Hydrophobic properties of films grown by torch-type atmospheric pressure plasma in Ar ambient containing C6 hydrocarbon precursor

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Abstract−The direct deposition of polymeric films with a torch-type atmospheric pressure plasma using benzene, n-hexane and cyclohexane in Ar was performed on several substrates. The surface morphologies of the films deposited with n-hexane and cyclohexane were uniformly smooth for all deposition thicknesses, and the typical water contact angle on the films indicating the degree of hydrophobicity was about 85°. However, the films deposited using benzene had a micro-coarse surface morphology and showed a superhydrophobic property with a water contact angle exceeding 150°. Some trace of oxygen incorporation was shown in all films due to the plasma deposition process in an air ambient. The small amount of oxygenated species did not lead to a decrease of hydrophobicity of the films.

Key words: Atmospheric Pressure Plasma, Surface Treatment, Hydrophobicity, Contact Angle, C6 Hydrocarbon

INTRODUCTION

Hydrophobicity has attracted interest for applications such as self-cleaning, prevention of snow adherence, and reduction of contamination. The maximum water contact angle of a smooth hydrophobic surface is typically about 110°, but with a rough hydrophobic surface, the contact angle can be higher than 150° [1-3].

Plasma polymerization is useful for depositing thin lms from several hydrocarbon precursors. In particular, atmospheric pressure plasma is very useful because it does not require a vacuum chamber and associated pumping system [4,5]. Plasma processes have been widely studied and developed for preparing several hydrophobic lms [6-8]. In a previous study [9] where the substrate was textured with an appropriate roughness and the film was produced with atmospheric pressure plasma of CH_4/Ar, which creates an extremely smooth layer on at surfaces, a water contact angle higher than <150° was realized. This implies that films deposited using atmospheric pressure plasma with hydrocarbon precursors can have superhydrophobicity and an extremely high water contact angle as long as appropriate roughness is provided.

An optimized process is thus needed for deposition of hydrophobic hydrocarbon films under the conditions of atmospheric pressure plasma. When using hydrocarbon precursors with different structures such as benzene, n-hexane, and cyclohexane for plasma polymerization, different surface properties will be obtained due to the differences in the molecular shape and electronic structure of each hydrocarbon precursor. This paper presents the surface characteristics of films deposited with a torch-type atmospheric pressure plasma using C6 hydrocarbon precursors such as benzene, n-hexane, and cyclohexane diluted with Ar gas.

EXPERIMENTAL

The deposition of hydrocarbon films on a substrate using atmo-spheric pressure plasma was carried out with a dielectric barrier discharge (DBD) torch plasma system as shown in Fig. 1. The AC powered electrode was composed of stainless steel with an out-diameter (OD) of 12 mm; the dielectric material for the DBD system was a quartz tube with a 20 mm OD and 2 mm thickness. A grounded electrode composed of a stainless steel net had the appearance of a wrapped quartz tube. Argon (99.999% purity) was used as a carrier gas and its total ow rate was fixed at 1 L/min. A separate gas stream containing the precursor was generated by owing Ar through a bubbler containing bezene, n-hexane, and cyclohexane liquid. The reagent gas stream ow rate was varied to obtain a certain concentration of precursor (1-5 vol%) in the mixed gas stream. The substrates were placed at a fixed position, located 1 mm apart from the DBD plasma torch. The water contact angle, as a measure of the hydrophobicity of the films, was evaluated with a lab-made analysis system. All measurements were carried out under ambient conditions (60% RH, ~20). X-ray photoelectron spectroscopy (XPS) was used to analyze the surface chemistry of the hydrocarbon film surfaces. XPS data were obtained with a VG Multilab using Mg-K_α with a X-ray source (1,253.6 eV) operated at 15 keV and 300 W. Chemical analysis of the films was monitored by Fourier-transform infrared spectroscopy (FTIR, FT-3000 MX Excalibur). The surface roughness of the hydrocarbon film was examined using atomic force microscopy (AFM, Nano Scope Multimode) and a silicon nitride tip was used as a probe. The thicknesses and the surface morphology of the lms deposited with benzene, n-hexane, and cyclohexane were monitored with an ultra high resolution scanning electron microscope (UHR-SEM, Hitachi S-4800).

