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## Properties of Low- $k$ ( $k \sim 2.05$ ) Plasma Polymer Films Deposited by PECVD Using Decamethyl-cyclopentasiloxane and Cyclohexane as the Precursors

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### 1. Introduction

As device features of integrated circuit (IC) continue to shrink, resistance  $\times$  capacitance (RC) delay greatly limits chip performance and reliability due to the increased power dissipation and metal line cross-talk in multilevel interconnects [1]. It is necessary to replace the present interlayer dielectric SiO<sub>2</sub> (a relative dielectric constant  $k \sim 4.1$ ) by materials with a low dielectric constant (low- $k$ :  $k \leq 3.5$ ). Plasma enhanced chemical vapor deposition (PECVD) of low- $k$  films has been studied intensively due to various advantages of the PECVD processes. PECVD with hydrocarbon precursors can produce so called "plasma polymers". Plasma polymers are quite different from chemically synthesized polymers [2]. Considering that plasma polymer films deposited using hydrocarbon precursors show relatively low  $k$  values and films containing Si atoms in their atomic networks are more thermally stable than plasma polymer films deposited with only pure hydrocarbons, PECVD deposition using a mixture of a hydrocarbon precursor and a Si-containing precursor is expected to produce films with both low  $k$  values and high thermal stability.

In this work, we investigated properties of plasma polymerized low dielectric constant films deposited using a mixture of decamethyl-cyclopentasiloxane (C<sub>10</sub>H<sub>30</sub>O<sub>5</sub>Si<sub>5</sub>: DMCPPO) and cyclohexane (C<sub>6</sub>H<sub>12</sub>: CHex) as the precursors. The films with reduced  $k$  values were obtained by PECVD deposition using mixture of an organic precursor and the Si-O containing precursor and annealing of the as-deposited films afterwards in an inert ambient at 400°C. It is considered that the annealing process for as-deposited PPDMCPSO:CHex thin films removes thermally unstable organic fragments and creates porosity in the films. In this report, plasma polymer films deposited from a mixture of DMCPPO and CHex were referred to as plasma polymerized decamethyl-cyclopentasiloxane:cyclohexane (PPDMCPSO:CHex) films, while films deposited from DMCPPO only and CHex only were referred to as PPCHex films and PPDMCPSO films, respectively.

### 2. Experiments

Deposition of plasma polymer films was performed using a PECVD system, which is described in detail elsewhere [3]. The base pressure of the deposition chamber of the PECVD system was  $\sim 10^{-6}$  Torr. Decamethyl-cyclopentasiloxane and cyclohexane precursors were

vaporized in bubblers kept at 75°C and 45°C respectively, and were carried into the deposition chamber using helium (He; 99.999%) carrier gas. The films were deposited on highly boron-doped p<sup>++</sup>-silicon (metallic silicon) and n-type silicon substrates at the same time. Deposition of the films was carried out at room temperature with He pressure of 1.5 Torr and plasma power of 15 W. After deposition, some of the samples were annealed at 400°C for 1hr in an N<sub>2</sub> ambient thermal furnace. Capacitances of the Al/plasma polymer/M-Si metal-insulator-metallic silicon (MIM) structures were measured to calculate the dielectric constants of the films. The frequency used for the capacitance measurement was 1 MHz. The leakage current characteristics of the thin films were investigated by measuring current through Al/plasma polymer/n-type Si(100) MIS structures. Fourier transform infrared (FTIR) absorption spectra were measured for the plasma polymer films deposited on n-type silicon substrates to investigate the chemical structures of the films. The insulating lifetime of the films for Cu diffusion was evaluated by bias-temperature stress (BTS) test. For the BTS experiment, TaN(50nm)/Cu( $\sim 200$  nm)/TaN(10nm)/PPDMCPSO:CHex/M-Si were fabricated [Fig. 1]. TaN(50nm) was for prevention of any possible oxidation of the Cu metal while TaN(10nm) was for Cu diffusion barrier during BTS test.

### 3. Results and Discussion

Figure 2 shows the relative dielectric constant  $k$  of plasma polymer films deposited at 1.5 Torr for plasma power of 15W. The  $k$  value of as-deposited PPDMCPSO and PPDMCPSO:CHex thin film was 3.5, and 2.45, respectively. As-deposited PPCHex film showed a very low  $k$  value of 2.0. After annealing at 400°C for 1 hour, the  $k$  value of PPDMCPSO:CHex film was reduced to 2.05 whereas that of the PPDMCPSO film was increased to 3.6. After annealing at 400°C, however, PPCHex did not show any residual thickness.

Figure 3 shows FTIR spectra of the films. FTIR spectra for the as-deposited PPDMCPSO, PPDMCPSO:CHex and PPCHex films are shown in Fig 3 (a), (c) and (e). The FTIR spectra for annealed PPDMCPSO and PPDMCPSO:CHex films at 400°C for 1hour are shown in Fig 3(b) and (d). The FTIR spectra of PPDMCPSO films [Fig. 3(a), (b)] has lower adsorptions peak of CH<sub>x</sub> (3200  $\sim$  2800 cm<sup>-1</sup>) than FTIR spectra of PPDMCPSO:CHex [Fig. 3(c) for as-depo-

sited samples, Fig. 3(d) for annealed samples] and PPCHex [Fig. 3(e)]. While the broad O-H ( $\sim 3400\text{cm}^{-1}$ ), C=O ( $\sim 1680\text{cm}^{-1}$ ) stretching adsorption peaks appeared in the PPDMCPSO thin film, those absorption peaks were not notable in PPDMCPSO:CHex and PPCHex. We believe that the relative dielectric constant  $k$  was decreased by including higher amount of hydrocarbon species compared to that of Si-related species for the as-deposited films. In the PPDMCPSO:CHex films, the  $k$  value decreased from 2.45 to 2.05 after annealing. This  $k$  value is in a similar range of the values of 2.19 - 2.2, reported for porous spin-on films where the nanoporosity induced in the deposited PPDMCPSO:CHex films by the removal of volatile C-H<sub>x</sub> species during the annealing reduced the  $k$  value [4].

