

Long-Lasting Hydrophilicity on Nanostructured Si-Incorporated
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Received August 13, 2010. Revised Manuscript Received September 19, 2010

We investigated the long-lasting hydrophilic behavior of a Si-incorporated diamond-like carbon (Si-DLC) film by varying the Si fraction in DLC matrix through oxygen and nitrogen plasma surface treatments. The wetting behavior of the water droplets on the pure DLC and Si-DLC with the nitrogen or oxygen plasma treatment revealed that the Si element in the oxygen-plasma-treated Si-DLC films played a major role in maintaining a hydrophilic wetting angle of $< 10^\circ$ for 20 days in ambient air. The nanostructured patterns with a roughness of ~ 10 nm evolved because of the selective etching of the carbon matrix by the oxygen plasma in the Si-DLC film, where the chemical component of the Si-Ox bond was enriched on the top of the nanopatterns and remained for over 20 days.

Introduction

Hydrophilic or superhydrophilic surfaces have been heavily studied for the various applications, such as water harvesting, self-cleaning, antifog, antibacteria, and cell culturing.^{1–4} Several methods, including TiO₂ coatings, surface modifications through dry or wet etching, and UV/O on various soft and hard materials, have been suggested for obtaining hydrophilic surfaces. Among these methods, plasma treatment using a dry etching technique is considered to be an important fabrication method for highly hydrophilic surfaces, and this method subsequently improves the adhesion strength between two different material systems, such as a polymer and a thin metal film and a polymer and an organic cell. Additionally, this surface treatment improves the wettability between water and solid surfaces.^{5–8} Hydrophilic surfaces have also been examined as biointerfaces, such as biocoatings of TiN, polymers, and amorphous carbon films, resulting in a better interfacial adhesion and biocompatibility for cells on the target surfaces.^{9–13} However, the long-term stability of the hydrophilic surfaces is a major concern for practical applications because of

the relatively high surface energy of the hydrophilic surfaces. Hydrocarbons can easily attach to the hydrophobic surfaces under air or humid conditions, reducing the surface energy and, in turn, deterring the hydrophilicity of the surface.¹⁴ A previous report suggested that the free siloxanes on polymeric materials migrate from the bulk to the surface through a porous hydrophilic silica-like layer.¹⁵

Diamond-like carbon (DLC) films are biocoating materials that have been intensively exploited in biological fields because of their well-known biocompatibility and mechanical performance characteristics, including antiwear, anticorrosion, and mechanical stability in aqueous and biological environments. DLC films do not exhibit any significant side effects for transplant materials or cell growth.^{16,17} In recent applications, functional elements such as F,¹⁸ P,¹⁹ and Si^{17,20} have been doped into a DLC matrix to improve its functionality, including its biocompatibility, wettability, and mechanical performance. In particular, Si-incorporated DLC (Si-DLC) films exhibit improved mechanical properties and corrosion resistance as well as biocompatibility.¹⁷ Roy et al.²¹ showed that a hydrophilic DLC was obtained using nitrogen and oxygen plasma treatment with a significant increase in the polar component on the surfaces. It also showed that hydrophilic DLC surface exhibited a better biocompatibility

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during in vitro tests because of its higher surface energy state, where a surface treatment with nitrogen or oxygen plasma increased the hydrophilic nature of the amorphous hydrogenated carbon or DLC (or a-C:H) films. However, because this hydrophilic surface is stable for only short period of a few days or even a few hours with its high surface energy, the hydrophobic nature of the film is recovered through the addition of new connections with components such as C, O, N, and hydrocarbons in ambient air, which is known as the aging phenomenon.^{22,23} Therefore, for a wide range of DLC film applications, the development of long-lasting hydrophilic surfaces should be examined in detail.

In this work, a long-lasting hydrophilic surface was investigated for a nanostructured Si-DLC film with a certain Si fraction range in the DLC matrix using a plasma treatment. The wetting behavior of water droplets on the pure DLC and the Si-DLC with the nitrogen or oxygen plasma treatments revealed that in the oxygen-plasma-treated Si-DLC films the Si element played a major role in maintaining the hydrophilicity with contact angle below 10° for 20 days in ambient air. The hydrophobic recovery of the Si-DLC films was traced with respect to the Si content in the Si-DLC matrix in terms of the binding energy of the DLC and Si-DLC films before and after aging by analysis with an X-ray photoelectron spectroscopy (XPS). The surface observation using atomic force microscopy (AFM) and transmission electron microscopy (TEM) showed that the oxygen-plasma-treated Si-DLC contained nanopatterns with a roughness of ~10 nm as well as a chemical enrichment of the Si-Ox near the surface region due to the selective etching of the carbon matrix by the oxygen plasma in the Si-DLC film. The pure DLC and Si-DLC films were exposed to air and water to examine any hydrocarbon contamination on the hydrophilic surfaces. These results showed that the hydrophobic recovery was significantly retarded on the samples that were immersed in water.