RESULTS AND DISCUSSION

The thickness of the films on the Si substrate was measured by cross-sectional SEM to analyze the deposition rate. The deposition conditions were as follows: an applied voltage of 9 kV; benzene, n-hexane, and cyclohexane concentration of 1, 3, and 5 vol% in Ar; a gap from the DBD-torch tip to the substrate surface of 1 mm;

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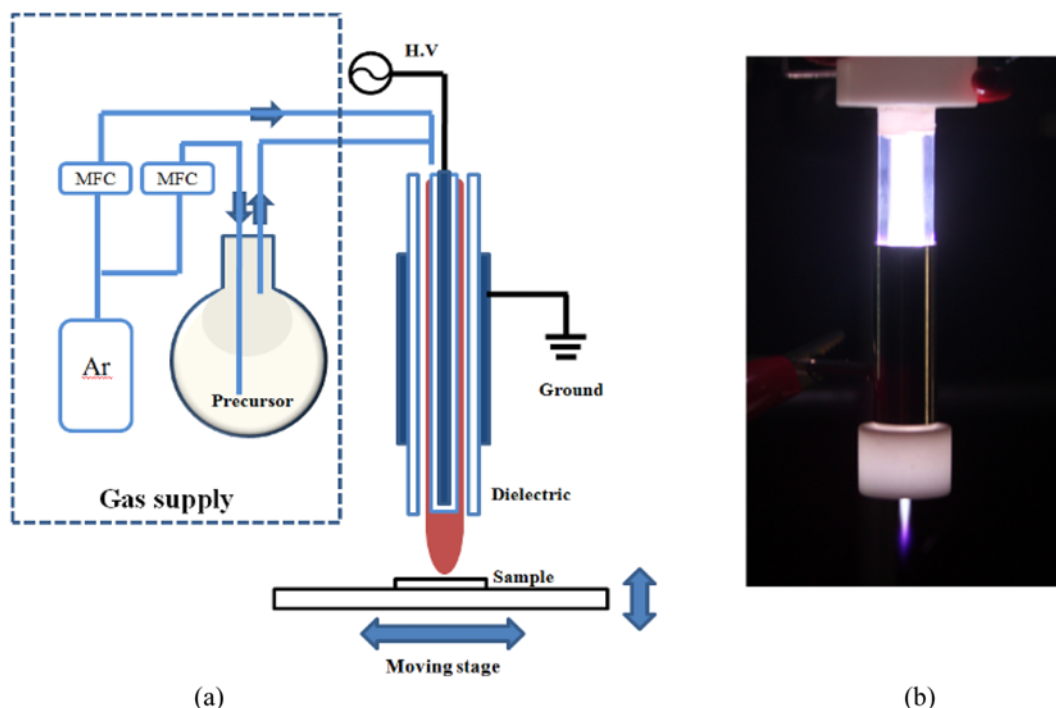E-mail: wglee@kangwon.ac.kr

Fig. 1. (a) Schematic diagram of torch-type atmospheric pressure plasma. (a) Deposition system; (b) Real shape of plasma generation in air.
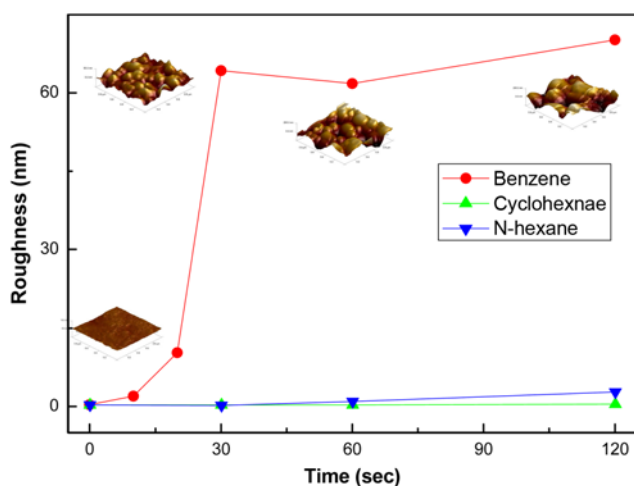

Fig. 2. Surface roughness of the films deposited with benzene, cyclohexane, and n-hexane, which were measured by AFM according to the deposition time.

and a total gas flow rate of 1 L/min. The thickness of the films deposited with n-hexane and cyclohexane for 5 min was ~1.0, ~3.0, and ~6.5 μm at precursor concentration of 1, 3, and 5 vol%, respectively. The resulting difference in the film deposition rate was not exhibited when the precursors were n-hexane and cyclohexane. Also, the films had an extremely smooth surface morphology on the flat substrates, as shown in Fig. 2. However, the film deposited with benzene precursor showed thickness of 2.5, 4.8, and 8.5 μm at the same concentrations, respectively. The growth rate of the film from benzene was almost twice that of the films prepared with n-hexane and cyclohexane at the same deposition conditions. From a comparison of surface roughness, the film prepared with benzene had a

surface morphology with relatively greater micro-coarseness and showed dependence of deposition time. The average roughness was about 60 nm at deposition time greater than 30 sec.