Figure 5 shows the leakage current characteristic of the films. The leakage current of the PPDMCPSO:CHex films ( $k=2.05$ ) have leakage current density of  $\sim 4 \times 10^{-7}$  A/cm<sup>2</sup> under 6.4 MV/cm.

Figure 6 shows characteristics of the TaN(50nm)/Cu(200 nm)/TaN(10nm)/PPDMCPSO:CHex/M-Si structure under bias-temperature stress. BTS experiments were performed in a N<sub>2</sub> ambient. Electric field used for the BTS was 1 MV/cm and the temperature used for the BTS was varied in the range of 250 - 350°C. From Fig. 6, it can be calculated that the low- $k$  PPDMCPSO:CHex film with the  $k$  value of 2.05 can be remaining insulating, when put adjacent to Cu/TaN(10nm), for 10 years at 167°C under 1 MV/cm.

#### 4. Summary

The  $k$  values of as-deposited PPDMCPSO and PPDMCPSO:CHex thin film were 2.45, and 3.5, respectively. As-deposited PPCHex film showed the lowest  $k$  value of 2.0.

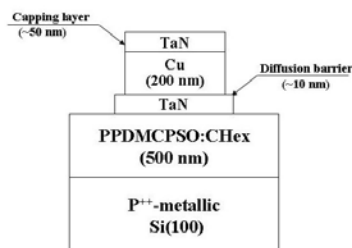


Fig. 1. Structure for BTS.

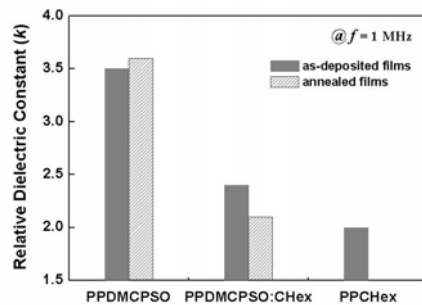


Fig. 2. The relative dielectric constant,  $k$  of plasma polymer films.

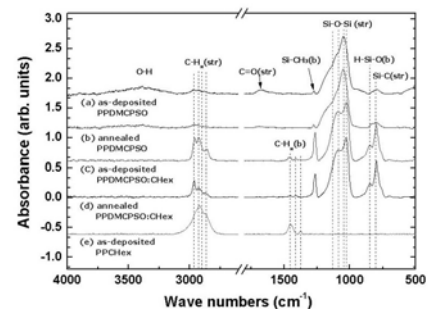


Fig. 3. The FTIR absorption spectra of plasma polymer thin films deposited on silicon substrate.

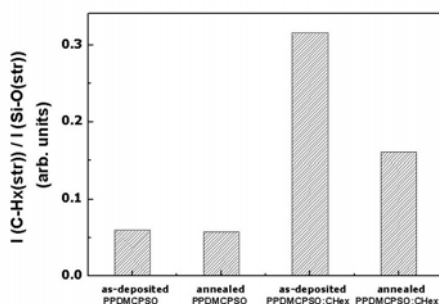


Fig. 4. The ratio of C-H<sub>x</sub>(str) peak intensity to Si-O(str) peak intensity.

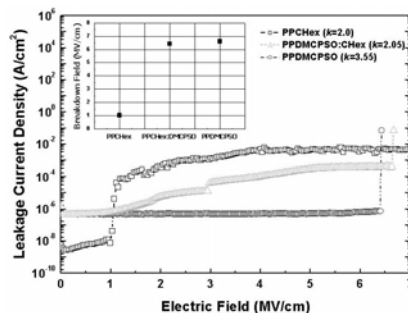


Fig. 5. I-V characteristics of the plasma polymer films.

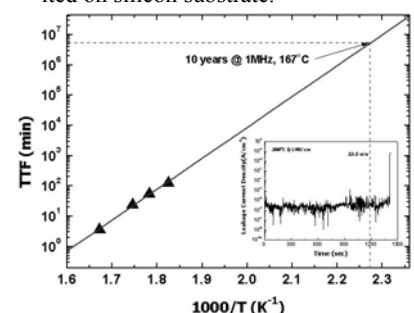


Fig. 6. The time to fail (TTF) plots of TaN/Cu/TaN/PPDMCPSO:CHex/Si structures under BTS at 1 MV/cm.

The FTIR spectra of PPDMCPSO films [Fig. 3(a), (b)] has lower adsorptions peak of C-H<sub>x</sub> than FTIR spectra of PPDMCPSO:CHex [Fig. 3(c),(d)] and PPCHex [Fig 3.(e)]. We think that for the as-deposited films, the relative dielectric constant  $k$  was decreased by including higher amount of hydrocarbon species compared to that of Si-related species. After 400°C-annealing, the  $k$  value of PPDMCPSO:CHex film decreased from 2.45 to 2.05. The leakage current density of PPDMCPSO:CHex film was  $\sim 4 \times 10^{-7}$  A/cm<sup>2</sup> under 6.4 MV/cm. For the BTS test, the PPCHex:DMCPSO ( $k=2.05$ ) film can be remaining insulating, when put adjacent to Cu/TaN(10nm), for 10 years at 167°C under 1 MV/cm. The results described above show that it is possible to decrease the dielectric constants of the PECVD-prepared PPDMCPSO:CHex film to 2.05, proving the extendibility of the PECVD low- $k$  films for future generations of ULSI chips.

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