Chemical structure evolution of low dielectric constant SiOCH films during plasma enhanced plasma chemical vapor deposition and post-annealing procedures

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Abstract Si-O-C-H films with a low dielectric constant were deposited on a p-type Si(100) substrate using a mixture gases of the bis-trimethylsilyl-methane (BTMSM) and oxygen by an inductively coupled plasma chemical vapor deposition (ICPCVD). High density plasma of about $\sim 10^{12}$ cm^{-3} is obtained at low pressure (<400 mTorr) with rf power of about 300W in ICPCVD where the BTMSM and O_2 gases are fully dissociated. Fourier transform infrared (FTIR) spectra and X-ray photoelectron spectroscopy (XPS) spectra show that the film has Si-CH_3 and OH-related bonds. The void within films is formed due to Si-CH_3 and OH-related bonds after annealing at 500°C for the as-deposition samples. The lowest relative dielectric constant of annealed film at 500 °C is about 2.1.

Ⅰ. Introduction

For the miniaturization of electronic circuits, many kinds of works are being taken including a search for new inter-metal dielectric (IMD) material with low dielectric constant and the optimizing of the formation condition. Present silicon dioxide (SiO_2) films as IMD layers will result in high parasitic capacitance and cross-talk interference in the high-density devices. Recently, many researchers have tried various organic or inorganic materials as an alternative to SiO_2[1~4]. Low dielectric materials used in ultra-large-scale integrated (ULSI) circuits should have a high thermal and mechanical stability up to 450°C and be compatible with the manufacturing processes of various micro-electronic parts including the etching, striping cleaning, and polishing. Silicon oxide-based low dielectric material containing alkyl groups have been attracted much attention for their higher thermal and mechanical stability than many organic materials. The spatial hindrance of alkyl groups will produce abundant nano-voids in film and decrease the dielectric constant[8, 9]. In the present work, the Si-O-C-H films with a low dielectric constant are deposited by an inductively coupled plasma chemical vapor deposition (ICPCVD) using a bis-trimethylsilyl-methane (BTMSM, H_9C_3-Si-CH_2-Si-C_3H_9) and an oxygen mixture gases [7]. In this study, the film properties at different deposition condition and before and after annealing will be presented, also we will discuss the chemical bonding structure of those films. Electrical properties such as the dielectric constant and refractive index were also investigated and discussed in terms of advantages for the film.

II. EXPERIMENTS

The Si-O-C-H films were deposited on a p-type Si(100) wafers using the mixture of BTMSM and oxygen gases and radio frequency (13.56MHz) ICPCVD system. The wafers were in a floating potential and not intentionally heated. The inductively coupled plasma was generated by means of a three turns coil, which was set around a quartz tube. A base pressure of ~a 10^{-7} Torr was reached before each deposition. The BTMSM precursor is a nontoxic, colorless liquid with a boiling point of 137 °C and 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. In this study, we have changed the BTMSM/(O_2+BTMSM) gases flow rate ratio from 25% to 85% and kept the total gas flow rate as constant of about 20 sccm. O_2 and BTMSM gases were introduced through a mass flow controller (MFC) into the reaction chamber, and the discharge pressure was measured with a Baratron gauge and kept it at about ~a 3.0 times 10^{-1} Torr. The electron density and electron temperature were measured by a fast injection Langmuire probe and calibrated by a microwave interferometer. The plasma density and the electron temperature with the RF power of a 300W were about 10^{12} cm^{-3} and 3eV, respectively. In this discharge condition, the concentration of radicals (Si, O, C, and Ar) were changed with the gas flow rate ratio, so the relationship between the relative gas flow rate ratio and film properties could be studied. To investigate characteristics of films, we carried out the post-annealing at 500°C for 30min in vacuum condition. FTIR spectroscopy, performed in absorbance mode with a model DA8 Bomem spectrometer, was used to determine the related Si-O and Si-CH_3 bonding configuration in the film. The bonding structure of the Si-O-C-H composite films was analyzed using XPS(VG Escable 200R). The thickness and the refractive index of the deposited Si-O-C-H composite films were measured by an ellipsometer. Electrical properties such as dielectric constant and leakage current density were investigated using a MIS(Al/Si-O-C-H film/p-Si) structure.

III. RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of Si-O-C-H composite films prepared with various flow rate ratios of BTMSM/(O_2+BTMSM) a mixture gases at RT. The spectra are generally broad overlapped due to the complex stoichiometry and amorphous nature of the film. The absorption of peaks at 1240 cm^{-1}, 962 cm^{-1} and 820 cm^{-1} were observed, which correspond with the Si- CH_3 symmetrical methyl deformation, and Si-CH_3 rocking mode and an end group of O-Si-CH_3 rocking mode, respectively [8-10]. The peaks at 1113 cm^{-1} and 442 cm^{-1} were the Si-O-C, and Si-O-Si asymmetrical stretching mode and rocking mode. A broad peak around 1600 cm^{-1} was came from OH absorption.

Another peak at 1680 cm^{-1} (it is more markedly for the annealed sample), it look like the stretching mode of C=O bond [11, 12]. These results show that there are not only main skeleton atomic Si-O-Si or Si-O-C groups, also there are many other groups such as OH, and C=O groups be formed in film, which deposited by plasma discharged method. From results, we know that in this film the Si atoms have Si-O, Si-C, and Si-Si states, the C atoms form C-Si, C-C/H and C-O bonds, and the O atoms form -OH, Si-O-Si, C-O-Si and O-C bond [13]. The intensity of the Si- CH_3 bond (1250 cm^{-1}) of the sample as function of BTMSM flow rate ratio is unchanged.

Figure 2 shows the FTIR spectra of the same sample as in Fig. 1 after in situ annealing at 500 °C for 30min in vacuum. In this figure, we obtained the intensity of the Si-CH_3 bond groups of the sample, with the flow rate ratio of BTMSM/(O_2+BTMSM) is similar as a deposited sample. However, the OH bond groups are not obtained. Increase the carbon content in organic siloxanes tends to lower the dielectric constant of the cured film. The Si-CH_3 bonds are reported to be more thermally stable than the Si-H bonds, and the OH-related bonds could be easily removed after post-annealing [5]. The peak become broaden is because of some C=O bond formed and add to the C-O peak for the annealing sample. The formation of voids within the film is due to Si-CH_3 and OH-related bond groups and as a result it caused low dielectric constants [4-6].

In order to investigate the Si-O-C bonding mode in the film, the deconvoluted spectra in the range from 1000 cm^{-1} to 1250 cm^{-1} is shown in Figure 3 and the peaks is resolved by Gaussian fitting. From Fig. 1, we know that the bonding near 1040 cm^{-1} is for the Si-O-Si asymmetric stretching mode, and the peaks near 1065 cm^{-1} and 1105 cm^{-1} are for Si-O-C asymmetric stretching mode in a ring link and open link, respectively [9]. The broad mode 1150 cm^{-1} is for the Si-O cage-like stretching mode [14]. The peak near 1240 cm^{-1} is best identified as for the Si-CH_3 bonding mode. Compared with the relative intensities of bonding modes in this range, the annealed samples show very little changes in the intensities for Si-CH_3 bond (1240 cm^{-1}), and the Si-C cage like bond (1153 cm^{-1}), but the intensities of Si-O-C bond (1113 cm^{-1}) in Si-O-Si open link and Si-O-Si bond (1040 cm^{-1}) decrease, and those of Si-O-C bond in Si-O-Si ring link increases simultaneously. For the other samples which have different BTMSM/(O_2+BTMSM) gas flow rate ratio, similar changes have also been found. This result means that for the Si-O-C-H composite film, the annealing at 500 °C for 30 minutes in vacuum would induce the re-arrangement of chemical bonds in the film. Some of the Si-O-Si open links will change into ring links in which the CH_3 organic groups have been attached. Because there is an aloof force between the CH_3 group and other part of Si-O-Si links, the space of void can be formed. In case of open links, the void can be filled easily by other open links. Therefore, we then infer the formation of the Si-O-C ring links by attaching CH_3 groups to the Si-O-Si ring links is good for forming the nano-size void in the film. As previously mentioned, the void formed in film can result in a low dielectric constant.

