

A comparative study of plasma polymerized organic thin films on their electrical and optical properties

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Received 21 November 2005; received in revised form 6 January 2006; accepted 9 February 2006

Available online 22 January 2007

Abstract

Plasma polymerized organic thin films were deposited on Si(1 0 0) and glass substrates by plasma enhanced chemical vapor deposition (PECVD) method using single molecular precursors. Cyclohexane, methylcyclohexane, and ethylcyclohexene were utilized as organic precursors, and hydrogen and Ar was used as a carrier gases, respectively. To compare the difference of the electrical and the optical properties of both the plasma polymerized pure organic thin films, we grew those films under the conditions of various radio frequencies (RF using 13.56 MHz) powers in the range of 20–50 W and deposition temperatures (25 and 100 °C). The composition changes and the electrical characteristics of as-grown thin films were analyzed with *I*–*V* and *C*–*V* techniques. The optical properties of the polymerized thin films were investigated by Fourier transformed infrared spectroscopy (FT-IR) and UV–vis spectrophotometer. As the plasma power was increased, the main IR absorption peak intensity of thin films was increased while the transmittance of the UV–vis spectra was decreased, indicating high cross-linked density. Based on *I*–*V* and *C*–*V* curves of the electrical property measurement, the best leakage current density of the ethylcyclohexane thin films obtained to be around 4.5×10^{-12} A/cm² at 1 MV/cm. © 2006 Elsevier B.V. All rights reserved.

Keywords: Plasma polymerization; Organic thin films; Electrical and optical properties

1. Introduction

As the integration level and speed of semiconductor devices increase, the reduction of the resistance \times capacitance (*RC*) delays in the metallization is becoming more important than before. The problems are propagation delay, cross-talk noise, and power dissipation due to *RC* coupling become significant due to increased wiring capacitance, especially interline capacitance between the metal lines on the same metal level [1]. Whereas the resistance is affected by conducting materials, the capacitance is mainly determined by dielectric materials [2]. Therefore, thin films with the relative low dielectric constant ($k < 3.0$) are under intense study due to their application as interlayer dielectrics for multilevel metallization of ultra large-scale integrated (ULSI) semiconductor devices. Low-*k* values are the two most important requirements for interlayer dielectrics.

Polymer thin films are considered as possible candidates for low-*k* materials due to their low-*k* values [3]. However, poor

adhesions with Si substrates and production difficulties have hindered their use in microelectronics. On the other hand, plasma enhanced chemical vapor deposition (PECVD) of polymer films (plasma polymerization) has many advantages that help to overcome these problems [4]. PECVD uses a glow discharge to create activated species such as radicals and ions from the original monomer, and the polymer films are deposited through various gas phase and surface reactions of these active species, including ablation of the deposited film.

In this study, we report here our results of the growth of polymer-like thin films on Si(1 0 0) and glass substrates in the deposition temperature range of room temperature and 100 °C using the cyclohexane, methylcyclohexane, and ethylcyclohexane precursor by PECVD method for low dielectric device applications. In addition, the effects of deposition temperature and plasma power on the electrical properties were mainly studied.

2. Experimental

The experiment was carried out in a made PECVD system which is consists of stainless steel. The Si(1 0 0) was used as substrate that cleaned and etched using acetone, isopropyl alcohol, HF solution, and DI water, sequentially. Glass was cleaned by same method without HF solution. After cleaning the samples,

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the pre-cleaned substrates were in situ pre-treated with Ar plasma to make an oxygen-free surface and/or a buffer layer for enhance film adhesion. The deposition was lasted for 5–10 min, depending on the RF power and deposition temperature because of made same thickness for our sample. The deposition pressure and temperature were $2\text{--}4 \times 10^{-1}$ Torr, and room temperature and 100°C . The substrates were heated using indirect heating (Hot-Wall system) method, and the deposition temperature was detected by K-type chromel-alumel thermocouple. The typical conditions of PECVD process applied in this study for film deposition are 20–50 W of RF power and 50 sccm of Ar carrier gas, and 50 sccm of H_2 bubbler gas for cyclohexane, methylcyclohexane, and ethylcyclohexane. Due to high vapor pressure of the precursor itself, it was not necessary to heat the source during deposition.