Experimental Details

1. Sample Preparation. The DLC and Si-DLC films were deposited on a P-type silicon substrate (100) through a radio-frequency-plasma assisted chemical vapor deposition (r.f.-PACVD) with a frequency of 13.56 MHz. The details of the deposition procedure were reported elsewhere.²⁴ Benzene and a mixture of benzene and diluted silane (SiH₄:H₂ 10:90) gases were used as the precursors for the deposition of the DLC and Si-DLC films, respectively. The substrates were initially cleaned with argon discharge for 5 min at a bias voltage of -400 V and a pressure of 0.49 Pa. An interlayer of amorphous silicon (a-Si:H) was deposited at a thickness of 2.5 nm to ensure that the DLC and Si-DLC films adhered better on the Si (100) wafers. Then, the DLC and Si-DLC films were deposited on the Si wafers at a bias voltage -400 V and a working pressure of 1.33 Pa for 10 min and 11 min 40 s, respectively, resulting in thicknesses of 1.0 and 0.55 μm, respectively, that were measured with an alpha-step profile meter (Alpha-step IQ surface profiler, KLA-Tencor). XPS (PHI 5800 ESCA system, Physical Electronics) confirmed that the Si fraction in the as-deposited DLC and Si-DLC films varied from 0 to 3.25 at %. The structure and mechanical properties of the Si-DLC film were previously investigated in detail.^{24–26} The atomic bond structures of the Si-DLC films were compared using Raman

spectroscopy (LabRAM HR, HORIBA Jobin-Yvon) before and after the films were modified.

Then, the DLC and Si-DLC films were modified with oxygen and nitrogen plasma in an r.f.-PACVD chamber at a bias voltage of -400 V and a pressure of 1.33 Pa for 10 min. The oxygen plasma treatment was used to etch the DLC and Si-DLC films, resulting in reductions of 0.2 and 0.06 μm in the thickness, respectively. For comparison purposes, an amorphous silicon (a-Si:H) film with a thickness of 25 nm was prepared on a Si substrate at a bias voltage of -400 V and a pressure of 1.33 Pa for 10 min, and this film was also modified with oxygen plasma under the same conditions as those of the other films to determine the effects of the Si fraction in the Si-DLC matrix.

2. Wetting Angle Measurement and Surface Analysis.

We characterized the wettability of the film surface by measuring the contact angles of deionized (DI) water droplets. For these experiments, 5 μL of DI water was dropped on the film surface, and the contact angle was measured using a contact angle goniometer (Rame-Hart) in ambient air at 15 °C with a relative humidity of 20–35% every 6 (first 3 days) and 24 h (after 3 days) for 20 days. The reported contact angles were collected by averaging measurements from five different spots on each sample. The surface energy of the samples was characterized using Owens method²⁷ with DI water and formamide liquid to investigate the aging behavior for 20 days. After the oxygen plasma treatment, both the pure DLC and the Si-DLC films were exposed to air and immersed in DI water, and the wetting angle of each sample was measured for 15 days using the same method as that described above to investigate the effects of air contamination on the long-term wettability.

The XPS measurements were performed for five samples, including the as-deposited Si-DLC films and the Si-DLC films with the N₂ and O₂ plasma treatments that were aged for 1 and 20 days. The samples were cleaned by a nitrogen gas blower before they were inserted into the spectrometer, but no cleaning process was performed once the samples were loaded. An Al Kα (1486.6 eV) X-ray source was used as the excitation source, and the anode was maintained at 250 W, 10 kV, and 27 mA at a chamber pressure of 2.67 × 10⁻⁸ Pa with a beam spot size of 400 μm × 400 μm. The peak position was calibrated using the C 1s peak at 284.6 eV. The curve fitting was carried out using a mixture of Gaussian and Lorentzian functions. An AFM (XE-70, Park Systems) that was equipped with a noncontact cantilever (910M-NCHR model, length = 125 μm, width = 30 μm, thickness = 4 μm, resonance frequency = 330 kHz, force constant = 42 N/m) was employed to observe the surface morphology of the films. The noncontact mode was chosen for these measurements with a scanning speed of 0.5 Hz and a scanning area of 1 μm × 1 μm. The surface roughness (R_q mode) was estimated by averaging three different profiles for each sample.

We prepared cross-sectional images of the specimens using a dual-beam focused ion beam system (FIB, Nova 600, FEI company) and analyzed them using a high-resolution transmission electron microscopy (HR-TEM, Tecnai, FEI). The microstructure and the chemical composition through the cross-section of the plasma-treated Si-DLC with a Si content of 1.24 at % were analyzed using HR-TEM at 200 kV in combination with scanning transmission electron microscopy (STEM)/energy dispersive X-ray spectrometry (EDS). Before the TEM sampling, a Cu thin layer of ~30 nm was deposited onto the Si-DLC film to prevent the ion beam from damaging the Si-DLC surface during the FIB sectioning.

