Characteristics of organic–inorganic hybrid plasma polymer thin films for low-κ ILD applications

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A B S T R A C T
This study investigated the effects of plasma power and tetraethylorthosilane (TEOS) to cyclohexene ratios on low-κ organic–inorganic hybrid plasma polymer thin films deposited on silicon (100) substrates. These films were deposited using a plasma enhanced chemical vapor deposition (PECVD) method, in addition to the electrical and mechanical properties of the resulting composites. Cyclohexene and TEOS were used as organic and inorganic precursors, respectively, with hydrogen and argon as precursor bubbler gases. Furthermore, additional argon was used as a carrier gas. The as-grown polymerized thin films were analyzed using ellipsometry, Fourier-transform infrared (FT-IR) spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The ellipsometry results showed the thickness of the hybrid thin film, and the FT-IR spectra showed that the hybrid polymer thin films were completely fragmented and polymerized between cyclohexene and TEOS. AFM results showed that polymer films with a smooth surface could be grown under various deposition conditions, while TEM and XRD showed that the hybrid thin film was an amorphous plasma polymer thin film without porosity. In addition, current–voltage (C–V) curves were prepared to calculate the dielectric constants. Post-annealing was applied to investigate the thermal stability of hybrid plasma polymer thin films in the hardness, Young’s modulus, thermal shrinkage, and the dielectric constant at 400 °C.

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1. Introduction
Advances in the development of ultra large scale integrated (ULSI) circuits have been hindered by difficulties during the introduction of materials into the multilevel interconnected structure of Si chips. Considerable research effort has been invested to replace the SiO₂ dielectric with materials having a significantly lower dielectric constant [1] due to the problems of propagation delay, cross-talk noise, and power dissipation. These problems are all caused by resistance–capacitance (R–C) coupling. The significance of these problems is amplified as a result of increased wiring capacitance, especially interline capacitance, between circuits on the same metal level. While resistance is affected by conducting materials, capacitance is determined primarily by dielectric materials [2]. The use of advanced inter-metal dielectrics to reduce capacitance may be more important than decreasing the resistivity by substituting aluminum with copper [3]. Therefore, thin films with relatively low dielectric constants (κ<3.0) are under intense study due to their application as interlayer dielectrics.

Polymer thin films are considered possible candidates for low-κ materials given their low κ values [4], an important requirement for interlayer dielectrics. The loss tangent, tan δ, is also an important property of dielectrics. Electric power is dissipated in all dielectric materials, usually in the form of heat. Since the dissipation factor (DF) is generally small, it varies depending on the dielectric material and the electrical signal frequency. In low dielectric constant (low-κ) materials, DFs of 0.1% to 0.2% are typical. A lower DF is usually an indication of quality capacitors when comparing similar dielectric materials [5,6]. Previous research has focused primarily on reducing the bulk dielectric constant by only considering existing chemically designed materials and porous materials with different porosity sizes. This research reports the use of porous materials for reducing the dielectric constants of interlayer dielectric materials. The hardness and Young’s modulus were mentioned in few papers, with low values below 0.3 and 10 GPa, respectively [7].

In this study, we investigated plasma polymer thin film deposition using a plasma enhanced chemical vapor deposition (PECVD) method on Si (100) substrates at room temperature using cyclohexene and TEOS precursors. The investigation looked for potential applications of low dielectric constant devices with improved hardness, Young’s modulus, and thermal properties. In particular, we examined the effects of deposition plasma power and the ratio of TEOS to cyclohexene on the dielectric constant.
2. Experimental procedures

Experiments were carried out in a homemade, stainless steel plasma enhanced chemical vapor deposition (PECVD) system. Silicon (100) wafers were cleaned by sequential sonication with acetone, ethyl alcohol, distilled water, and isopropyl alcohol. Substrates were cleaned by in-situ Ar plasma bombardment at 100 W for 15 min. Hybrid polymer thin films were deposited by PECVD at room temperature. Cyclohexene and tetraethylorthosilicate (TEOS) were utilized as the organic and inorganic precursors, respectively. Three co-deposition precursor ratios of TEOS to cyclohexene were selected: 1:10, 3:10, and 5:10. Each precursor was preheated to 60 °C or 80 °C and was bubbled with 50 sccm (standard cubic centimeter per minute) hydrogen with 5, 15, or 25 sccm argon gas. An additional 50 sccm argon was used as the carrier gas. The deposition time lasted up to 30 min depending upon the RF (radio frequency using 13.56 MHz) power used to deliver a uniform film thickness of 300 nm. Typical film deposition conditions for the PECVD process were 20–60 W of RF power at a pressure of $4.0 \times 10^{-1}$ Torr.

