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A study on the influence of carbon contents on dielectric constant of SiOC films by thermal treatment

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Carbon doped silicon oxide (SiOC) films with low dielectric constant films were deposited on p-type Si(100) substrates using a mixture gases of the bis-trimethylsilymethane(BTMSM) and oxygen gas by an inductively coupled plasma chemical vapor deposition. The Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy spectra were employed to investigate the porosity and the atomic concentration in the films. After annealing at 400℃ in vacuum, the carbon contents of the deposited film was increased, but the film density decreased. Therefore, the annealed SiOC composite films have the lowest relative dielectric constant (k = 2.1).

1. Introduction

As the design rule of intergrated circuit (IC) devices approaches 0.1㎚ and beyond, resistance-capacitance (RC) delay in the multilevel interconnections has become the determining factor in over all chip performance [1]. This is due to wiring extension that increases the conductor resistance as well as the signal cross-talk. Reducing the dielectric constant(k) of insulation layers has been regarded as one of the effective way to solve RC delay and cross talk problems [3]. The Silicon dioxide (k = 3.9~4.2) of present IMD(Inter Metal Dielectric) film, is difficult to solve of the problem of RC delay and cross-talk [1,2]. Therefore, a new low dielectric material is urgingly required for the IMD film in order to improve device performance[1,2,3].

Recently, many researchers have pro -posed a variety of organic and inorganic materials as an alternative to SiO_2, such as hydrogensilsequioxane(HSQ)[4], fluorine -doped silicon oxide[5], fluorinated amorphous carbon,[6] methylsisequioxane (MSQ)[7] and carbon doped silicon oxide[8], etc. Among these materials, SiOC film has many advantages as compared with other low dielectric materials since it has higher thermal and mechanical stability [9]. The reason for the low dielectric constant of SiOC films was a decrease in the SiOC film density, which resulted from the replacement of Si-O bonds with Si-CH_3 (alkyl group) bonds [10, 11]. However, a study on the influence of carbon contents in the SiOC film is insufficient.

In this work, the quantitative relationship between the dielectric constant and the concentration of carbon is shown. In addition, we investigated the film density of SiOC films by FT-IR(Fourier Transform Infrared), which is discussed together with the analysis of XPS(X-ray photoelectron spectroscopy).

2. Experiments

The SiOC composite films were deposited using a BTMSM (bis-trimethylsilymethane, H_9C_3-Si-CH_2-Si-C_3H_9) and an oxygen mixture gases in a ICPCVD (Inductively Coupled Plasma Chemical Vapor Deposition) generated 13.36MHz RF power supply. The ICPCVD plasma is generated by means of 3 turns mode which is set around a quartz tube. We sustained the base pressure 10^{-4}Torr before each deposition and the SiOC composite films were deposited on *p*-type Si(100).

The BTMSM precursor is a nontoxic, colorless liquid with a boiling point of 137℃ and melting point of -41℃. The BTMSM :O_2 flow rate ratio are 3:17, 10:10, 17:3(sccm) and the total gas flow rate was kept about 20sccm. As deposited SiOC films were annealed at 400C for 30min.

Ellipsometry was employed to determine the film thickness and the refractive index of the SiOC films. The chemical structure of the SiOC films was investigated by FT-IR. XPS was used to investigate the influence of carbon contents on the dielectric constant of the SiOC films. The Dielectric constant of SiOC films was measured by C-V (1MHz) meter using the MIS (Al/SiOC/*p*-Si) structure.

3. Results and discussion

Figure 1(a) shows the C 1s electron orbital spectra of as deposited and annealed SiOC films, which were deposited at the gas flow rate ratio with O_2/BTMSM=3/17. The C 1s electron orbital spectrum consists of Si-C bond (282.9eV) [12-14]. After annealing SiOC film, the relative area of Si-C bond is increased more than that of as -deposited film (from 64.2% to 35.8%). Also figure 1(b) indicates that the C 1s electron orbital spectra of as deposited and annealed SiOC films, which were deposited at the gas flow rate ratio with O_2/BTMSM=17/3. In spite of different flow rate ratio, the C 1s peak area is increased during annealing.(from 81.4% to 18.6). The binding energy shifts to higher energy position in all of samples after annealing [12,13].