Results and Discussion

Figure 1a,b show the droplet images on the Si-DLC film surfaces that were modified with nitrogen and oxygen plasma taken after they were exposed to ambient air for 1 (left column)

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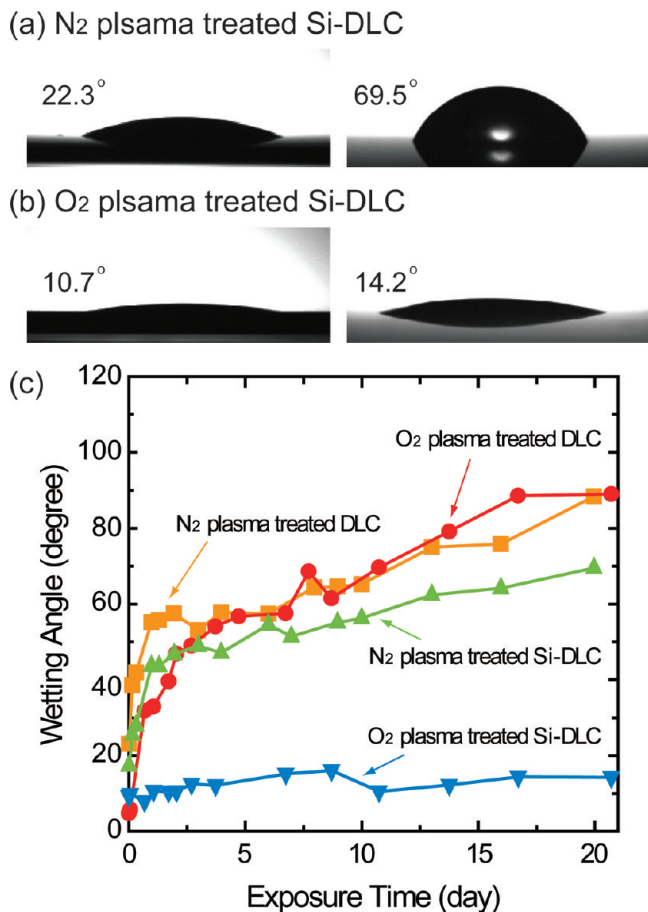


Figure 1. Optical microscopic images of the DI water droplets on (a) the nitrogen- and (b) the oxygen-plasma-treated Si-DLC films with increasing exposure time to ambient air. The left and right columns were taken on the first and 20th days after the plasma treatment, respectively. (c) Contact angle behaviors of the nitrogen- and oxygen-plasma-treated DLC and Si-DLC films as a function of the exposure time in ambient air.

and 20 days (right column). For the Si-DLC films that were modified with the nitrogen plasma, the wetting angle changed from 17.4 to 22.3° within 6 h and reached a value of 69.5° after 20 days in Figure 1a,c. However, the Si-DLC with the oxygen plasma treatment maintained its hydrophilic nature, with a wetting angle from 10 to 14° in ambient air for 20 days in Figure 1b,c. In Figure 1c, the detailed measurements indicated that the hydrophilic surface of the Si-DLC films that were modified with oxygen plasma lasted for a long period of time. The wetting angle of the DLC films that were modified with nitrogen and oxygen plasma increased to the values for the untreated films after 20 days, whereas the Si-DLC film that was modified with oxygen plasma maintained its initial hydrophilic properties for a longer period of time. Therefore, the Si component in the DLC matrix, along with oxygen treatment, played a role in maintaining the hydrophilic nature of the films under ambient air.

The effects of the Si component in the DLC film on the wetting behavior of the Si-DLC films were further studied to examine the long-term stability of the hydrophilicity at various Si concentrations from 0 to 3.25 at %. These films were also compared with the a-Si:H film (equivalently higher Si fraction near 100 at %) in Figure 2. Prior to the surface modification using oxygen plasma, the wetting angles of all of the films ranged from 73 to 78° and remained unchanged as the aging time increased through

