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Synthesis of N-doped Ethylcyclohexane Plasma Polymer Thin Films with Controlled Ammonia Flow Rate by PECVD Method

Hyunjin Seo, Sang-Jin Cho, and Jin-Hyo Boo*

Department of Chemistry, Sungkyunkwan University, Suwon 440-746

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In this study, we investigated the basic properties of N-doped ethylcyclohexene plasma polymer thin films that deposited by radio frequency (13.56 MHz) plasma-enhanced chemical vapor deposition (PECVD) method with controlled ammonia flow rate. Ethylcyclohexene was used as organic precursor with hydrogen gas as the precursor bubbler gas. Additionally, ammonia (NH_3) gas was used as nitrogen dopant. The as-grown polymerized thin films were analyzed using ellipsometry, Fourier-transform infrared [FT-IR] spectroscopy, UV-Visible spectroscopy, and water contact angle measurement. We found that with increasing plasma power, film thickness is gradually increased while optical transmittance is drastically decreased. However, under the same plasma condition, water contact angle is decreased with increasing NH_3 flow rate. The FT-IR spectra showed that the N-doped ethylcyclohexene plasma polymer films were completely fragmented and polymerized from ethylcyclohexane.

Keywords : Thin film, PECVD, N-doped ethylcyclohexene plasma-polymer, Optical and chemical properties

I. Introduction

The existing semiconductor technology lets a silicone material make integrations by a top-down form developed by nano- or molecule technology merged with nanotechnology, biotechniques, and information technology and by a bottom-up method to constitute a device and a circuit with self-alignment of atoms and molecules. Those are common opinions of a majority of experts. In spite of the basic consensus by such experts, the progress in the nano and molecule device research field is very slow, and it is much worse now. There are many causes as possible reasons, but it is recognized that the following are still in question: 'the choice of the stable molecule and design technology,' 'self-alignment technology of atoms and molecules,' and 'technology to form a molecule and contact between the metal electrode for stability' [1,2]. The realization of nanosize electronics expects the development of bottom-up strategies such as chemical synthesis, self alignment of atoms and molecules, and self-assembled supramolecule. In fabricating the bio-application material, the diamond-like carbon [DLC] films have been a good candidate for some applications such as blood-contacting devices [3] and cell-contacting materials [4] due to their excellent mechanical properties [5-7]. In this work, nitrogen-doped ethylcyclohexane plasma poly-

* [E-mail] jhboo@skku.edu

mer was deposited by nitrogen injection during PECVD process with ammonia gas. Also, N-doped ethylcyclohexane plasma polymerized thin films were investigated on the surface properties such as surface energy and structural effects.

II. Experimental

The experiment was carried out in a homemade stainless steel PECVD system. Si(100) wafers were wet-cleaned by sonication with acetone, ethyl alcohol, distilled water, and isopropyl alcohol and dried by N_2 gas blowing. Also, substrates were dry-cleaned by *in situ* Ar plasma bombardment with 60 W for 15 min. The plasma polymer thin films were deposited by PECVD method. Ethylcyclohexane was utilized as organic precursor. Ethylcyclohexane was preheated up to 60°C and bubbled by 50 sccm of hydrogen gas. The deposition time was 1 hour to make the same thickness at 20 nm. The deposition pressure and temperature were 4.0×10^{-1} Torr and 25°C, respectively. The typical conditions of the PECVD process applied in this study for film deposition are 0, 5, 10, 15, and 25 sccm of NH_3 gas flow. The chemical bonding type of plasma polymer thin films was investigated by FT-IR spectroscopy (Vertex 70, Bruker Optik Gmbh, Ettlingen, Germany). Moreover, Raman shift of each thin film was investigated by FT-Raman spectroscopy [8]. Surface wettability was measured according to water contact angle measurements (Attension, KSV Instruments, Ltd., Helsinki, Finland). The *ex-situ* ellipsometry data of all investigated films were produced by an ellipsometer (GC5A automatic ellipsometry, Gaertner Scientific Corporation, Skokie, USA) at 632 nm to investigate the relationship of film density with the doping amount of nitrogen. Transmittance and bandgap energy of the N-doped ethylcyclohexane plasma polymer thin film were investigated by a UV-Vis spectrophotometer (Optizen 2120UV Plus, Mecasys Co., Ltd., Daejeon, Korea).