The concentrations of reactive species in n-hexane/Ar and cyclohexane/Ar plasma were not high enough for condensation and formation of particulates in the gas phase. This implies that the reactive radical concentration in the plasma was not high enough for solid particulate formation in the gas phase [10,11], and consequently the reactive species diffused to the substrate surface where heterogeneous reactions took place. In the case of benzene, it has an optimum molecular structure in terms of increasing the probability of particle formation in the gas phase during the plasma deposition process [12,13]. This led to the production of a film with rough surface morphology as shown in Fig. 3.

The chemical composition of the lm was determined with XPS. Fig. 4 presents the XPS survey spectra of the hydrocarbon lms. Although the precursor gas contained only carbon and hydrogen, the plasma-deposited lms had an oxygen element. This was due to the activation of air in the atmospheric plasma. The C 1s high resolution spectra did not show discernible structures other than a broad main peak at 285 eV. A small asymmetric tail in the high binding energy side is ascribed to oxygenated species. The O 1s peak was centered at <533 eV [14]. It is noteworthy that the lm deposited in atmospheric pressure plasmas contained oxygenated species, but still had hydrophobic water contact angle. The oxygen and water molecules in the air were also activated in the plasma [15]. If the detected oxygenated species are mostly present at the surface, a fairly hydrophilic surface will be produced, which will give a low water contact angle.

Fig. 5 presents the FTIR spectra of the plasma-deposited lms using benzene, n-hexane, and cyclohexane. The peaks at 2,960, 2,930, 2,870, 1,450, and 1,380 cm^{-1} correspond to the vibrations of asym-
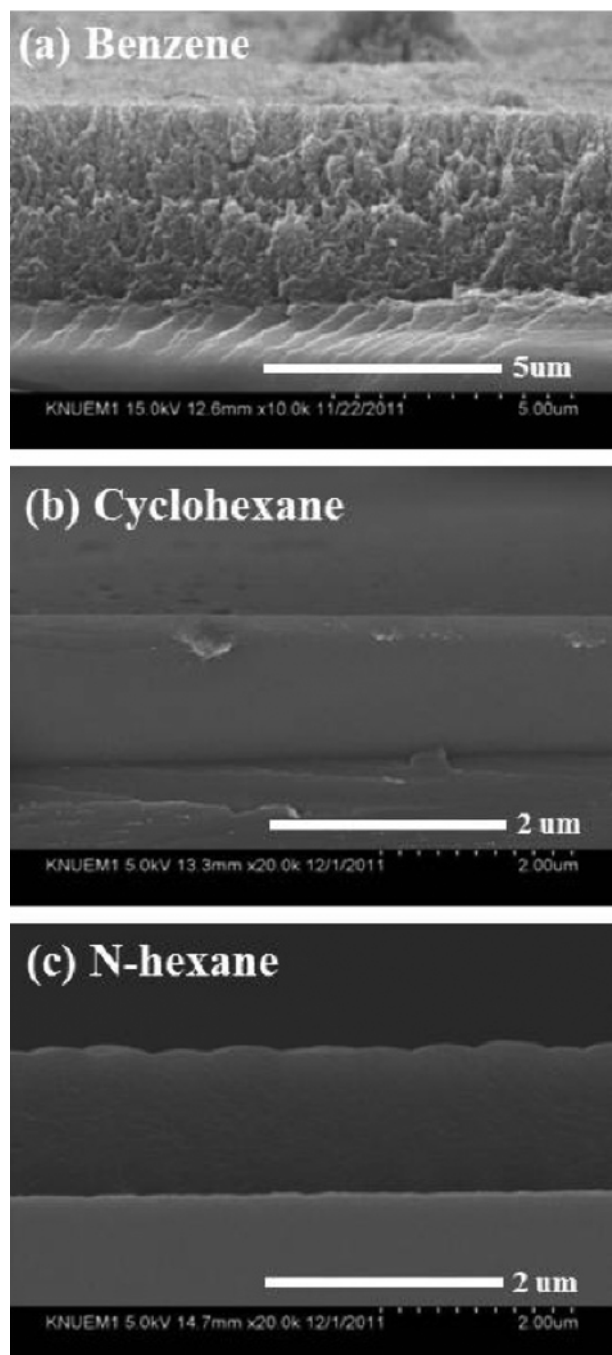
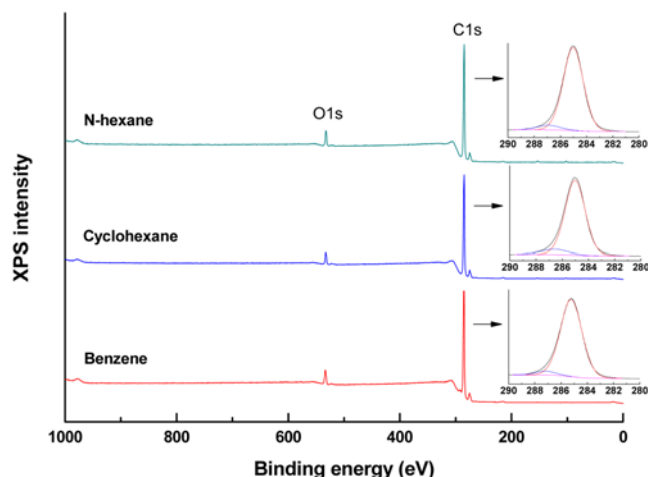**Fig. 3. Cross-sectional SEM images of the films deposited from benzene, cyclohexane, and n-hexane.**

