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ICPCVD방법으로 만든 Organosilicate 박막의 Organic 특성에서의 유전상수

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Dielectric Constant at Organosilicate Films with Organic Properties by ICPCVD

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ABSTRACT

Organosilicate films have three properties such as organic, hybrid and inorganic according to the flow rate ratio between oxygen and Bis-trimethylsilymethane(BTMSM, H9C3-Si-CH2-Si-C3H9) precursor. The films with organic properties decreased the dielectric constant because of the pore in final materials. In this study, it was researched the porosity of organosilicate films with organic properties from Bruggeman effective medium approximat-ion model. The porosity of this films is due to the rich alkyl group, and increasing the porosity decreased the dielectric constant of the film.

Key Words : Organosilicate films, Porosity, Cross link breakdowb, Low-k, Organic properties

Ⅰ. INTRODUCTION

Low-k materials are needed in ultra-large-scale integration(ULSI) device performance, because they reduce signal propagation delay time, and cross-talk noise.

Many researchers have proposed various low-k materials[1~5]. Recent research efforts have focused on the preparation of porous materials. The dielectric candidates have been examined by spin-on or CVD. Organosilicate films as non-polar organic polymers have the lower dielectric constant due to the presence of lighter C and H atoms vs. Si and O. The properties of organosilicate films using BTMSM precursor are divided into three properties, organic, hybrid, and inorganic[6]. It is known that the dielectric constant of the porous materials reduces by porosity and decreasing polarizability. In the case of organosilicate films with organic properties, the corporation of non-polar and space-occupying groups such as a R group increase free volume in a silicate network.

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Optimized loading of R groups in a silicate network makes pores by steric force and electrostatic force. The result is a reduction in dielectric constant of organosilicate films. In this paper, the origin of low dielectric constant in organosilicate films with organic properties analyzes by the Bruggeman effective medium approximation(EMA) model. The porosity was predicted approximately using the Bruggemans EMA model. The porosity was in proportion to the relative carbon concentration. The relative carbon concentration of organosilicate films deposited with O_2/BTMSM($[(CH_3)_3Si]_2CH_2$) was examined from deconvolution of samples spectra by Fourier transform infrared spectroscopy(FTIR). Organosilicate films increased the relative carbon concentration after annealing and than decreased the dielectric constant.

II. EXPERIMENTS

The Si-O-C composite films were deposited on the p-type Si(100) substrate by ICPCVD with rf power at 13.56MHz. The precursor mixed with BTMSM and O_2 was used. The flow rate ratio of O_2:BTMSM(Ar) was 10:10 sccm. THe carrier argon gas was 10 sccm, and O_2 was also 10 sccm. The deposition temperature was room temperature, and the post annealing was done at 300℃ and 500℃ for 30minutes in vacuum. The BTMSM is vaporized and carried by inert argon gas with a thermostatic bubbler(maintained at 40℃ to the reaction chamber). To prevent recondensation of BTMSM, all of the gas delivery lines were heated and kept at a constant temperature of 40℃. High density plasma of about 1012cm-3 was obtained at low pressure with rf power of about 300W in ICPCVD, and the working pressure of ~10-5 Torr was reached before each experiment. The inductively coupled plasma was generated by means of a three turns coil, which was set around a quartz tube. The depoistion depends on the parameters such as the flow rate of O_2/BTMSM, the rf power and the working pressure. The FTIR spectra of samples were deconvoluted and researched the relative carbon concentration after annealing. The dielectric constant of the films was measured using the MIS(Al/Si-O-C film/p-Si) structure.

III. RESULTS AND DISCUSSION

The dielectric constant of the films was shown in Fig. 1.

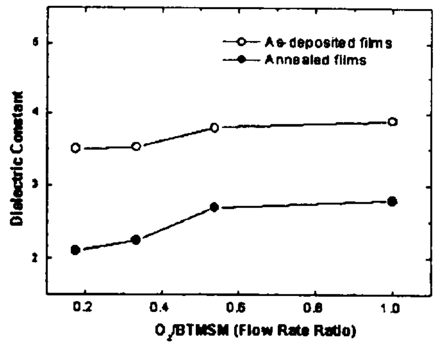


Fig. 1. The dielectric constant.

Figure 2 shows the FTIR spectra of as-deposited films. The FTIR survey-scan spectra of the annealed films were similar to that of as-deposited films.

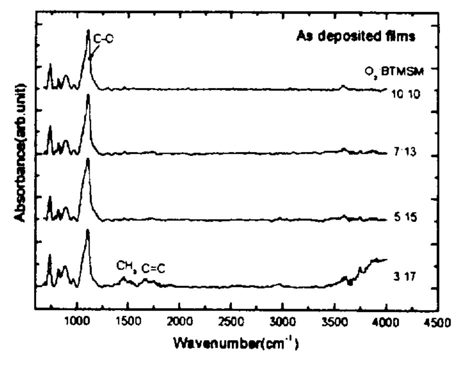


Fig. 2. The FTIR spectra of as-deposited films.