The as-grown plasma polymerized thin films were ex situ characterized with FT-IR and UV–vis. Impedance analyzer was utilized for the determination of I – V curve for leakage current density and C – V for dielectric constants, respectively. C – V characteristics were measured using Boonton 7200 Capacitance Meter for electrical properties.

3. Results and discussion

Fig. 1 shows FT-IR spectra of plasma polymerized methylcyclohexane thin films. In Fig. 1, we can see two strong absorption peaks at about 2910 , 2800 , and 1400 cm^{-1} . The absorption peak at 2910 cm^{-1} can be assigned to the aliphatic C–H stretching mode by methyl group. And the polymers produce C–H bending modes around 1400 cm^{-1} . The small absorption peaks around $1400\text{--}1600\text{ cm}^{-1}$ may attribute to C–C and C=C stretching vibration. We could also see the increase of absorption peak intensities whenever the polymerization was carried out at high RF power.

Fig. 2 also shows FT-IR spectra of plasma polymerized ethylcyclohexane thin films that was grown on Si(1 0 0) substrates at 100°C with different RF power. We can see three strong absorption peaks at 2910 , 2800 , and 1450 cm^{-1} . The absorption peak at 2910 cm^{-1} can be assigned to the aliphatic C–H stretching mode of methylene group. And the methylene group can assign the absorption peak at 1450 cm^{-1} to the CH_2 bending mode. Comparing this with Fig. 1, C–H stretching peak of Fig. 2 increases with increasing RF power. And C=C stretching peak appears at about 1700 cm^{-1} [5]. These peaks also increase with increasing RF power.

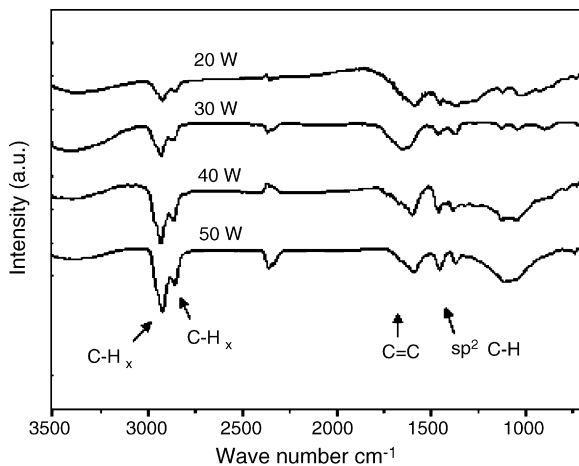


Fig. 1. The FT-IR spectra of methylcyclohexane as-grown thin films at different RF power.

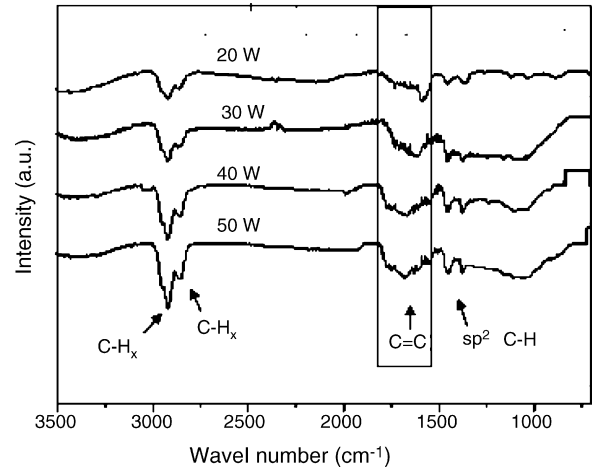


Fig. 2. FT-IR spectra of ethylcyclohexane monomer as-grown thin films at 100°C .

