicated the chemical shift in FTIR spectra of annealed SiOC. 32, 34 and 36 samples were the red shift and the others were the blue shift owing to the Si-O right shoulder increasing. The increase of Si-C left shoulder bonding and reduction of Si-O bonding by the

oxygen attack to the Si-CH<sub>3</sub> at 1260 cm<sup>-1</sup> caused the red shift. The blue shift depended on the strong Si-CH<sub>3</sub> at 1260 cm<sup>-1</sup> or Si-O at 1120 cm<sup>-1</sup> as polar sites. The Si-CH<sub>3</sub> at 1260 cm<sup>-1</sup> as the increase of Ar gas flow rate moved to higher wave number and the Si-O at 1120 cm<sup>-1</sup> increased the intensity as decrease the Ar gas flow rate.

Figure 7 was the dielectric constant and the chemical shift in SiOC film with various Ar gas flow rates. In the 32, 34 and 36 samples with the red shift, the sample 34 was the lowest dielectric constant 2.4. In spite of low dielectric constant, samples with blue shift has the problem as leakage current due to the polarity. Therefore, high degree of amorphous SiOC film due to the red shift will be good for the interlayer dielectric materials.

#### 4. Conclusion

SiOC film was prepared by capacitively coupled plasma chemical vapor deposition. SiOC by FTIR analysis showed the chemical shift according to the polarity. The red shift was due to the elongation of bonding length between atoms and lowering the polarity. However, the blue shift originated from the condensation effect between atoms and reduction of the bonding length. Therefore, SiOC with red shift became the high degree amorphous structure and obtained the lowest dielectric constant 2.4. The high degree of amorphous SiOC film with the red shift does not involve the peak of 33°. The blue shift in SiOC originated from the polar site and then increased the hardness. The capacitance and thickness decreased after annealing process and then also decreased the dielectric constant of SiOC. The degree of amorphism was decreased after annealing, because of the decrease of polarity. Moreover, the reduction of hardness at SiOC with red shift was good to serve the flexible substrate due to the high degree of amorphism.

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