Ex-situ ellipsometry thickness measurements for all investigated films were calculated using an ellipsometer with a wavelength range of 193 to 1000 nm. The surface morphology was investigated using contact mode atomic force microscopy (AFM). High resolution transmission electron microscopy (HR-TEM) images showed the atomic arrangement of the hybrid thin film, and X-ray diffraction (XRD) patterns showed the crystallinity of the hybrid thin film. The types of chemical bonding in plasma hybrid polymer thin films were investigated using Fourier-transform infrared (FT-IR) spectrometry. We used double-sided polished Si (100) substrates in transmittance mode IR analysis, and IR spectra were transformed to absorption

![Fig. 1. Growth rates (nm/s) of thin films under specific conditions.](image1)

![Fig. 2. AFM images and root mean square (RMS) roughness, indicating changes in surface morphology, with increasing deposition RF power and TEOS ratio.](image2)
spectra. In addition, these films, with a built up metal–insulator–silicon–metal (MISM) structure, were analyzed using a multi-frequency precision LCR (L, inductance; C, capacitance; R, resistance) meter. This analysis was necessary for the preparation of C–V curves in order to measure the dielectric constant and the DF at 1 MHz of frequency. The nanoindentation depth used was 300 nm. Nanoindentation results were considered in all analysis up to a penetration depth \( h \leq t_f/10 \), where \( t_f \) is the thickness of the hybrid plasma polymer film on Si substrate [8]. Plasma polymer thin films were annealed at temperatures from 200 to 500 °C under an Ar atmosphere for 5 min using rapid thermal process (RTP). Thermal shrinkage of the film thickness was investigated in order to determine the thermal stability. Additionally, the hardness, Young’s modulus, and the dielectric constant were investigated after post-annealing.

3. Results

We measured the growth rates (nm/s) of thin films under specific deposition conditions (Fig. 1). The growth rates normally increased with increasing TEOS ratio and increasing RF power, although the growth rates at 40 W and 50 W were almost the same, while the growth rate at 60 W decreased because of plasma etching. However, the growth rate of the 5:10 thin film consistently increased with increasing RF power. From these results, we saw that larger proportions of TEOS led to more easily deposited hybrid thin films, although too high a concentration of TEOS led to high thin film growth rates by PECVD. Thus, only the 5:10 sample growth rate increased proportionally with increasing RF power.

Fig. 2 shows the AFM images and root mean square (RMS) roughness, which indicate that a change in surface morphology occurred with increasing deposition RF power and TEOS ratio. Usually, plasma affects the as-grown plasma polymer through plasma heating and plasma bombardment effects [9,10]. However, RMS roughness values did not change significantly under conditions of increased RF power or TEOS ratio, indicating in this case that the plasma effects of the hybrid plasma polymer were negated by plasma co-deposition. Thus, the cyclohexene–TEOS hybrid plasma polymer thin film had a smooth surface and good surface uniformity under all deposition conditions.

As shown in Fig. 3, the TEM images and XRD patterns showed the atomic arrangement of the hybrid plasma polymer thin film without a crystalline structure. The distance between atoms in the plasma polymer thin film was somewhat decreased with increasing RF power because the ion density of the plasma increased with increasing RF power [11]. High RF power leads to faster plasma deposition due to the higher reaction energy. In addition, there was no porosity because the plasma polymer thin film consisted entirely of condensed matter. We didn’t observed any XRD peaks from the hybrid thin films, except for Si (200) and Si (400) peaks from the silicon (100) substrate, indicating that the hybrid plasma polymer thin film was an amorphous hydrocarbon plasma polymer (Fig. 3c).

The chemical bonding of plasma polymerized thin films was analyzed using FT-IR absorption over a range of 4000–600 cm\(^{-1}\) (Fig. 4). The IR spectra exhibited an absorption band at 1050 cm\(^{-1}\), corresponding to a Si–O stretching vibration band. Moreover, absorption bands at 792–892, 1380–1457, 1712, 2870–2960, and 3260–3660 cm\(^{-1}\) corresponded to Si–CH\(_3\), CH\(_x\) (bending vibration mode), C O, CH\(_x\) (stretching vibration mode), and –OH bands, respectively [12]. The intensity of the CH\(_x\) peak (2960 cm\(^{-1}\)) decreased with increasing RF power (Fig. 4). Generally, C O and –OH groups have high dielectric constants because of their high polarizabilities. From the IR spectra, absorbance of these functional groups was increased by increasing the RF powers of hybrid thin film deposition, thus the dielectric constant was also increased [13]. The intensity of the Si–O band also increased with a higher TEOS bubbling rate. From this result, the TEOS precursor was well controlled by Ar bubbling. Additionally, the IR spectra showed

![Fig. 3. TEM images and XRD patterns of 20 and 60 W of RF power with 1:10 TEOS ratio.](image-url)
that cyclohexene and TEOS were ionized by the plasma, as their IR spectra post plasma differed completely from that of the original liquid precursors.