III. Results and discussion

Fig. 1 shows the images of water contact angle that obtained from the N-doped ethylcyclohexane plasma polymer thin films deposited with different NH_3 flow rate between 0 and 50 sccm under 60 W of plasma power. With increasing the NH_3 flow rate, water contact angle was gradually decreased from 29.64° to 21.41°, indicating that the film is changing with more hydrophilic surface due to relatively high nitrogen content in the films at large NH_3 flow rate. Decreasing of contact angle shows the increasing surface energies of the N-doped ethylcyclohexane plasma polymer thin films with increasing NH_3 flow rate. Additionally, decreasing of contact angle indicates an indirect cause of the increasing ammonia amounts in the N-doped ethylcyclohexane plasma polymer thin films. The change of water contact angles as a function of NH_3 flow rate was shown in the Fig. 2. The water contact angles were decreased by increasing the NH_3 flow rate, suggesting that the surface energies of the N-doped ethylcyclohexane plasma polymer thin films were changed into a more hydrophilic surface by the high flow rate of ammonia gas. When 50 sccm of NH_3 gas was inserted during the PECVD process, the water contact angle was decreased up to 21° which was the lowest value in this study.

We also deposited the N-doped ethylcyclohexane

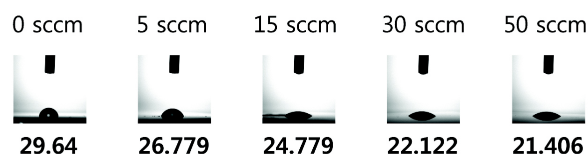

Figure 1. Contact angle images of the N-doped ethylcyclohexane plasma polymer thin films deposited at plasma power of 60 W and with changing the NH_3 flow rate from 0 to 50 sccm.

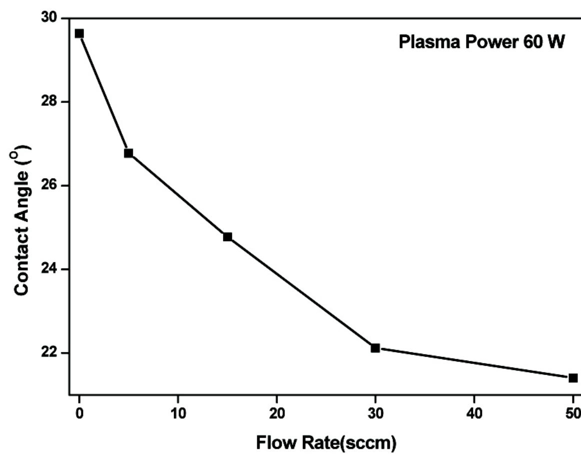

Figure 2. Contact angle changes of the N-doped ethylcyclohexane plasma polymer thin films deposited with changing the NH_3 flow rate from 0 to 50 sccm.

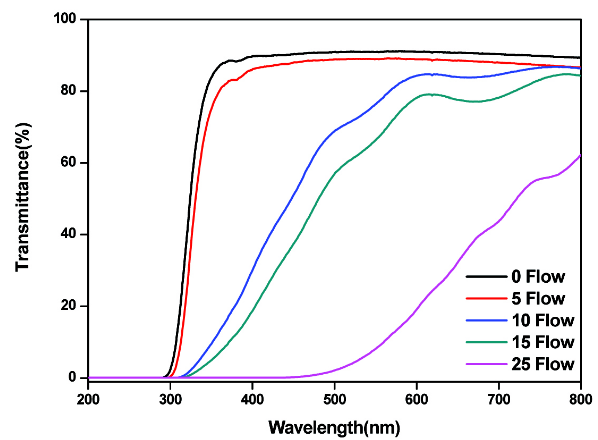

Figure 4. Changes of optical transmittance of the N-doped ethylcyclohexane plasma polymer thin films deposited at different NH_3 flow rate and fixed plasma power of 60 W.

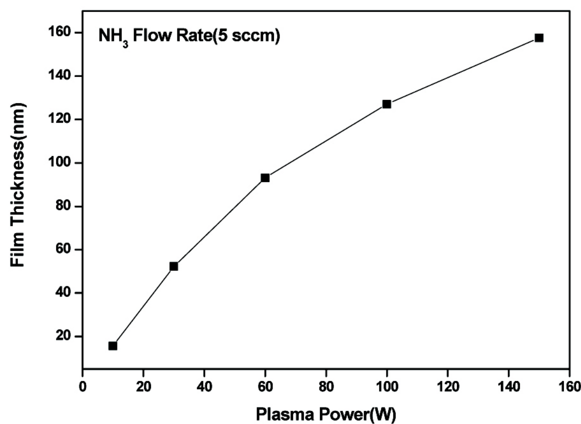

Figure 3. Variation of film thickness with plasma power. All N-doped ethylcyclohexane plasma polymer thin films were deposited under NH_3 flow rate of 5 sccm and different plasma power.