To confirm the O-Si-O, Si-C, C-H and C-O bonds in the film, the XPS narrow scan spectrum of the C 1s, and O 1s peak is deconvoluted by fitting the data with a number of Gaussian peaks, which deposited with gas flow rate of BTMSM/(O_2+BTMSM)=50 % and annealed at 500 °C for 30 minutes in vacuum ambient, are given in Fig. 4. From the spectra we know that the carbon peaks of is composed of C-Si (282.7eV), C-C/H (284.8eV), and C=O (286.8eV) bonds for both the before and after annealing sample have much more changes. After annealing, the C-Si bond intensity decrease, which shows the some of Si-CH_3 groups have been removed, which is useful for further formation the void in film. Furthermore, the intensities of the peak at 284.5eV(C-C/H) and the peak at 286.6eV(C=O) increased after annealing. The C-C bond intensity increasing can be interpreted as carbonization effect of high temperature annealing. The reason of assigning peak at 286.8eV as C=O bond in C 1s spectra is that there is a peak appeared at about 1680 cm^{-1} in FTIR spectra for the after annealing sample, which is exactly corresponding to the C=O bond absorption.

Figure 5 shows the atomic concentrations of Si-O-C-H films with as-deposited and annealed at 500 °C for 30 minutes as a function of flow rate ratio BTMSM/(O_2+BTMSM). The atomic concentration in the as deposited film nearly not changed at different gas flow rate ratio. It kept about 70at.% oxygen, 27at.% silicon, and 3at.% carbon, which the film radical ratio was of about $SiO_{2.6}C_{0.1}H_x$. After 500 °C annealing, the relative atomic concentration of O decrease, and that of Si and carbon increase, especially when the gas flow rate ratio of BTMSM/(O_2+BTMSM) was larger than 65 % concentration of O will change from 65 to 54at.%., and the concentration of C will change from 5.0 to 15at.%. At gas flow rate ratio of 85 %, the film radical rate was $SiO_{1.7}C_{0.5}H_y$. This result shows that there are some H-O groups or H_2O be remove from the film. To realize the integration scheme, we use XPS depth profile to investigate the as-deposited Si-O-C-H film, which has grown from O_2 and BTMSM with flow rates of 10 sccm and 10 sccm, respectively.

The dielectric constants and refractive indexes of as-deposited and post-annealing films at 500°C for 30 minutes with various BTMSM/(O_2+BTMSM) gas flow ratio are shown in Fig. 6. In this Fig. 6, we know that the dielectric constants of the post-annealing films, and with the flow rate ratio of BTMSM/(O_2+BTMSM) precursors increase, the dielectric constant and refractive index both is increased. In the case of O_2/BTMSM ICPCVD method, the dielectric constant decrease after annealing indicates that the water could be removed from the film without decreasing the Si-CH_3 bond by post-annealing [1]. Therefore, we assume that a rearrangement of a bond configuration in the film resulted in a void with a preexisting atomic scale nanoporosity in the film [1, 5]. This result suggested that the low BTMSM/(O_2+BTMSM) gas flow rate ratio is better for the formation of the main skeleton Si-O-Si structure which play the role of decreasing dielectric constant in Si-O-C-H film.

To investigated the effect of substrate temperature in film characters, we have deposited films with different

substrate temperature of room temperature (RT, about 25°C), 70°C and 150°C at a same gas flow rate of BTMSM/(O_2+BTMSM)=25 %. C-V test results shows that with the substrate temperature increase the calculated dielectric constant of film increase. At RT the condition, the dielectric constant is about 3.1, at 70°C and 150°C, they are about 3.7 and 3.9, respectively. This results dhow decrease the deposited temperature is easy to combine more CH_3 into the film and produce more voids in film. XPS composition analysis for those sample shows, in RT deposited film the atomic ratio of Si:C:O was 27.8% : 2.82% : 69.4%, and at 150°C, was 28.3% : 0.9% : 70.8%, this also proves that the film deposited at RT can incorporate more Si-CH_3 groups into film.