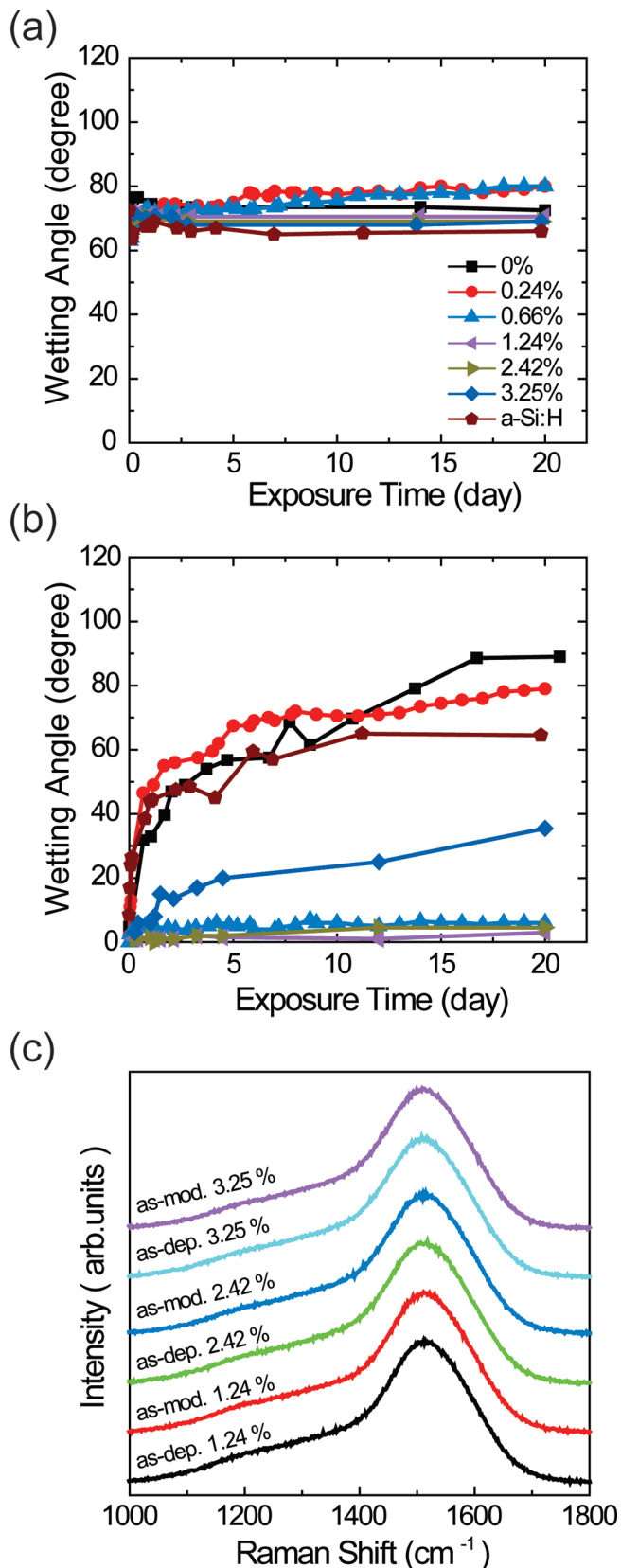


Figure 2. Contact angles of (a) the as-deposited and (b) the oxygen-plasma-treated Si-DLC films as a function of the Si at % fraction in the Si-DLC films at different exposure times to ambient air. (c) Raman spectra of the Si-DLC films before (as-dep.) and after (as-mod.) the oxygen plasma treatment.

exposure to ambient air (Figure 2a). All of the Si-DLC films had superhydrophilic surfaces with contact angles of < 5° just after

(or within 1 h of) the surface modification with oxygen plasma. For the pure DLC film with a Si fraction of 0 at %, the hydrophobic nature of the film was rapidly recovered within 5 days, whereas the Si-DLC films with specific Si fractions ranging from 0.66 to 2.42 at % maintained their hydrophilic nature for at least 20 days. The hydrophobicity of the Si-DLC films with higher Si fractions (2.66 at %) exhibited a gradual recovery. Notably, in Figure 2, the amorphous Si (a-Si:H) surface with the oxygen plasma treatment exhibited a rapid recovery from the superhydrophilic state (almost near 5°) to the hydrophobic state (~65°) within 5 days. This value was similar to the value for the as-deposited a-Si:H film in Figure 1e. Therefore, for the Si-DLC films, a specific range of Si fraction corresponded to the long-term stability of the hydrophilicity that was associated with the oxygen plasma treatment.

In Figure 2c, the shape of the Raman spectra did not significantly change for the Si-DLC films with various Si fractions before and after the oxygen plasma treatment. All of the spectra were typical of hydrogenated amorphous carbon (a-C:H) and were characterized by a broad D-peak shoulder near $1318.1 \pm 2.4 \text{ cm}^{-1}$ and a G-peak near $1523.2 \pm 1.6 \text{ cm}^{-1}$. The G-peak was induced by the lattice vibration in the graphite-like hexagonal ring, and the D-peak was associated with the existence of graphitic clusters with short-range crystallinity.²⁶ The measurements in Figure 2c indicated that chemical bond structures of the Si-DLC films were relatively unaffected by the oxygen plasma treatment.

In Figure 3, the binding energies of the Si-DLC films were measured using the XPS analysis before and after the plasma treatment at various aging times to determine the main factors in maintaining the hydrophilic properties for a longer period of time. The deconvoluted binding energies of C 1s and Si 2p are shown for the as-deposited Si-DLC films (2.66 at % Si) in Figure 3a. Figure 3a shows that the C 1s spectrum was composed of two peaks corresponding to the sp^2 (C=C) and sp^3 (C-C) bonds at 284.4 and 285.5 eV, respectively.^{21,28,29} The Si 2p spectrum was deconvoluted into three components with a strong peak for the Si-C bond at 100.5 eV and small peaks for the Si-C and SiO₂ bonding at 100.5 and 103.4, respectively.^{21,30,31} For the as-modified Si-DLC film with nitrogen plasma, the C 1s spectrum (Figure 3b) was deconvoluted into several components for the host peaks of the C=C and C=N bonds at 284.4 and 285.7 eV, respectively, along with the small peaks for the C-C, C=O, and Si-C bonds at 285.5, 288, and 282.4 eV. The Si 2p spectrum was also deconvoluted into three components for the host peak of the Si₃N₄ bond at 102.3 eV and the small peaks for the Si-C and SiO₂ bonds at 100.5 and 103.4, respectively.^{32,33} The spectrum of the Si 2p region indicated that the nitrogen plasma treatment reduced the Si-C bonded network, and the nitrogen removed a considerable amount of carbon and led to formation of the C=N and Si₃N₄ bonded networks on the surface. However, after 20 days of exposure to ambient air, the C=N bonded network was clearly reduced in the C 1s region, but the C=O bonding slightly increased. The deconvoluted spectrum of the Si 2p region