Fig. 4. XPS spectra and high resolution C1s spectra positioned at 285 eV of the hydrocarbon films deposited with benzene, n-hexane, and cyclohexane precursors in the Ar plasma (precursor concentration=1 vol%, applied voltage=9 kV, deposition time=5 min).
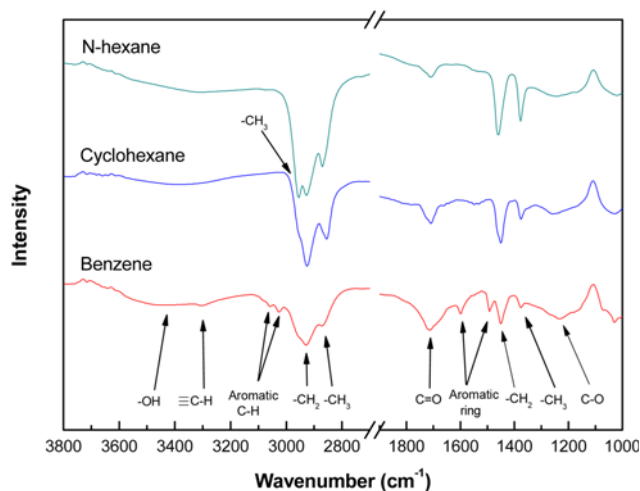

Fig. 5. FTIR spectra of the hydrocarbon films deposited with benzene, n-hexane, and cyclohexane precursors in Ar plasma (precursor concentration=1 vol%, applied voltage=9 kV, deposition time=5 min).

metric CH_3 stretching, asymmetric CH_2 stretching, symmetric CH_3 stretching, CH_2 deformation, and CH_3 deformation, respectively [16]. Especially, in the case of benzene, the peak at 3,305 cm^{-1} is assigned as CH triple bond stretching, and the peaks related to the aromatic rings at 1,600-1,500 cm^{-1} indicate that the benzene molecule is preserved to some degree in the deposited film. The broad peak at 3,450 cm^{-1} was due to the hydroxyl groups, and the weak peaks at 1,710 and 1,610 cm^{-1} can be assigned to carbonyl groups (C=O). The peaks at 1,105 and 1,260 cm^{-1} are ascribed to C-O vibrations. These oxygenated species are attributed to activation of air molecules inside the atmospheric plasma. Compared to the case of

using cyclohexane, the lm from n-hexane had a signicant symmetric CH_3 stretching peak (2,960 cm^{-1}). The CH_3 groups in the cyclohexane precursor lm are believed to have been generated by recombination reactions of the cyclohexane fragments.