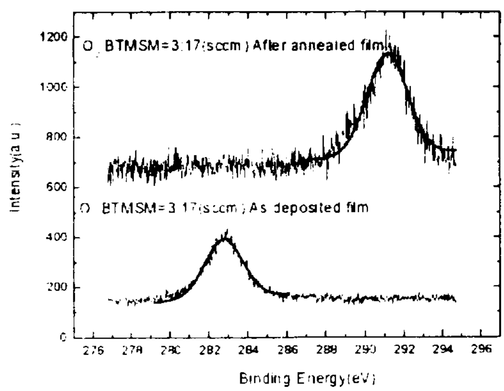

Fig. 1. (a) The C1s XPS narrow scan spectra of the SiOC composite films with the gas of O_2:BTMSM flow rate ratio as 17:3(sccm)

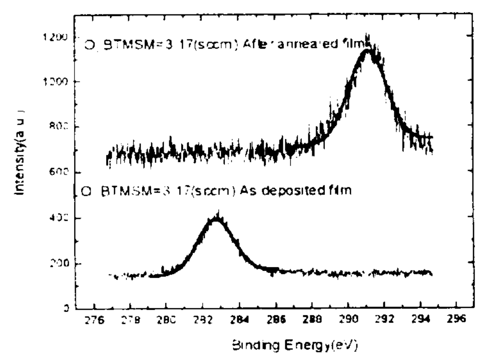

Fig. 1. (b) The C1s XPS narrow scan spectra of the SiOC composite films with the gas of O_2:BTMSM flow rate ratio as 3:17(sccm)

These tendencies indicated that the atomic concentration of oxygen affected the C 1s chemical shift in the annealed sample.

These results show that the atomic concentration of carbon is higher in the annealed film than the as-deposited film.

Figure 2 shows the FT-IR spectra of as deposited and annealed SiOC composite film, which was deposited with O_2/BTMSM gas flow rate ratio at 3:17(sccm). It could be seen from Fig.2 that there are Si-CH_3 (889, 1276 cm^{-1}), Si-O-C(Si)(1048 cm^{-1}), and CH_x(2965.7 cm^{-1}) bonds [12-16]. This peak has a clearly separated Si-O peak at 1104 cm^{-1} and it is an indicator of the existence of the porosity. [14].

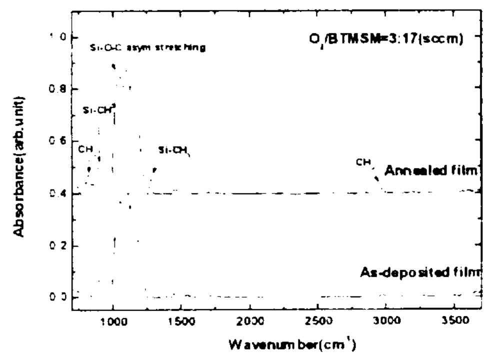

Fig. 2. The FT-IR spectra of the SiOC films prepared with the gas O_2:BTMSM flow rate ratio as 3:17(sccm)

The absorption peak at 889, 1276 cm^{-1}, which is Si-CH_3 bending mode, intensity is increased by annealing. The increment of Si-CH_3 peak intensity during annealing is associated with an increasing fraction of carbon contents, as indicated in Fig. 1(b).

It is means that the atomic concentration of oxygen decreased by annealing, and the atomic concentration of carbon increased by annealing [13]. Fig. 3 show the atomic concentration of SiOC films before and after annealing at 400C for 30minutes as a function of O_2/BTMSM flow rate ratio. From this figure we can see that the atomic concentration of as-deposited film almost keep constant while the mixture gas flow rate ratio of O_2/BTMSM change from 17:3 to 3:17, but the situation is different for annealing films. The relative atomic concentration of oxygen decrease in the after annealed SiOC film but atomic concentration of carbon increased [12].