exhibited a clear reduction in the Si₃N₄ bonding and the presence of a small amount of Si-N bonding. The bonds between C and -N and Si and -N were polar components with electronegativities of 0.5 and 1.2 Pauling units, respectively.^{21,34-36} The presence of the C=N and Si₃N₄ bonding on the surface of the Si-DLC film that was modified with nitrogen plasma increased the polar component of the film's surface energy, which increased the hydrophilicity of the film. As the exposing time increased in ambient air, the C=N and Si₃N₄ bonding significantly decreased for the Si-DLC film that was modified with nitrogen plasma, and the film became hydrophobic.

In Figure 3d, the C 1s spectrum for the Si-DLC film that was modified with oxygen plasma showed that the oxygen plasma treatment clearly reduced the C=C and C-C bonds on the as-deposited Si-DLC film surface corresponding to broad peaks for the C-O and C=O bonds at 286.1 and 288 eV, respectively. However, in the Si 2p region, a strong SiO₂ peak and two small Si-Si and Si-O bonded networks were detected on the as-modified surface.³⁷ After exposure to ambient air for 20 days, the deconvoluted spectrum of the C 1s region indicated that the large peak for the C=C bonded network was almost unchanged, but the peaks for the C-O bonded network became smaller, whereas the deconvoluted spectrum of the Si 2p region was almost unchanged in Figure 3e. The oxygen-plasma-treated Si-DLC films contained the bonds between C and -O, and Si and -O, and both of these bonds were highly polar with electronegativities of 1.0 and 1.7 Pauling units, respectively.³⁴ The C-O bonding on the oxygen-plasma-treated Si-DLC film slightly decreased, and the Si-O₂ bonds were almost unchanged (similar to the Si 2p regions in Figure 3d,e). Therefore, the surfaces remained hydrophilic after 20 days of air exposure. OH (Si-OH) groups were also expected on the surfaces of the oxygen-plasma-treated Si-DLC films, increasing the polar component.³⁸ However, these groups were not easily detected in the XPS spectra.

The surface energy of the polar component of the Si-DLC films was estimated at various Si fractions with increasing aging time in Figure 4. As the Si atomic fraction was varied from 0 to 3.25 at % in the Si-DLC films, the surface energy of the films was almost constant in the range from 8.7 to 11.44 dyn/cm, but the surface energy of the films significantly increased up to 56.5 dyn/cm after the oxygen plasma treatment. After aging for 20 days, the surface energies of polar components of the pure DLC and the 3.25 at % Si-DLC films decreased to 36.8 and 44.5 dyn/cm, respectively. However, the surface energy of the polar components of the Si-DLC films with specific Si fractions of 1.24 and 2.42 at % only slightly changed to 56.0 to 56.5 dyn/cm, which agreed well with the contact angle behavior in Figure 2. Here the increase in the Si-C bonded network of the Si-DLC film with a Si fraction of 3.25 at % explained the decrease in the polar component of the surface energy of the film.²⁵

The surface morphology of the films was assessed as a function of the Si content using AFM in Figure 5. The surface roughness of the as-deposited films was similar for various Si contents and was comparable to the roughness of the Si (100) wafer. After the oxygen plasma treatment, the surface roughness of these films dramatically changed. In particular, the Si-DLC with 1.24 at % Si exhibited a roughness of 13.93 nm, whereas the modified Si-DLC