We also have investigated relative dielectric constant of as-deposited sample and annealed sample. After annealing, dielectric constant were decreased from 3.6 to 2.1.

IV. Conclusion

Low k Si-O-C-H films were deposited by RF (13.56MHz) ICPCVD system with a BTMSM precursor and oxygen mixture gases. BTMSM is vaporized and carried by inert argon gas from a thermostatic bubbler (maintained at 40°C) to the reaction chamber. The BTMSM/(O_2+BTMSM) gases flow rate ratio change as 25%, 50%, 65%, 75%, and 85% so as to keep the total gas rate constant at about 20sccm. The chamber base pressure and work pressure were about ~3.0 $\times 10^{-1}$ Torr, respectively. The film compositions deposited is about 27 at.% Si, 70 at.% O and 3 at.% C, after annealing C concentration will increase and O will decrease. Carbon bond in Si-O-C-H film has C=O bond except C-H, C-C, Si-C and C-O bonds. Suitable low gas flow rate ratio and low substrate temperature is good for lowing the dielectric constant. The void within films is formed due to Si-CH_3 and OH-related bonds for post annealing at 500°C. The relative dielectric constant of annealed film at 500°C is about 2.1.

Acknowledgements

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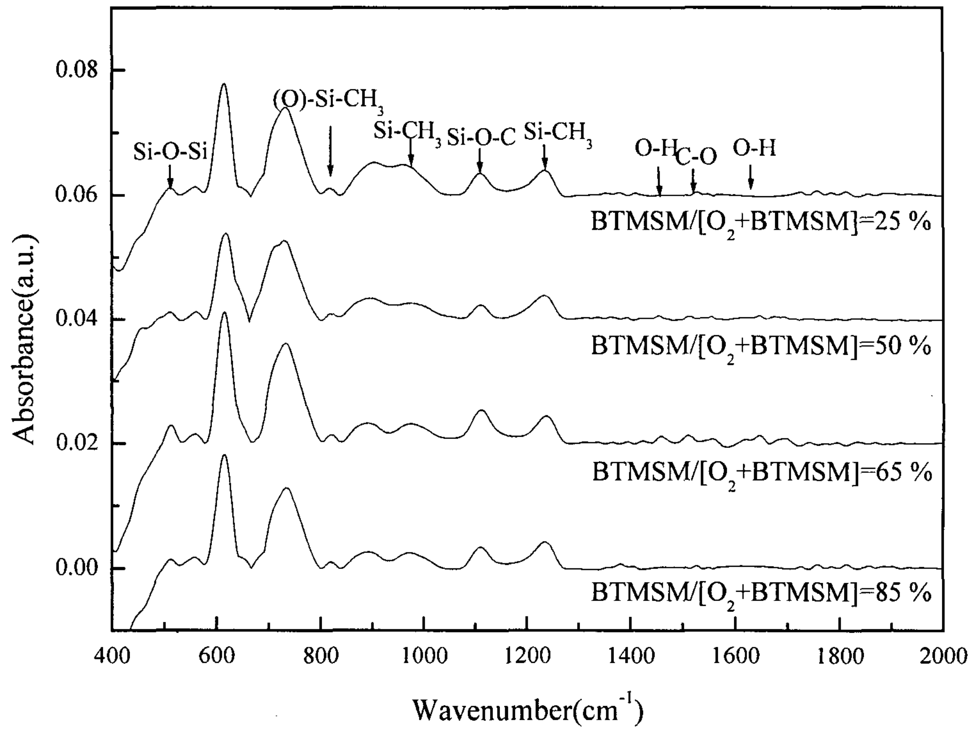


Fig. 1. FTIR spectrum of the Si-O-C-H films prepared with different BTMSM/(O_2+BTMSM) ratios as from 23% to 85% at RT. The discharge conditions are P_w = 200 mTorr, $P_{r.f.}$ = 300 W. Electron density is 2.0×10^{12} cm^{-3}.