Fig. 3 show UV–vis transmittance spectra of the plasma polymerized thin films that were deposited at room temperature under the condition of Ar: $\text{H}_2 = 1:1$ and different RF powers. From both figures, we could see a change of optical transmittance in the range $300\text{--}350\text{ nm}$ with a sharp slope and a high value of constant transmission from 350 to 2500 nm . Higher transmittance than 80% could be obtained from the methylcyclohexane films grown at RF power of below 100 W . However, the optical transmittance was gradually decreased with increasing RF powers due a degree of to C–C or C=C bonds in the film layers.

Fig. 4 also shows UV–vis transmittance spectra of the plasma polymerized ethylcyclohexane thin films that was grown at 100°C under the same deposition condition of Fig. 2. The transmittance and optical band gap of the films also have a decreasing tendency with increasing RF power. The reason for the blue shift tendency is mainly due to the higher degree of C=C bonds formation in the film layers. This result indicates that the ethyl group of the ethylcyclohexane molecule is easily ionized by the plasma effect. Also with increasing RF power ethylcyclohexane films may have relatively higher degree of cross-linking and C=C bonding, those of methylcyclohexane films, because

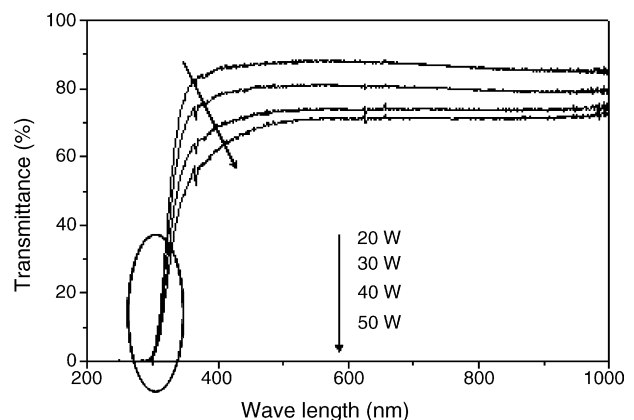


Fig. 3. UV–vis transmittance spectra obtained from the methylcyclohexane thin films that grown on glass at various RF powers.

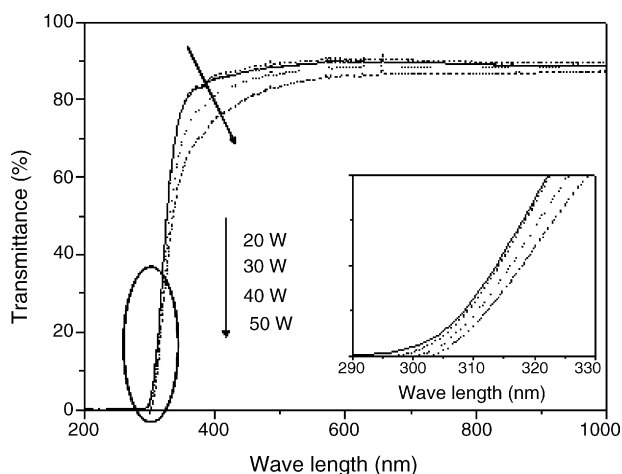


Fig. 4. UV-vis transmittance spectra obtained from the ethylcyclohexane thin films that grown on glass at 100 °C and various RF powers.

the ethyl group of ethylcyclohexane molecule produces much radical with increasing RF power.

Also, in the case of the ethylcyclohexane films, on the other hand, the optical transmittance was relatively lower than that of the methylcyclohexane films. From these results, we could make a conclusion that with increasing the RF power and number of carbon contents in the functional group precursor, the optical transmittance of organic thin film has decreases. This suggests that with increasing RF power, high degree cross-linking density of the electrons could be overlapped, resulting in formation of more stable polymers. The increase of absorption peak intensity with increasing the RF power can be explained with either the increase of carbon contents or the scattered reflection caused by plasma bombardment. This indicates that more high quality films can deposit using high RF power. Thus, we obtained better crystalline polymer thin films from the condition of 50 W RF power.