plasma polymer thin films with changing plasma power from 10 to 150 W under the same NH_3 flow rate of 5 sccm. Fig. 3 shows the variation of film thickness with different plasma power. The film thickness was determined by measuring a refractive index of the grwoing plasma films with ellipsometry. We took the refractive indices of Si and SiO_2 as 3.42009 and 1.53757, and we obtained the average refractive index value of the N-doped ethylcyclohexane thin films to be 1.432, respectively. From the Fig. 3, we can make conclusion that the film thickness is almost linearly increased with plasma power, signifying that the NH_3 flow rate is not much affected to the film growth rate within 50 sccm folw rate. This means that plasma power as well as pressure will be major parameter for influencing the growth rate of plasma polymerization.

Optical property of the as-grown plasma polymer thin films were also observed by UV-visible spectrometer. Fig. 4 shows the variations of optical transmittance obtained from the N-doped ethylcyclohexane plasma polymer thin films that grew with different NH_3 flow rate. From the Fig. 4, we found that the transmittance is decreased and the maximum level of survey spectrum is moved toward higher wavelength (so called red-shift) with increasing the NH_3 flow rate, reflecting different optical energy band gap as well as increasing refrective index. This indicates that with increasing NH_3 flow rate, the plasma polymerized films has larger optical band gap and more longer polymer chains with possibly different thickness. That's why there was decreasing tendancy of opical transmittance of the as-grwon N-doped ethylcyclohexane plasma polymer thin films with different optical band gap and thickness. The stretch vibration, bending vibration and bonding state of the

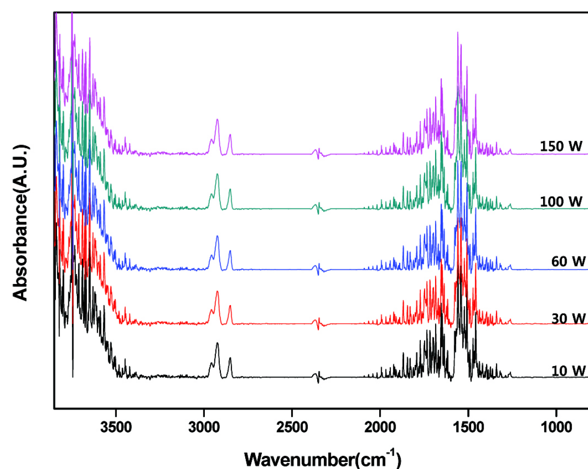

Figure 5. FT-IR spectra of the N-doped ethylcyclohexane plasma polymer thin films deposited at different plasma power and fixed NH_3 flow rate of 5 sccm.

plasma-polymerized thin films that grew with different plasma power were analyzed by FT-IR absorption over a range of 4,000 to 600 cm^{-1} as shown in the Fig. 5. The N-H bending peak and C-N stretching peak are appeared at 1,640-1,550 cm^{-1} and 1,350-1,000 cm^{-1}, respectively. While the C-Hx strecting and overtone peak is observed at 3,000-2,800 cm^{-1}, reflecting that NH_3 and ethylcyclohexane are fragmented and recombinized in the plasma, resulting in polymerization with their ion and/or radical sepcies on the substrate surface. From the FT-IR spectroscopy and contact angle measurements, the chemistry and surface energy of the N-doped ethylcyclohexane plasma polymer thin films were changed by nitrogen amounts and plasma power.

IV. Summary

N-doped ethylcyclohexane plasma polymer thin films were deposited on Si(100) by the PECVD method. Growth of N-doped ethylcyclohexane plasma polymer thin film is influenced by both NH_3 flow rate and plasma power. Thus, we can control the optical and chemical properties of the N-doped ethylcyclohexane plasma polymer thin film by controlling of either plasma power or ammonia flow rate. With increasing plasma power, film thickness is gradually increased while optical transmittance is drastically decreased. However, water contact angle is decreased with increasing NH_3 flow rate. IR spectra and the difference of the fingerprint region between monomer and N-doped ethylcyclohexane plasma polymer show that N-doped ethylcyclohexane plasma polymer thin film was fabricated by nitrogen gas injection during the PECVD process.

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