Images of water droplets on the films with benzene, n-hexane, and cyclohexane produced on Si water, alumina, and a slide glass substrate are shown in Fig. 6. The water contact angles are plotted as a function of deposition time. The maximum contact angle was about 85° regardless of the type of substrates and film thickness. This value is very close to the water contact angle of polycarbonate (about 83°) [17]. It was reported that CH_4/Ar plasma produces an extremely smooth polymer lm on a surface containing CH_2 backbones and CH_3 side groups [9]. On flat substrates, the water contact angle of the CH_4/Ar plasma film was ~90°, but on a rough surface such as cotton, the contact angle reached 150°. The water contact
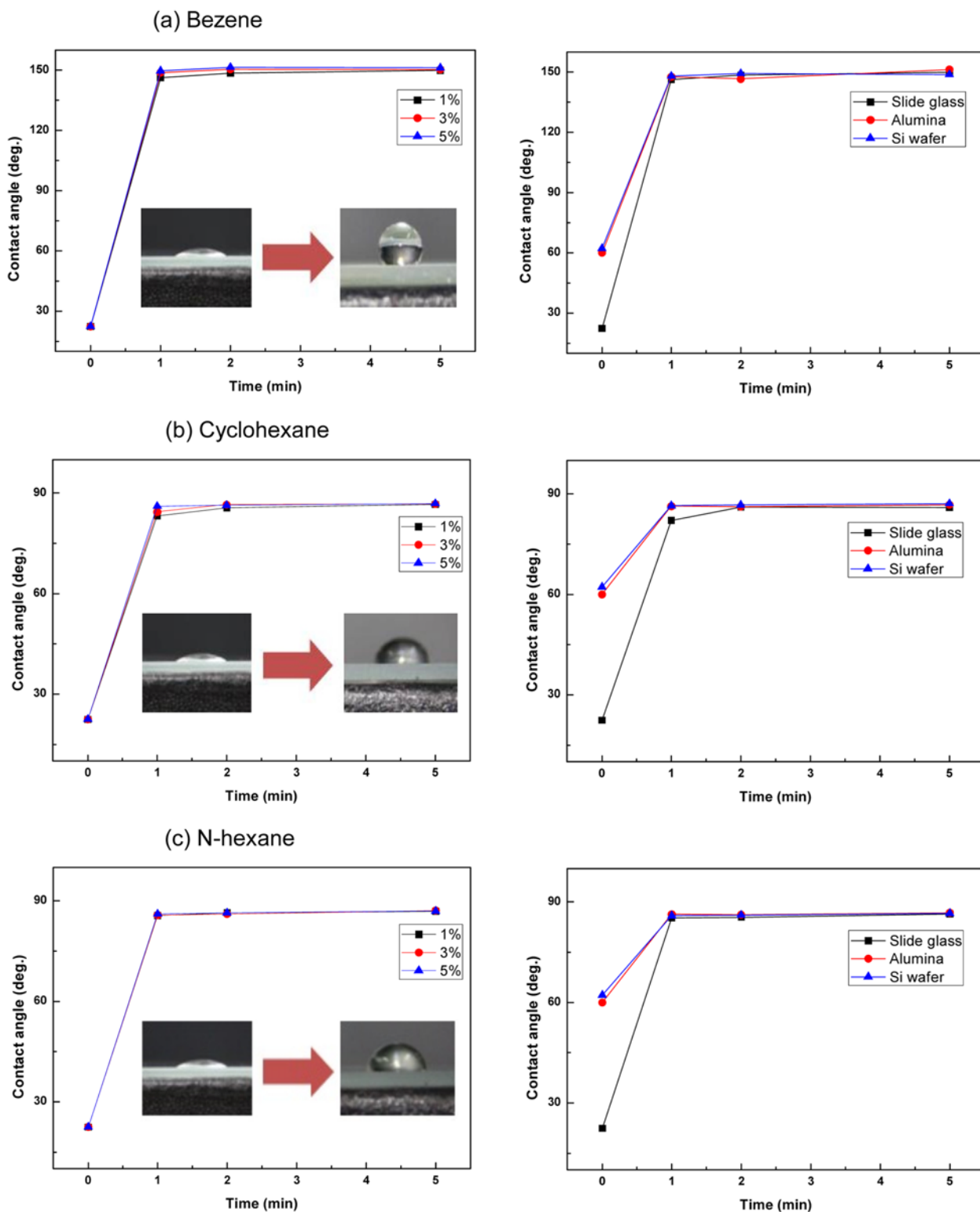
Fig. 6. Water contact angle on the films deposited with benzene, cyclohexane, and n-hexane precursors in Ar plasma according to the deposition time. The left side figures show the effect of precursor concentration and the right side figures show the effect of the substrate. Optical images present the initial water droplet on a bare silicon substrate and a droplet on a silicon substrate coated with a hydrocarbon film for 5 min.

angle of films deposited with benzene was more than 150°, thus showing superhydrophobic surface properties.