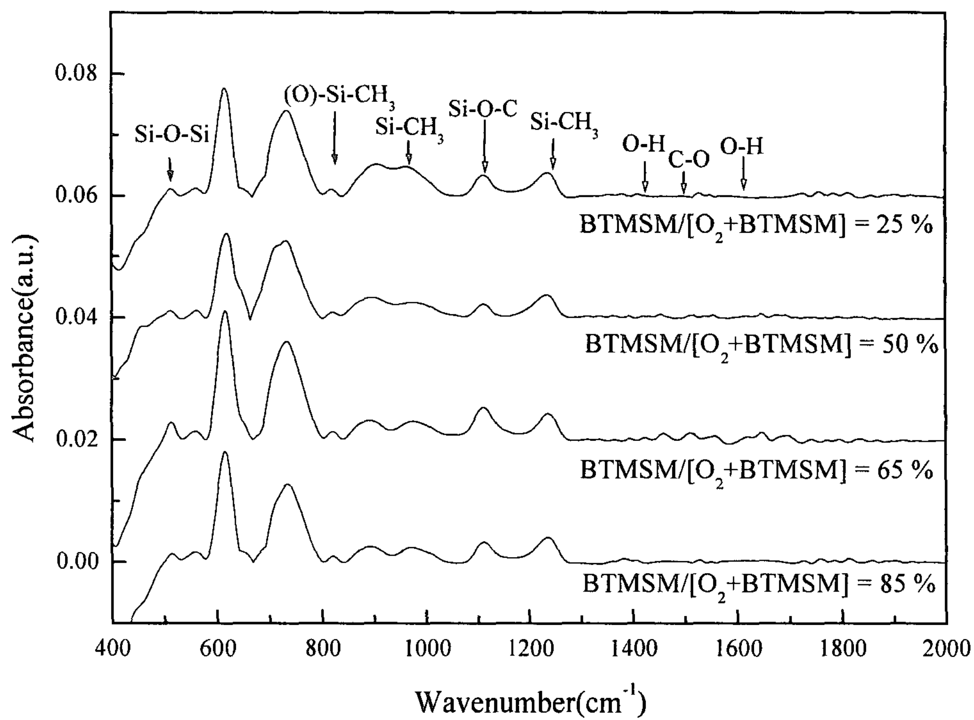


Fig. 2. FTIR spectra of the annealed samples at 500°C for 30 min.