It is known that Si-O asymmetric stretching vibration mode is broad from the peak at 950cm^{-1} to the peak at 1350cm^{-1}, and Si-CH_3 peak at 1270cm^{-1} appears. But in the case of organosilicate films with organic properties, Si-CH_3 peak at 1270cm^{-1} does not appear and C-O asymmetric stretching vibration mode becomes narrow from the peak at 1000cm-1 to the peak at 1250cm^{-1}[6-8]. In the figure 3, organo- silicate films with organic properteis show the C-O stretching vibration mode from the peak at 1000cm^{-1} to the peak at 1250cm^{-1}. The FTIR spectra of as-deposited films enlarged partly to confirm the range of main peak actually. The FTIR spectra of samples were deconvoluted and researched the relative carbon concentration after annealing. Figure 4 shows the relative carbon concentration in as-deposited films and annealed films. The relative carbon concentration of C-O data of deconvoluted data is much than that of O-C-O data.

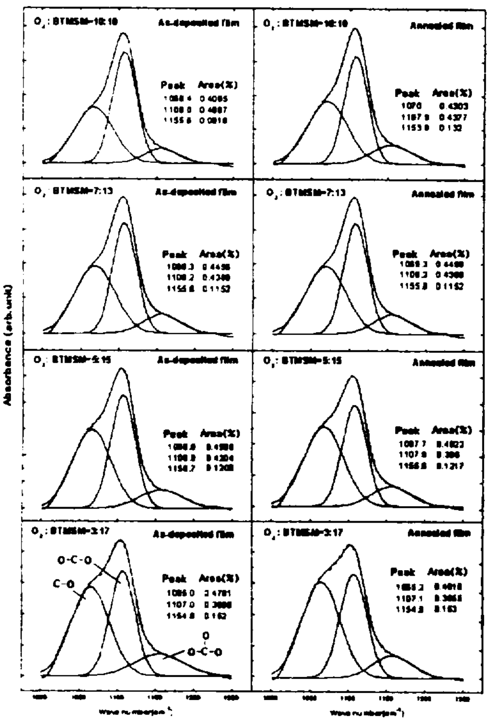


Fig. 3. FTIR spectra from 1000cm^{-1} to 1250cm^{-1}.

The relative carbon concentration of C-O data in as-deposited films increased after post annealing processor, and decreased according to increase the flow rate ratio O_2/BTMSM.

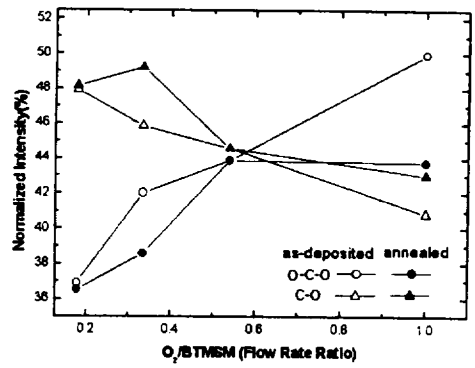
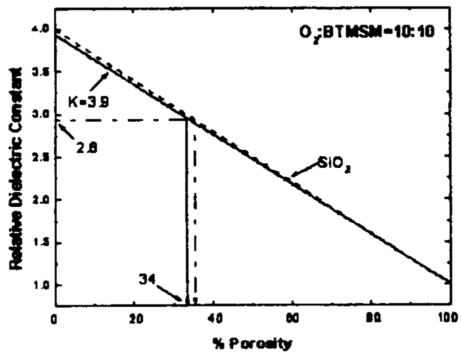


Fig. 4. The relative carbon concentration.

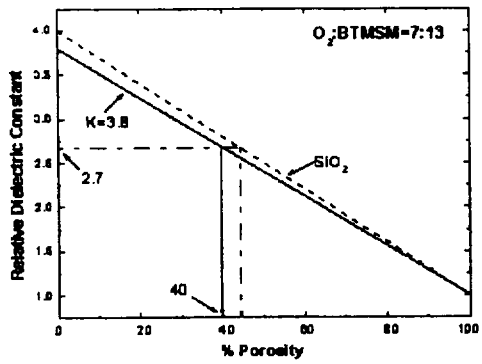
These results are the same as the Fig. 1 and Fig. 2, therefore, the dielectric constant of organosilicate films decrease according to increase the carbon concentration in the films with organic properties. The dielectric constant of the films is concerned about the density of the films, and the density of the films is a function of the porosity. The effect of porosity on dielectric constant can be predicted using the Bruggemans EMA model such as equation(1).