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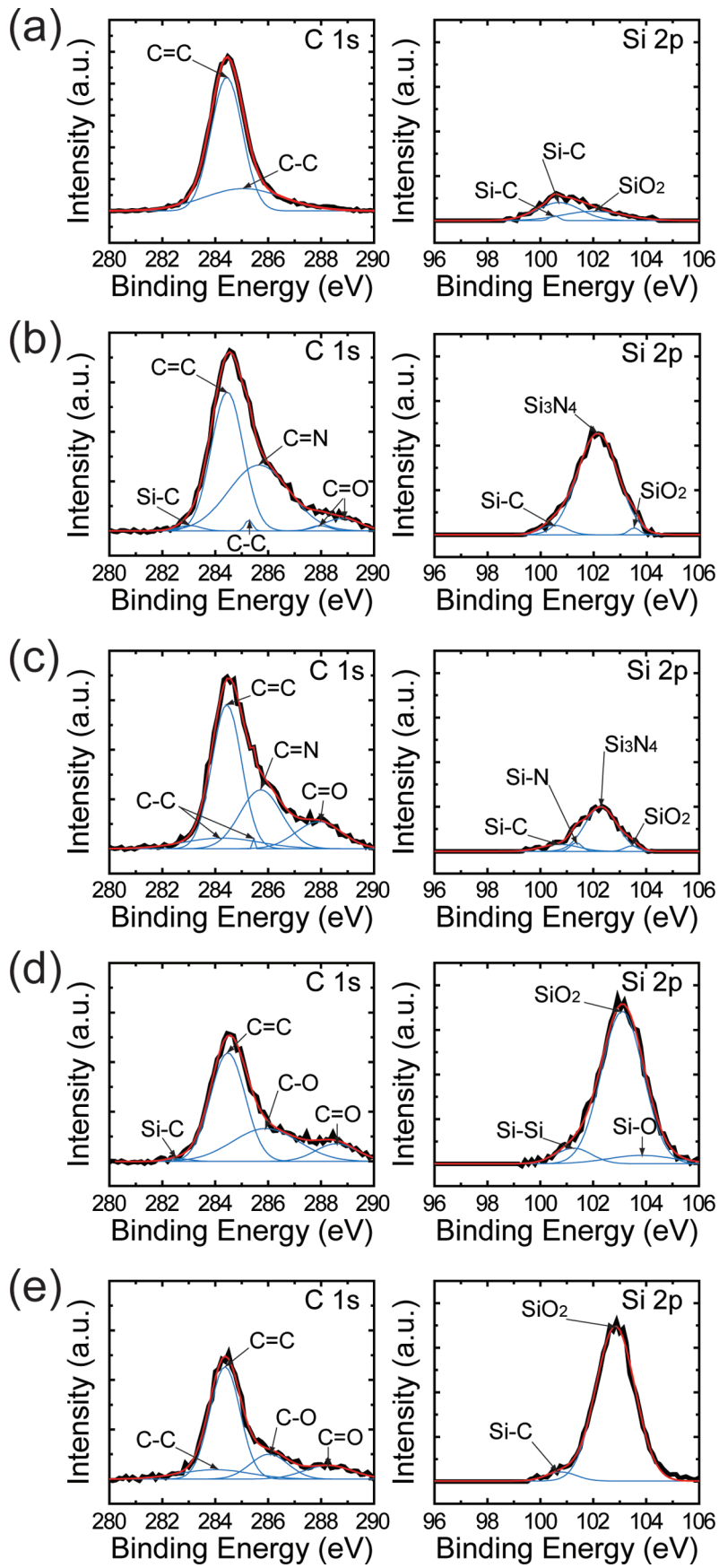


Figure 3. XPS spectra of the Si-DLC films in the C 1s and Si 2p binding energy regions of (a) the as-deposited Si-DLC, (b) the as-modified Si-DLC with nitrogen plasma, (c) the aged Si-DLC for 20 days with nitrogen plasma, (d) the as-modified Si-DLC with oxygen plasma, and (e) the aged Si-DLC for 20 days with oxygen plasma.

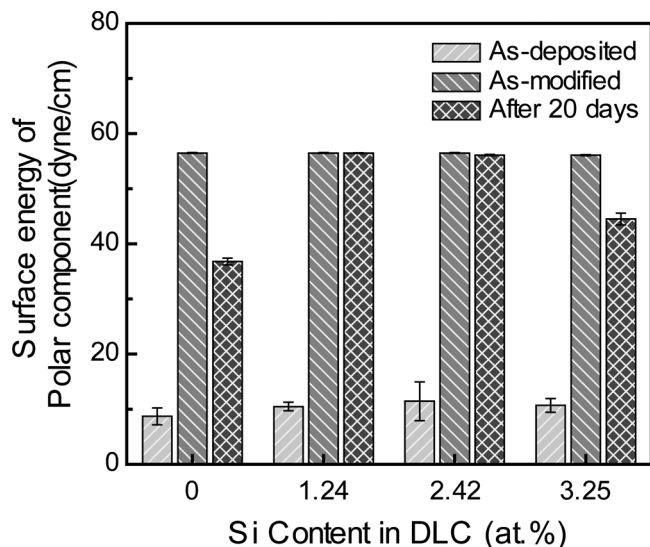


Figure 4. Variations in the surface energy of the oxygen-plasma-treated Si-DLC films as a function of the Si at % fraction in the films.

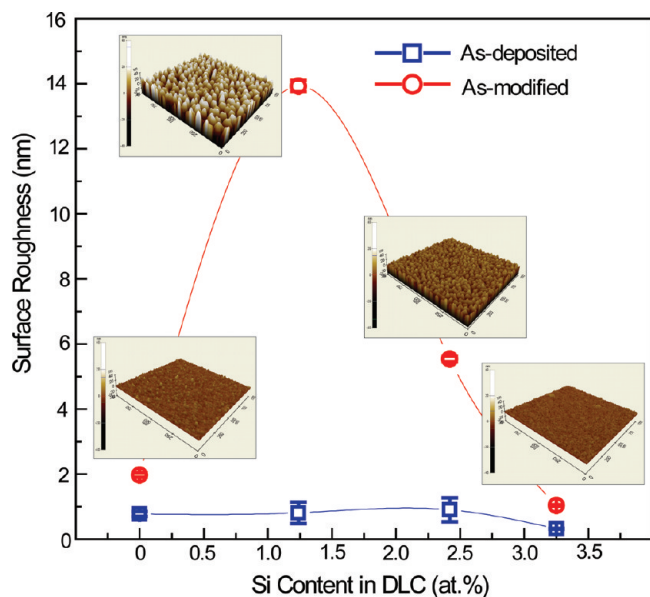


Figure 5. Surface roughness variations of the as-deposited (□) and the as-modified (○) DLC and Si-DLC films as a function of the Si at % fraction in the films. The inserted AFM images show the 3-D surface morphologies of the films.