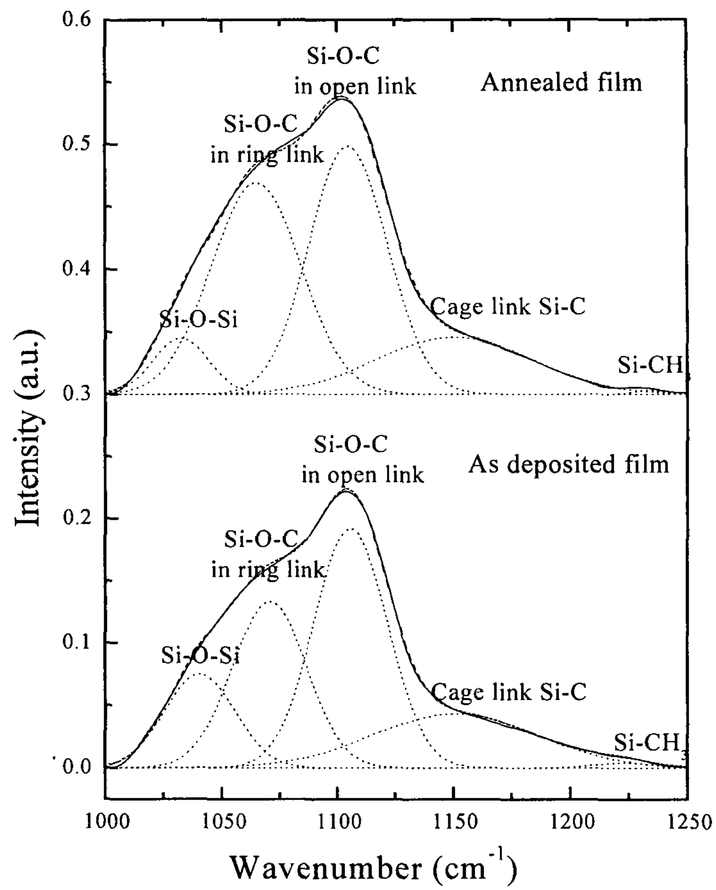
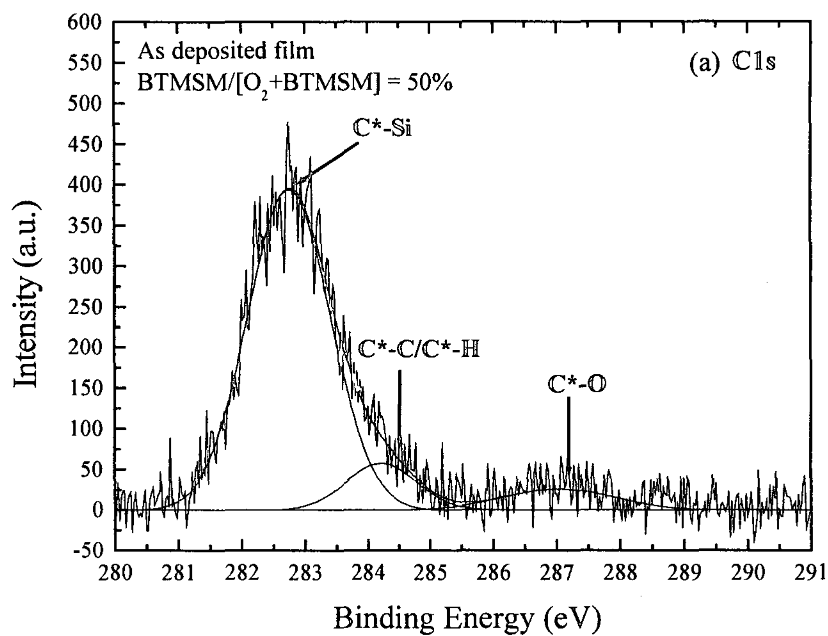
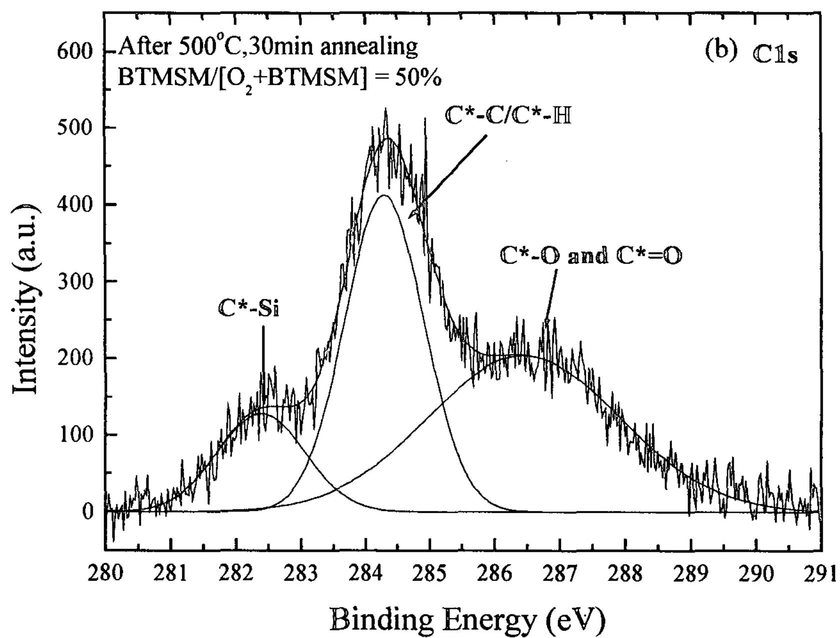
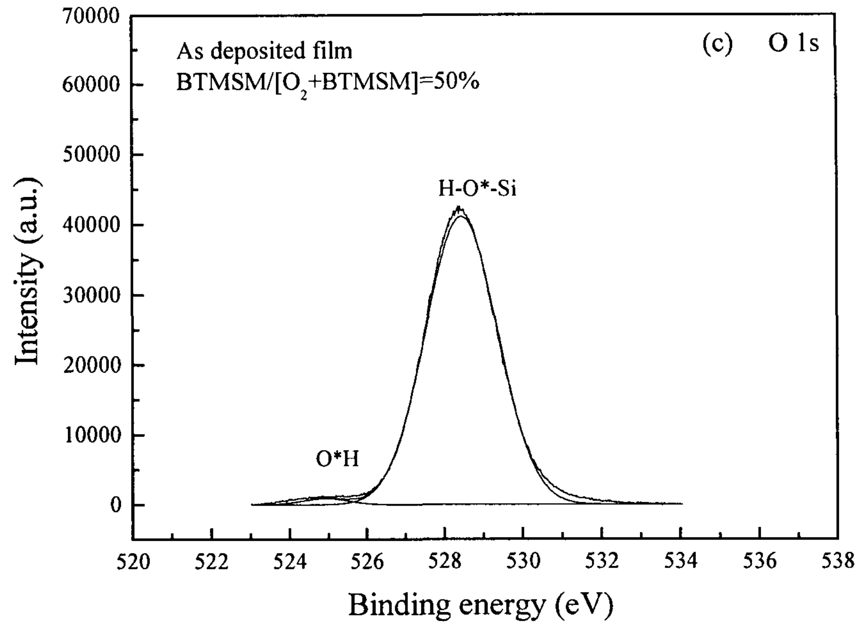