The dielectric constants of the as-deposited film were determined as a function of RF power and TEOS ratio (Fig. 5a). Dielectric constants increased with increasing RF power and higher TEOS ratio because of the increased polarizability and the Si–O group of the thin films. For the deposited thin films, the lowest dielectric constant was 2.71 from deposition at 20 W of RF power with a 1:10 TEOS to cyclohexene ratio. Moreover, the dielectric constant plateaued at approximately 4.2. In addition, the dielectric constants of a pure plasma polymer thin films were also determined (Fig. 5a). All values were located between 2 and

![Fig. 4. FT-IR absorption spectra over a range of 4000–600 cm⁻¹ used to identify the bonding in plasma polymerized thin films.](image)

![Fig. 5. Dielectric constants and dissipation factors of the as-deposited films as a function of RF power and TEOS ratio.](image)

![Fig. 6. (a) The hardness and Young’s modulus, (b) the thermal shrinkage of thickness, and (c) the dielectric constants by post-annealing.](image)
2.4. However, according to the increased silicon content ratio, the dielectric constant was increased by SiO because the dielectric constant of SiO is almost 4. The dissipation factor, or loss tangent (tan δ), is another important property of the ILD materials [5]. All dissipation factors of the hybrid thin film were less than 0.08%, with the DF value at 1 MHz being the lowest, at 0.0496% (Fig. 5b). Thus, these films had low DFs and could potentially be useful as low-κ ILD materials for semiconductors.

The hardness, Young’s modulus, thermal shrinkage, and dielectric constant were determined after post-annealing up to 500 °C. The hardness value of the 20 W, 5:10 sample remained at 1 GPa until 400 °C post-annealing. Additionally, Young’s modulus was not changed much by the post-annealing process because of SiO (Fig. 6a). However, the hardness and Young’s modulus of the 20 W, 1:10 sample dramatically increased during post-annealing. The thermal shrinkage was reduced by increasing the SiO content in the hybrid thin film (Fig. 6b). For the 20 W, 5:10 sample, the thermal shrinkage of thickness at 400 °C was less than 10% of the as-deposited film thickness. The thickness of the pure organic and 1:10 hybrid plasma polymer thin films were dramatically increased by post-annealing because CH₃ groups with a low amount of SiO are thermally unstable. The CH₃ groups could be degassed by post-annealing. The dielectric constant of the 20 W, 5:10 sample was nearly unchanged by post-annealing until 400 °C (Fig. 6c). However, post-annealing dramatically increased the dielectric constant of the sample with a low amount of SiO. Therefore, a higher amount of SiO led to electric thermal stability up to a temperature of 400 °C.

4. Conclusions

The growth rates of organic–inorganic hybrid polymer films were influenced by the RF power and the TEOS to cyclohexene ratio. A plasma etching effect occurred during PECVD, and we observed that the as-grown hybrid films had –CH₃, C O, –OH, and Si–O functional groups, as well as IR spectral patterns that differed from those of the liquid precursors, indicating that the thin film was polymerized between cyclohexene and TEOS. Moreover, the number of Si–O functional groups was controlled solely by the TEOS bubbling rate, not the RF power. Thus, we were able to predict the dielectric constant with RF power and TEOS ratio changes. The dielectric constant increased with increased deposition RF power and TEOS ratio. The lowest dielectric constant was 2.71 at 20 W of RF power and a TEOS to cyclohexene ratio of 1:10. The DFs for all of the hybrid films were less than 0.08%, with the lowest DF of 0.0496% occurring at a deposition power of 30 W and a TEOS ratio of 1:10. The optimum dielectric constant was 2.71 from deposition at 20 W of RF power and a TEOS ratio of 1:10. At these same conditions, the DF was 0.0718%. Increasing the SiO amount led to an increase in the dielectric constant. However, it also led to increases in the thermal stabilities of the hardness, Young’s modulus, shrinkage, and the dielectric constant. Consequently, more research into organic–inorganic hybrid films is needed to investigate increasing thermal stability with a low dielectric constant.

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