Study on the characteristics of ThioPP thin films for low-k applications

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Abstract. The thiophene plasma polymer was deposited on silicon(100) substrates by PECVD (Plasma Enhanced Chemical Vapor Deposition) with homemade stainless steel vacuum chamber. Thiophene was utilized as organic precursor with hydrogen gas as bubbling gas. Argon gas was used as a carrier gas. To analyze the electrical properties of the plasma polymerized thin films, the plasma-polymer thin films were grown under various RF power condition. The as-grown plasma-polymer thin films were analyzed by atomic force microscopy (AFM), scanning electron microscopy (SEM), measuring the capacitance, impedance analyzer, ellipsometry, Fourier Transform Infrared spectroscopy (FT-IR), and water contact angle measurement. AFM and SEM images showed smooth surfaces of thin films with increasing RF power. An impedance analyzer was utilized for the measurements of I-V curves (for leakage current density) and capacitance (for dielectric constant). Refractive indices were increased by increasing RF power. The IR spectra showed that the plasma polymer thin films have totally different chemical functionalities from liquid thiophene precursor, as well as the changing chemical functionalities of the thin films caused by various RF powers. The best dielectric constant is 2.52 in this study.

Introduction

There has been an increase of interest in the use of glow discharge for the polymerization of a number of organic and organometallic compounds [1, 2]. Among many CVD methods, PECVD process is very efficient method to produce homogeneous organic thin films on large area substrates, offering good control over the film properties [3–7]. Plasma polymerization is known as a unique method of organic thin film deposition [8].

The advances in the performance of the (ULSI) have been hindered in recent years by the difficulties of the introduction of materials in the interconnect part of the Si chip technology while a large effort was invested for many years to replace the SiO2 dielectric with materials having a significantly lower dielectric constant [9]. Because the problems which are propagation delay, cross-talk noise, and power dissipation due to resistance-capacitance (R-C) coupling become significant due to increased wiring capacitance, especially interline capacitance between the metal lines on the same metal level. Whereas the resistance is affected by conducting materials, the capacitance is mainly determined by dielectric materials [10]. The use of advanced inter-metal dielectrics to reduce the capacitance seems to be more important than the decrease of the resistivity provided by the substitution of aluminum by copper [11]. Therefore, thin films with the relative low dielectric constant (k<3.0) are under intense study due to their application as interlayer dielectrics. Polymer thin films are considered as possible candidates for low-k materials due to their application as interlayer dielectrics. Polymer thin films are considered as possible candidates for low-k materials given their low-k values [12].

In this study, we investigated on the plasma-polymer thin films on Si (100) substrates at room temperature by a plasma enhanced chemical vapor deposition (PECVD) method using thiophene precursor for low dielectric constant device applications. In addition, the effects of deposition of the plasma power on the dielectric constants were mainly studied.

Experimental Procedure

The experiment was carried out in a homemade stainless-steel PECVD system. Silicon(100) wafers were wet-cleaned by sonication with acetone, ethyl alcohol, distilled water, and isopropyl alcohol; and dried by N2 gas blowing. Also, substrates were dry-cleaned by in-situ Ar plasma bombardment with 100 W for 15 min. The plasma polymer thin films were deposited by PECVD method. Thiophene was utilized as organic precursor. Thiophene was preheated at up 60 °C, and bubbled by 50 sccm of hydrogen gas. Additionally, 50 sccm of argon gas was used as a carrier gas. The deposition time was lasted 30 min to make same thickness, 300 nm. It depended on RF power. The deposition
pressure and temperature were $3.5 \times 10^{-1}$ Torr and room temperature ($25^\circ C$). The typical conditions of PECVD process applied in this study for film deposition are 20, 40, 60, 80, and 120 W of RF power.

Surface roughness was measured by non-contact mode AFM (Park Systems, 910M-NCHR). Also, the surface morphology of plasma polymer thin films was measured by field emission SEM (FE-SEM) (JEOL, JSM700F). The $\kappa$ values were determined from the measurement of the capacitance in the metal-insulator-silicon-metal (MISM) structure of Al/hybrid polymer thin film/Si/Al. The capacitance was determined at 1MHz with the MISM structure by precision LCR meter (Hewlett-Packard, HP 4284B). Leakage current density was investigated by a semiconductor parameter analyzer (Hewlett-Packard, HP 4145B) such as l-V curve with 1 MV/cm of field. Chemical bonding type of plasma polymer thin films was investigated by FT-IR (Bruker Optik, Vertex 70). The ex-situ ellipsometry data of all investigated films were produced by the ellipsometer (Gaertner, GC5A automatic ellipsometry) at 632 nm. Surface wettability was measured according to water contact angle measurements (KSV Instruments, attension).

**Experimental Procedure**

Fig. 1 (a) – (c) shows the AFM 2D images and RMS roughness. It shows changes of surface morphologies with increasing deposition RF power. Usually, plasma affects the as-grown plasma polymer through plasma heating and plasma bombardment effects [13, 14]. In this result, the RMS roughness values increase with increasing RF power. It means that plasma bombardment is effective in surface roughness. Also, Fig. 1 (d) – (f) shows the morphology of plasma polymer surface by FE-SEM. Surface morphology shows the increasing surface density of plasma polymer thin films with increasing RF power. Therefore, SEM result shows the same trend of AFM image result.

Fig. 1. AFM images ($5 \times 5 \mu m^2$) of the surface of (a) 20; (b) 60; (c) 120 W of RF power and SEM images of surface morphology of (d) 20; (e) 60; (f) 120 W of RF power.