films gradually became smooth with a roughness of 1.55 nm as the Si fraction increased in the Si-DLC films. Notably, the surface roughness on the a-Si:H film was 0.298 and 0.191 nm before and after the plasma treatment, respectively, which was similar to the surface roughness of 0.76 nm for the as-deposited DLC films. In Figure 5b, nanoscale patterns formed on the Si-DLC films after the oxygen plasma treatment because of the selective etching of the carbon matrix during the oxygen plasma treatment. The cross-sectional profile of the oxygen-plasma-treated Si-DLC with 1.24 at % of Si that was aged over 20 days was further measured using TEM EDS in Figure 6a, and the compositional changes for C, Si, and O were determined through the thickness of the film. Figure 6b revealed that larger amounts of Si and O accumulated on the top surface of the nanopatterns (< 6 nm in depth) of the Si-DLC matrix because of the selective etching of the carbon matrix

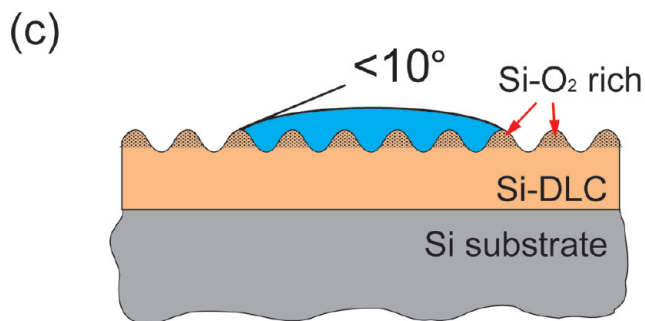
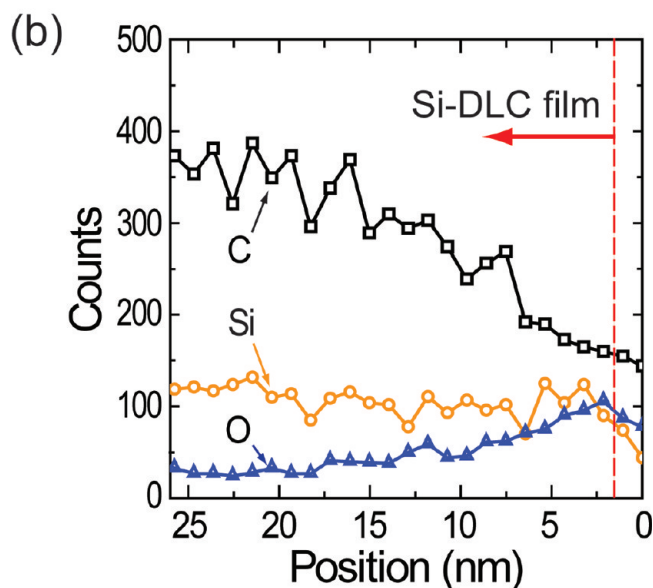
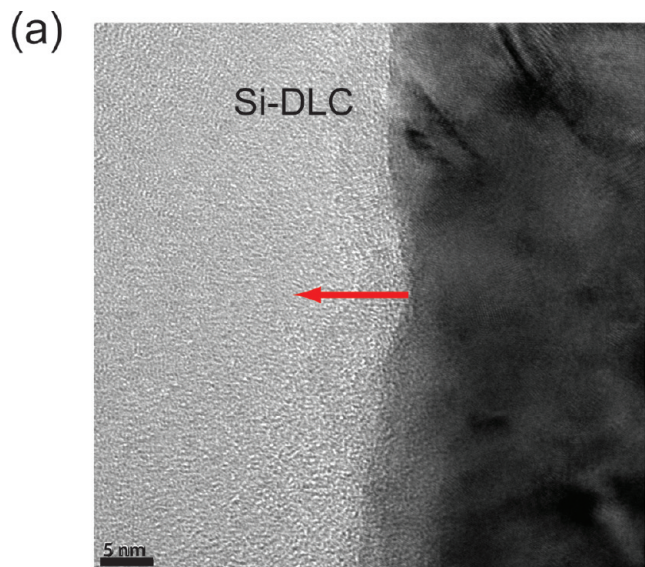


Figure 6. (a) TEM image of the modified 1.24 at % Si-DLC film with oxygen plasma. (b) Compositional variation with respect to C, O, and Si from the TEM EDS analysis through the thickness of the film. (c) Schematic describing the Si-O₂ rich nanopatterns of the Si-DLC film after oxygen plasma treatment.

in the Si-DLC films during the oxygen plasma treatment. As the oxygen plasma treatment progressed, the carbon matrix was etched faster than the Si component in the Si-DLC matrix, resulting in the accumulation of relatively higher Si and O contents