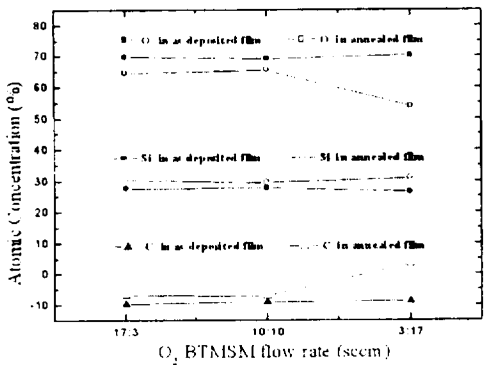

Fig. 3. The Atomic concentration of as-deposited and post annealing films with the gas of O_2:BTMSM flow rate ratio

decreased by the increase of carbon contents: it is resulted in the decrement of the dielectric constant.

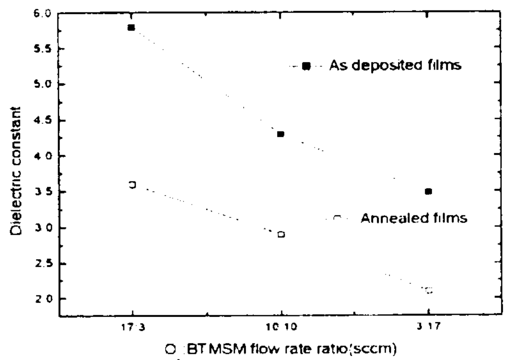

Fig. 4. The Dielectric constant of as-deposited and after annealed films with the gas flow rate ratio.

It is the same results as indicated in previously the FT-IR spectra. The dielectric constants for as-deposited and annealed films with different O_2/BTMSM gas flow rate ratio were shown Fig. 4. This figure indicate that the dielectric constant decrease after annealing.

The reason for low dielectric constant has two main reasons. First is the atomic concentration of carbon. From Fig.4, the dielectric constant of annealed film is lower than as deposited film because that this reason can be interpreted by the change of the polarization after annealing as become generally known that the polarization depends on the bonding length between atoms. The bonding length of Si-C is shorter than the bonding length of Si-O in general. Therefore, the polarization of annealed SiOC film was

That is, we can expect that the dielectric constant of annealed sample is lower than that of as-deposited sample. Second, the dielectric constant has something to do with the film density. The Dielectric constant decreases as film density decrease, Fig. 2 indicates that the intensity of separated peak was increased by annealing. The intensity of separated peak show the porosity, so annealed film increases the porosity. The film density decreased as a function of porosity. In these reason, we found that the dielectric constant of SiOC film is decreased by annealing. The lowest dielectric constant is 2.1 after annealed sample with the gas flow rate ratio of O_2/BTMSM at 3:17.

4. Conclusion

The SiOC composite films were deposited

by RF (13.56MHz) ICPCVD system with a BTMSM source gas and oxygen reactive gas. The gas flow rate ration varied 17:3. 10:10. 3:17(sccm) and we annealed the as-deposited films at 400C for 30 minutes. The SiOC composite films, it was found that the atomic concentration of carbon increased after annealing by XPS and FT-IR spectra. From FT-IR spectra, the SiOC composite films have porosity and the film density was decreased during annealing. Therefore, we found that after annealed films decrease the dielectric constant and after annealed film decrease the atomic concentration as a whole, so we can guess that the dielectric constant of annealing film is lower than that of as deposited film. Therefore, the low dielectric constant of the SiOC films mainly results from reduction of the oxygen contents and the increase of carbon contents by annealing.

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탄소가 첨가된 SiO_2 박막의 열처리에 따른 탄소 농도 영향에 대한 연구

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Abstract 본 연구에서는 ICPCVD 방법으로 BTMSM 과 산소 가스를 이용하여 차세대 반도체 소자에 적용가능한 저유전 박막인 SiOC 박막의 열처리 전후의 탄소 농도가 유전상수에 끼치는 영향에 관하여 연구하였다. 열처리 후에 산소의 농도가 다소 감소하며 탄소의 농도가 약간 증가함을 XPS 와 FT-IR 을 통하여 확인할수 있었으며 열처리 후의 SiOC 박막의 최저 유전 상수는 2.1이었다.