Fig. 2 shows the refractive indices of plasma polymer thin film with RF power. Refractive index was increased by increasing deposition RF power. Refractive indices shows the same trend of AFM and SEM. Density of plasma polymer thin film was increased by increasing the deposition RF power due to increasing RF power led to increase cross-link in plasma polymer [15]. Thus, increasing the RF power led to increase refractive index [16, 17].

Fig. 2. Refractive index ($N_d$) of plasma polymer with RF power.

Fig. 3. Dielectric constant ($\kappa$) of plasma polymer with RF power.

Fig. 4. Leakage current density ($A/cm^2$) of plasma polymer with RF power.
The dielectric constant of a material can also be calculated from the refractive index, as expressed in

$$\kappa(\lambda) = n^2(\lambda) - k^2(\lambda) + 2i n k(\lambda),$$

where $\kappa$ is a relative dielectric constant, $n$ is a real part of a refractive index, $k$ is the extinction coefficient, $i = -1$, and $\lambda$ is the wavelength of the light source.

The pure electronic contribution to the dielectric constant ($\kappa$) was calculated from the refractive index obtained in the UV/Vis region. Since the extinction coefficient ($k$) of SiO$_2$-based materials is normally negligible in this region, the relative dielectric constant ($\kappa$) in Eq. (1) can be simply expressed as [18, 19],

$$\kappa = n^2.$$  

Therefore, the dielectric constant could be predicted based on the measurement of the refractive index. However, dielectric constant decreased from 20 W to 60 W after than increased as shown in Figure 3. The lowest value was 2.52 ± 0.04 at 60 W of RF power. The dielectric constants measured at 1 MHz consist of electronic, ionic and dipolar contributions. Refractive index related with electronic polarization. Thus, it means that change of dipolar or ionic polarization was highly effective on real dielectric constant of plasma polymer thin film within 20 – 60 W of RF power.

![Fig. 5. IR spectra of plasma polymer with RF power.](image)

![Fig. 6. Water contact angles of plasma polymer with RF power.](image)

Fig. 4 shows leakage current density (A/cm$^2$) of plasma polymer thin film. The insulating properties of the films were determined by measuring the leakage current density under different applied field. As shown in Fig. 4, there is a changing of the leakage current densities with various RF power. Increasing RF power of the plasma led to increasing the plasma ion density and also the plasma-heating effect. Thus, the leakage current densities decreased under influence of the film density that increased in a range of 20 – 60 W which the plasma-heating effect had weak. This indicates that the pinhole-free films were deposited at 60 W of RF power. On the other hand, the leakage current densities increase by damage by increased the plasma-heating effect and plasma etching effect over 80W of RF power. The lowest leakage current density of the films was $1 \times 10^{-9}$ A/cm$^2$ at 1 MV/cm, indicating that the film deposited at 60 W of RF power was insulating enough to be used as interlayer ultralow-$\kappa$ dielectrics in a semiconductor [20–23].

The bonding state of the plasma polymerized thin films was analyzed by FT-IR absorption over a range of 4000–600 cm$^{-1}$, as shown in Fig. 5. The IR spectra exhibit an absorption peak at 1154 and 1050 cm$^{-1}$, corresponding to the Si-O stretching vibration band. Bands ranging from 1446, 1463, 1525, 1591, 1703, 2870–2960, and 3260–3660 cm$^{-1}$ corresponded to Si-CH$_3$, S=O, C=S, C=O, CH$_x$ stretching vibrations, and –OH bands, respectively [24]. From Fig. 5, the intensity of the CH$_x$ (2960 cm$^{-1}$) and C=O peaks were decreased with increasing RF power. Also, the peak intensity of C=C increased with decreasing peak intensity of CH$_x$ (2960 cm$^{-1}$) as RF power increased, therefore film density could be increased through higher RF power. Additionally Si-CH$_3$ peak was decreased with increasing deposition RF power.

Si-O, S=O, C=S, C=C, C=O, and –OH groups had high dielectric constant because of high polarizability [25]. From the IR spectra, intensities of these groups were changed by increasing RF power, thus the dielectric constants were changed with increasing RF power. Intensities of 1154 and 1446 peaks were rapidly decreased with increasing RF power. Thus, in the early, the dielectric constant was decreased with increasing RF power until 60 W. However, S=O and C=S were rapidly increased from 80 W of RF power. As the result, the dielectric constant was increased with high RF power such as over 80 W of RF power.

Figure 6 shows water contact angles of plasma polymer with RF power. The water contact angle was increased until 60 W of RF power, and then contact angle was decreased from 80 W of RF power. This trend accorded with IR data.
Conclusion

After Plasma polymer thin films were deposited on Si(100) by PECVD method using Toluene single precursor. AFM and SEM images show the increasing film density with increasing RF power. Also, refractive indices were increased with increasing RF power by increasing the degree of cross-link in plasma polymer. Dielectric constant could be expected to increase with increasing RF power. However, dielectric constant was increased from 80 W of RF power. The increase of polarization in plasma polymer thin film was investigated by IR and water contact angles. The dielectric constant was highly influenced by polarization. Thus, we can predict the trend of dielectric constant change by IR and water contact angle. In addition, the plasma polymer thin film that was deposited at 60 W of RF power showed a leakage current density of $1 \times 10^{-7}$ A/cm$^2$ at 1MV/cm. The result showed the best low-$\kappa$ material deposited at 60 W of RF power. Its dielectric constant is 2.52.

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