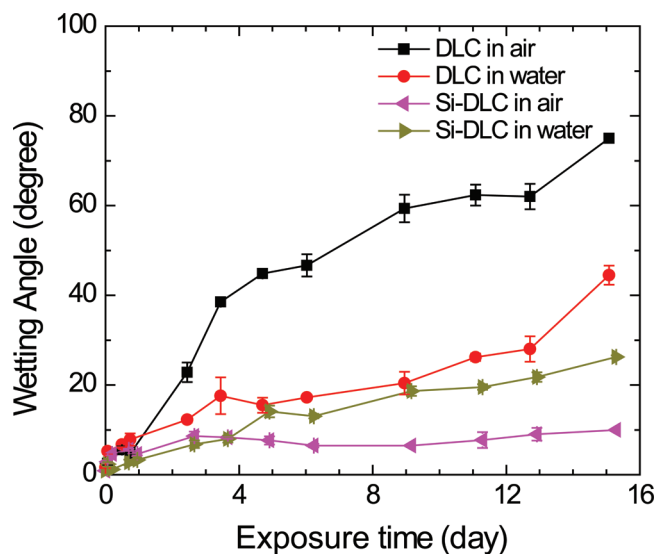


Figure 7. Contact angle behaviors of the oxygen-plasma-treated pure DLC and Si-DLC films with 1.24 at % of Si as a function of the exposure time in ambient air and the immersion time in DI water.

on the top surface of the nanopatterns on the Si-DLC film (Figure 6c), which also agreed with the XPS analysis in Figure 3e.

After the oxygen plasma treatment, two samples (DLC and Si-DLC with 1.24 at % of Si) were exposed to air and immersed in DI water, and the hydrophobic recovery was traced for 15 days to investigate the effects of air contamination on the surface wettability of the films. Similar to the results previously discussed, the wetting angle of the DLC film changed from superhydrophilic to hydrophobic as the aging time increased in Figure 7, whereas the Si-DLC film exhibited a long-lasting superhydrophilic ($<20^\circ$) behavior. However, the DLC and Si-DLC films gradually increased wetting angles up to 45 and 25°, respectively, which were slightly higher than those of the Si-DLC film that was exposed to air but significantly lower than those of the oxygen-plasma-treated DLC film. Therefore, the hydrophobic recovery of the DLC films was significantly suppressed in DI water. Therefore, the surface of the pure DLC film that contacted and absorbed the water molecules was protected from the hydrocarbons in air, which are believed to contaminate the hydrophilic surface, enhancing the hydrophobic recovery after a certain duration. Even though further experiments and analysis are required, these results suggested that the hydrocarbon contamination from air affected the surface wettability of the plasma-treated surfaces.

Conclusions

The conditions for the long-lasting hydrophilicity of the DLC and Si-DLC films were investigated using oxygen and nitrogen plasma treatments. The as-deposited DLC and Si-DLC films with hydrophobic characteristics were modified to hydrophilic films after the plasma treatment. In a short period, the hydrophobic properties were rapidly recovered after the films were exposed to ambient air. However, on the oxygen-plasma-modified Si-DLC films with a specific Si fraction ranging from 0.66 to 2.42 at %, the hydrophilicity lasted for over 20 days.

From the XPS analysis, C=N, Si₃N₄, Si-N, C-O, C=O, Si-O₂, and Si-O bonds were observed on the as-modified film surfaces with the nitrogen and oxygen plasma, but less C=N and Si₃N₄ bonding existed with increasing aging time. However, the polar component of the Si-O₂ bonding exhibited almost no change on the Si-DLC film surfaces that were modified with the oxygen plasma. The surface nanostructures formed through the selective etching of the carbon matrix in the Si-DLC films, resulting in a surface roughness of up to 13.93 nm in the specific fraction range of 1.24 to 2.42 at % Si. In the depth profiling TEM EDS analysis for the Si-DLC with 1.24 at % of Si after 20 days of air exposure, the bonds between Si and -O were detected on the top surface of the nanostructured patterns and played a key role in prolonging the hydrophilicity for a long period on the Si-DLC coated surfaces. The water immersion experiments for the DLC and Si-DLC films showed that the water wetting angles of the pure DLC and Si-DLC films that were immersed in DI water were slightly higher than those of the Si-DLC film that was exposed to air but relatively lower than those of the pure DLC film. Therefore, the air contamination affected the surface wettability on the plasma-treated surfaces.

The DLC film can be used for various applications, including nonwetable or antifog coatings on windshields for automobiles as well as biocoatings such as the contact lens, where the hydrophilic Si-DLC coating can improve the wettability and the scratch resistance of the lens for longer life times because of the long-term stability of the wettability of the DLC films.^{18,39}

Acknowledgment. This work was partially financially supported by a grant (code no. 2010K000298) from the Center for Nanostructured Materials Technology under the 21st Century Frontier R&D Programs of the MEST, Korea (M.-W.M., K.-R.L.) and by Kyungpook National University (J.W.Y., S.-S.K.).

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