$$f_1 \times \frac{k_1 + k_e}{k_1 + 2k_e} + f_2 \times \frac{k_2 + k_e}{k_2 + 2k_e} = 0 \qquad (1)$$

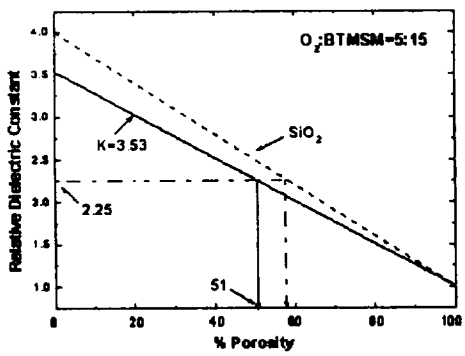
Where f1,2 represents the fraction of the two components, k1,2 the dielectric constant of the components, and ke the materials effective k. The simple EMA model assumes two components such as the solid wall material and voids. Thermal conductivity decreases with increasing porosity as the propagation of thermal energy flow through the films are interrupted by the nano pores. Fig. 5 shows the relative porosity calculated from the results of the dielectric constant using the EMA model.The relative porosity of annealed films decreases with increasing the O2/BTMSM flow rate ratio.



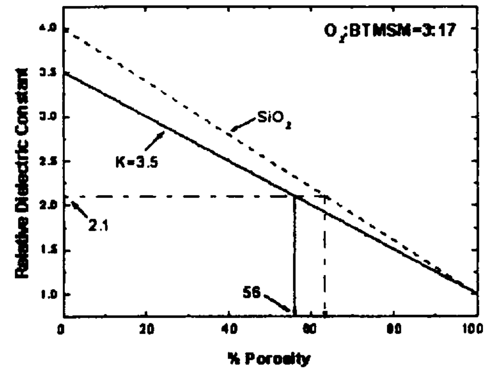
(a) Annealed film with O2:BTMSM=10:10,



(b) Annealed film with O2:BTMSM=7:13,



(c) Annealed film with O_2:BTMSM=5:15,



(d) Annealed film with O2:BTMSM=3:17,

Fig. 5. The r더ative porosity by the EMA model.

The relative porosity of films with O2/BTMSM flow rate ratio as 0.17, 0.33, 0.53 and 1.0 are 56%, 51%, 40% and 34%, respectively. These results are simply explained at the Fig. 6.

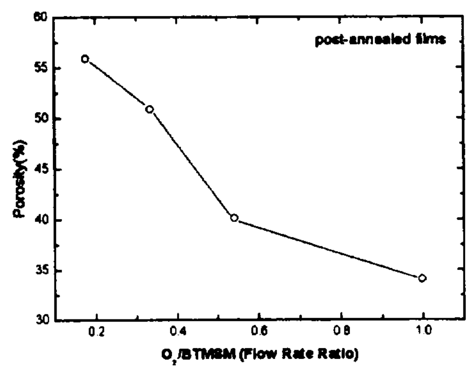


Fig.6. The porosity of the post annealed films.

Consequently, organosilicate films with high carbon concentration obtain high porosity, and then decrease the dielectric constant. The C-O data of Fig. 3 has directly influence on the porosity, and the porosity and C-O data are proportion to each other. The dielectric constant in organic inorganic hybrid type silicate materials such as organosilicate films depends the porosity and low ionic polarizability. The effect of the porosity is due to the electron-releasing group and the effect of low ionic polarizability is due to the electron-withdrawing group. The origin of the electron-releasing group and the electorn withdrawing group are very different, therefore the bonding structure of the organosilicate film due to these groups is also different like as cross -link structure and cross-link breakdown structure[6]. In the range of the flow rate ratio O_2/BTMSM=1, organosilicate films have organic properties because of the electron rich of the electron-releasing group in C-H hydrogen-bonded system. Therefore the films can have porosity, and the increasing the porosity decreased the dielectric constant of the films. It is confirmed by FIIR analysis that organosilicate films with pores increase the relative carbon concentration according to decreasing the dielectric constant. Porosity of organosilicate films with organic properties by the analysis method of EMA model decreased according to change the flow rate ratio O_2/BTMSM.

IV. Conclusion

Organosilicate films deposited using O2/BTMSM precursor by ICPCD. The porosity of organosilicate films with organic properties were investigated by FTIR and EMA model. The relative high carbon concentration reduced the dielectric constant. Increasing the porosity of organosilicate films with organic properties decreased the dielectric constant. The FTIR main peak of organosilicate films with organic properties is C-O asymmetric stretching vibration mode from the peak at 1000cm^{-1} to the peak at 1250cm^{-1}. C-O deconvoluted data is directly concerned with the porosity in organosilicate films.

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