Fig. 3. The deconvoluted spectra of Si-O-C bonding mode in the wave number range from 1000 cm^{-1} to 1250 cm^{-1} of the same sample as in Fig.1.


As deposited film
BTMSM/[O2+BTMSM] = 50%
(a) C1s
C*-Si
C*-C/C*-H
C*-O
Intensity (a.u.)
Binding Energy (eV)


After 500°C,30min annealing
BTMSM/[O2+BTMSM] = 50%
(b) C1s
C*-C/C*-H
C*-O and C*=O
C*-Si
Intensity (a.u.)
Binding Energy (eV)



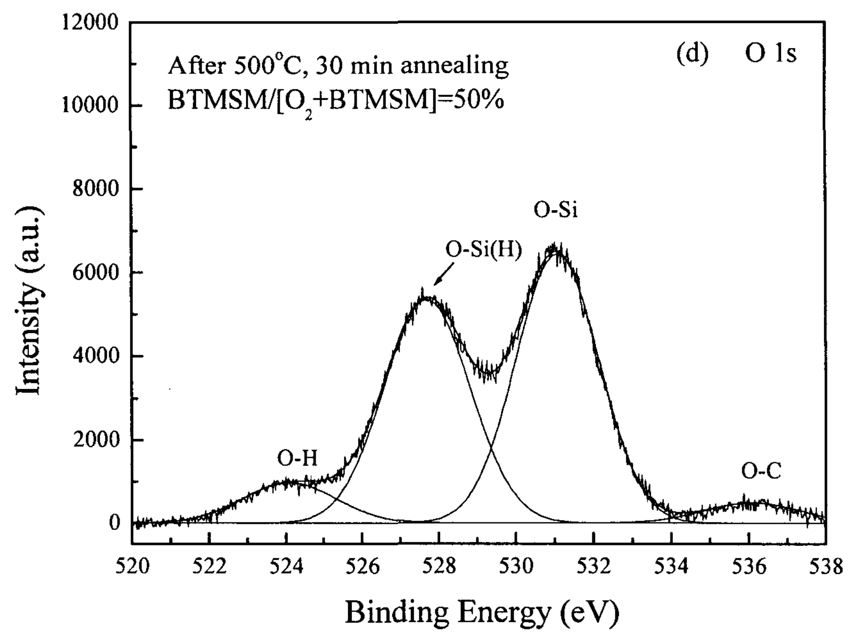


Fig. 4. The C 1s and O 1s XPS narrow scan spectra of the Si-O-C-H composite film and after annealing film with gas flow rate of BTMSM/(O_2+BTMSM) as 50%.