Figs. 5 and 6 show the changes of the dielectric constants and the leakage current densities obtained from the polymerized thin films that grown at 100 °C and various RF powers with

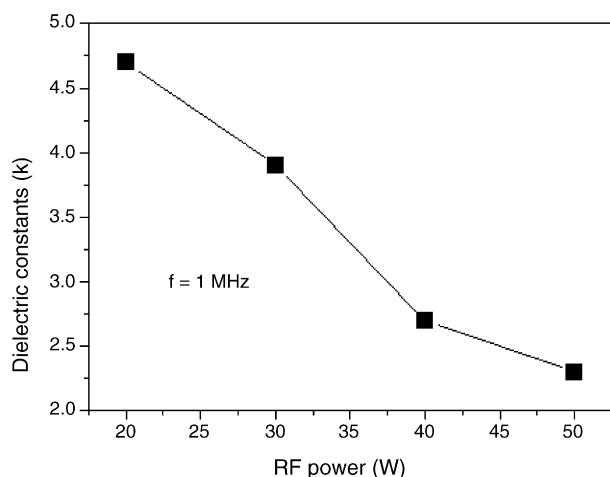


Fig. 5. Changes of dielectric constants as a function of RF powers about cyclohexane polymer thin films.

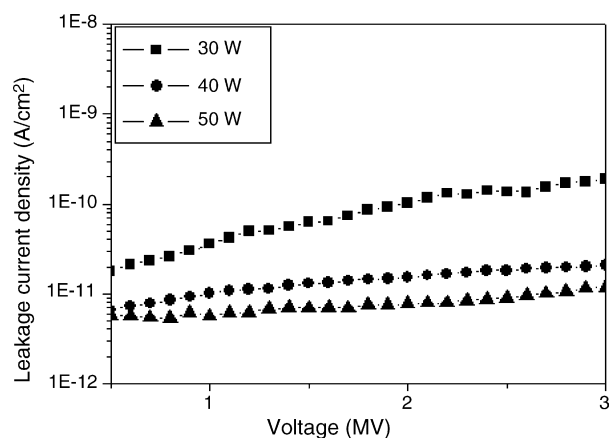


Fig. 6. Changes of leakage current density as a function of RF powers about cyclohexane polymer thin films.

Ar:H₂ = 1:1. Fig. 5 shows the variation of dielectric constants obtained from experimentally observed C–V curves using the MIS structure as a function of RF powers. With increasing RF power, the obtained dielectric constants decreased from 4.7 to 2.3. Fig. 6 shows the leakage-current densities for the cyclohexane thin films grown at 100 °C and various RF powers with Ar:H₂ = 1:1. From Fig. 6, we determined the insulating properties of the films by measuring the leakage-current density (*J*) with different applied fields (*F*). As the plasma power increase from 30 to 50 W, the leakage-current densities decreased and the breakdown did not occur until 1 MV. This indicates that the films have a compact structure with high density and are free of pin-holes, which lowers leakage current density and increases breakdown field. The best leakage current density at RF power of 50 W was measured to be about 10^{−11} A/cm² at 1 MV/cm, suggesting that this polymer-like thin film can be used as the insulating material microelectronic devices.