These results suggest that when a stable process for moderate

hydrophobic films is applied, the degree of hydrophobicity can be controlled by modifying the surface roughness of the substrates. The strong advantages of atmospheric pressure plasma can be exploited

for continuous in-line manufacturing of hydrophobic hydrocarbon film using various precursors, and it can be applied to any surface regardless of the type of substrate.

CONCLUSION

This study showed that a torch-type atmospheric pressure plasma with benzene/Ar, n-hexane/Ar and cyclohexane/Ar can be used to effectively deposit hydrophobic lms on several flat substrates. The films prepared with n-hexane and cyclohexane precursor showed a relatively smooth surface morphology and had a uniform water contact angle along with constant film deposition thickness on the flat substrates. The films from n-hexane/Ar or cyclohexane/Ar plasma exhibited a water contact angle of about 85°. Otherwise, the films deposited with benzene precursor showed almost two-fold greater deposition rate at the same conditions relative to those deposited with n-hexane and cyclohexane. The films produced using benzene showed a micro-coarse surface morphology and revealed a superhydrophobic surface property with a water contact angle of over 150° due to the coarse surface.

REFERENCES

1. S. Shibuichi, T. Onda, N. Satoh and K. Tsujii, *J. Phys. Chem.*, **100**, 19512 (1996).
2. D. Öner and T. J. McCarthy, *Langmuir*, **16**, 7777 (2000).
3. Z. Yoshimitsu, A. Nakajima, T. Watanabe and K. Hashimoto, *Langmuir*, **18**, 5818 (2002).
4. R. Foest, F. Adler, F. Sigeneger and M. Schmidt, *Surf. Coat. Technol.*, **163/164**, 323 (2003).
5. H. KaKiuchi, Y. Nakahama, H. Ohmi, K. Yasutake, K. Yoshii and Y. Mori, *Thin Solid Films*, **479**, 17 (2005).
6. T. Ishizaki, N. Saito, Y. Inoue, M. Bekke and O. Takai, *J. Phys. D: Appl. Phys.*, **40**, 192 (2007).
7. K. Teshima, H. Sugimura, Y. Inoue, O. Takai and A. Takano, *Appl. Surf. Sci.*, **244**, 619 (2005).
8. S. W. Myung and H. S. Choi, *Korean J. Chem. Eng.*, **23**, 505 (2006).
9. J. H. Kim, G. M. Liu and S. H. Kim, *J. Mater. Chem.*, **16**, 977 (2006).
10. M. Mikikian, L. Couedel, M. Cavarroc, Y. Tessier and L. Boufendi, *Eur. Phys. J. Appl. Phys.*, **49**, 13106 (2010).
11. K. Takahashi and K. Tachibana, *J. Vac. Sci. Technol. A*, **19**, 2055 (2001).
12. J. Perrin, J. Schmitt, C. Hollenstein, A. Howling and L. Sansonnents, *Plasma. Phys. Controlled Fusion*, **42**, B353 (2000).
13. K. A. Foglein, I. Babievskaya, P. T. Szabo and J. Szepvolygi, *Plasma Chem. Plasma Process*, **23**, 233 (2003).
14. J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of X-ray photoelectron spectroscopy*, Physical Electronics Inc., Minnesota (1995).
15. S. H. Kim, J. H. Kim and B. K. Kang, *Langmuir*, **23**, 8074 (2007).
16. S. H. Lee, Z. R. Dilworth, E. Hsiao, A. L. Barnette, M. Marino, J. H. Kim, J. G. Kang, T. H. Jung and S. H. Kim, *ACS Appl. Mater. Interfaces*, **3**, 476 (2011).
17. D. S. Won, T. K. Kim and W. G. Lee, *Surf. Interface Anal.*, **42**, 1209 (2010).