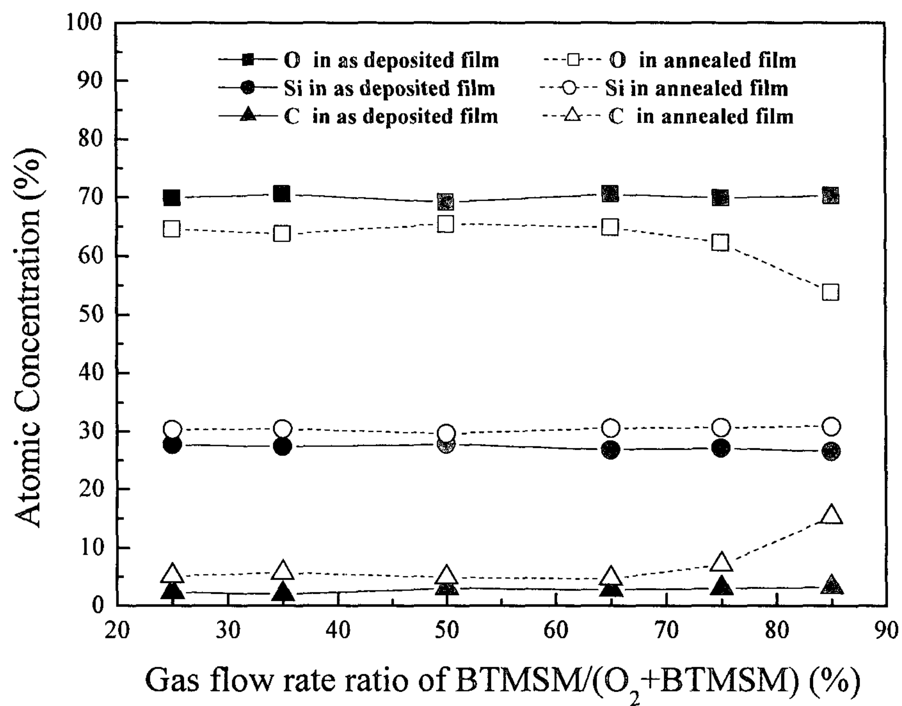


Fig. 5. Atomic concentration as a function of gas flow rate for the deposited film and post annealing sample.

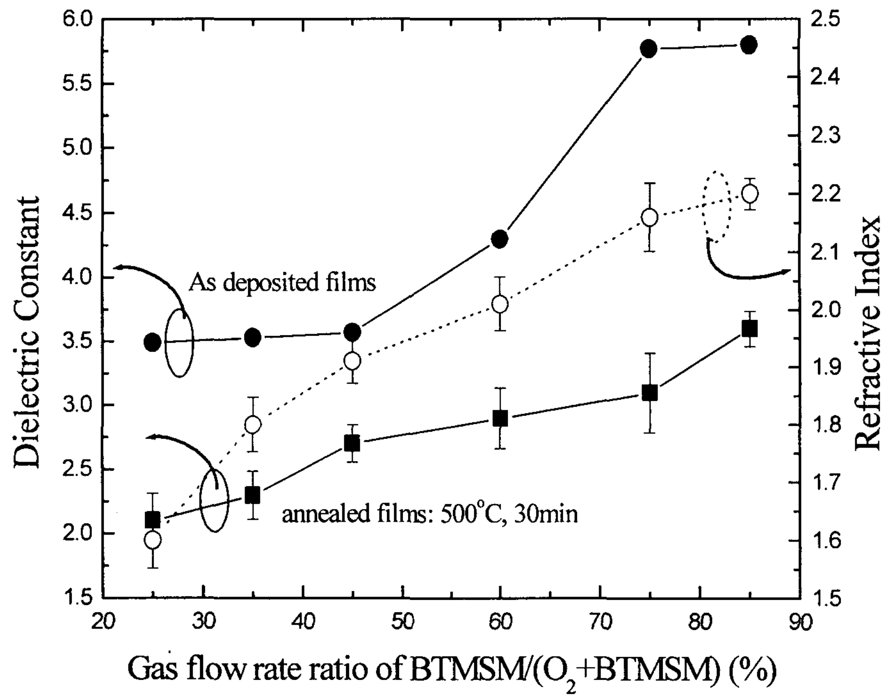


Fig. 6. Dielectric constant and refractive index changes with gas flow rate ratio.