For comparative study, we also have deposited the plasma polymerized ethylcyclohexane thin films using ethylcyclohexane monomer precursor. Figs. 7 and 8 show the dielectric constants and leakage current densities for the ethylcyclohexane thin films that was grown at 100 °C and various RF powers

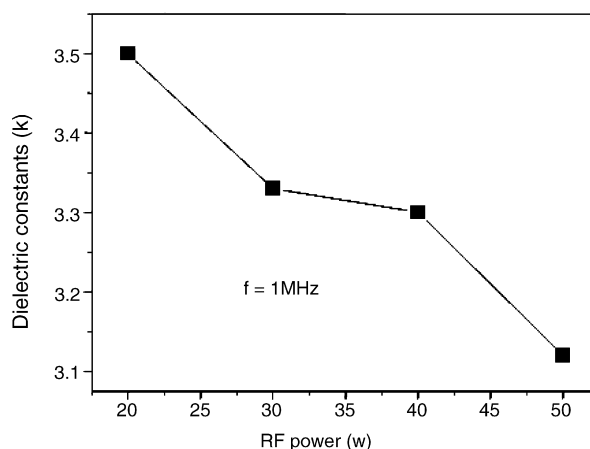


Fig. 7. Changes of dielectric constants as a function of RF powers about ethylcyclohexane polymer thin films.

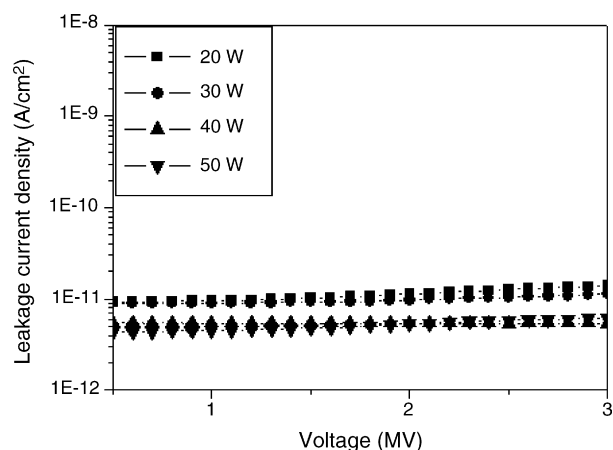


Fig. 8. Changes of leakage current density as a function of RF powers about ethylcyclohexane polymer thin films.

with Ar:H₂ = 1:1. Fig. 7 shows the variation dielectric constants using MIS structure as a function of RF power. The dielectric constants were decreased from 3.5 to 3.1 with increasing the RF power, resulting in the similar behavior as Fig. 5. From Fig. 8, we determined the insulating properties of the films by measuring the leakage current density (J) with different applied field (F). As the plasma power increased from 20 to 50 W, the leakage current densities decreased and the breakdown did not occur until 1 MV. This indicates that films have a compact structure with high density and are free of pin-holes, which lowers leakage current density and increases breakdown field. The best leakage current density of ethylcyclohexane film grown at RF power of 50 W was measured around 4.5×10^{-12} A/cm² at 1 MV/cm. From the electrical properties, we thus suggest that our polymer-like thin films can be used in both the insulating material for microelectronic devices.

4. Conclusions

Polymer-like organic thin films were deposited at the range of 25 and 100 °C temperature with a PECVD method using the organic precursors such as cyclohexane, methylcyclohexane, and ethylcyclohexane monomers. The best dielectric constant and leakage current density of a plasma polymerized organic thin film was obtained to be 2.3 and 10^{-12} A/cm² at 1 MV/cm, respectively. From our study, FT-IR and UV–vis results show that the as-grown transparent organic films have high degree cross-linking density with high transmittance. From our study, we realized that relatively more dense organic film with the ethylcyclohexane monomer than methylcyclohexane monomer because the ethyl group of ethylcyclohexane molecule produced much radical with increasing RF power.

Acknowledgments

Support of this research by the Korea–Germany Plasma Center Project through Ministry of Commerce, Industry, and Energy in Korea, is gratefully acknowledged. This work was also supported by the BK21 project of the Ministry of Education, Korea Research Foundation Grant (KRF-2005-005-J11902), and by the Center for Advanced Plasma Surface Technology at the Sungkyunkwan University.

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