

Characterization of Acetylene Plasma-Polymer Films: Recovery of Surface Hydrophobicity by Aging

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Aging phenomena of plasma polymer films were studied by using the surface analysis techniques of contact angle measurement, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and atomic force microscopy (AFM). The polymer films were grown on an aluminum substrate by using a plasma polymerization method from a gas mixture of acetylene and helium, and the films were subsequently modified to have a hydrophilic surface by oxygen plasma treatment. Aging of the polymer films was examined by exposing the samples to water and air environments. The aging process increased the hydrophobicity of the surface, as revealed by an increase in the advancing contact angle of water. XPS analysis showed that the population of oxygen-containing polar groups increased due to the uptake of oxygen during the aging, whereas TOF-SIMS analysis revealed a decrease in the polar group population in the uppermost surface layer. The results suggest that the change in surface property from hydrophilic to hydrophobic nature results from the restructuring of polymer chains near the surface, rather than compositional change of the surface. Oxidative degradation may enhance the mobility and the restructuring process of polymer chains.

Key Words: Aging, Plasma polymer, Hydrophilicity, XPS, TOF-SIMS

Introduction

Plasma technology has been widely used as a surface modification method for introducing unique properties onto the surface of materials of various compositions and topographic shapes, owing to its advantage as relatively simple, fast, and clean methods.¹⁻⁷ When the plasma modification method is applied to polymer surfaces, however, chemical properties of the modified polymer surfaces often gradually change with time, thereby limiting the durability of the surfaces in industrial application. An important property of polymer surfaces for practical application is hydrophilicity, which determines the wettability, printability, and cohesion/adhesion properties of the surfaces.^{1,3,8} Change in hydrophilicity of polymer surfaces with time under ambient conditions, the so-called 'aging' process, is crucial for applications of polymer surfaces, and extensive research efforts have been made to understand the mechanism of the aging process in terms of surface compositional and structural changes.^{1,9-20}

Hydrophobic recovery of a modified, hydrophilic polymer surface upon aging originates from the intrinsic restructuring mechanism of the polymer surface to reduce the free energy of the polymer-air interface.^{1,9-15} Extrinsicly, ambient contaminants may also neutralize the acidic or basic polar functional groups or charged centers present at the surfaces, thereby decreasing the surface hydrophilicity.¹⁴⁻²⁰ The mechanism of such hydrophilicity changes may be able to be understood through investigations with surface-sensitive analysis techniques. X-ray photoelectron spectroscopy (XPS)^{14,21-26} and infrared spectroscopic methods^{21,23-25} have often been used for this purpose. Angle-resolved XPS (AR-XPS) studies of

modified polymer surfaces have also been performed, which enable to examine the compositional change in the surface region within a depth of several nanometers.^{15,19,25} However, the AR-XPS method may have a limited application in such measurements due to the effects of surface topography and a limited electron collection angle.¹⁹ Hydrophilicity of a solid surface is probed most widely by measuring the contact angle of water,^{21,26} and this method reflects the property of the topmost surface layer within a depth less than 1 nm,^{27,28} much shallower than the probing depth of XPS. Secondary ion mass spectrometry (SIMS) experiment is sensitive to the top molecular layer of surfaces, owing to its principle based on sputtering of the surfaces by ion bombardment. SIMS has a probing depth comparable to contact angle measurements. However, static SIMS techniques have been used only rarely for the examination of polymer aging processes, partly due to the fact that a quadrupole mass analyzer has a low (about unity) mass resolution, and with such an instrument it is difficult to unambiguously identify the molecular species with various elemental compositions existing at polymer surfaces.^{28,29} Recent instrumental developments for time-of-flight (TOF) SIMS have greatly improved the resolution of a TOF mass analyzer, which enables us to distinguish the molecular fragments at close masses without further sample treatments such as chemical derivatization and isotope labeling.^{26,28-32} Several previous TOF-SIMS studies of polymer surfaces have reported a good correlation between the molecular information obtained by TOF-SIMS experiment and the wettability from contact angle measurements.^{33,34}

In the present work, we prepared polymeric coating films on an aluminum substrate by using a glow-discharge plasma

technique with acetylene gas as a monomer³⁵ and He as an auxiliary gas.^{9,36} Such a polymerization method is commonly called plasma polymerization, and the polymeric material thus formed, a plasma polymer.²⁴ In contrast to conventional polymers, plasma polymers do not have regularly repeating structural units, and they are thought to possess random, three-dimensional network structures formed through relatively high probability of cross-linking of various molecular fragments generated in the plasma phase.²² The acetylene plasma polymer prepared by this method was then further treated with oxygen plasma to transform the film surface to become hydrophilic.^{12,37} The aging process of the hydrophilic surface of plasma polymers was examined in water and air environments. Contact angle measurement, XPS, TOF-SIMS, and atomic force microscopy (AFM) were employed to examine the aging process and its plausible mechanism.

Experimental

The plasma polymerization and the plasma surface treatment were performed in a batch pilot system at LG Electronics Inc. The system was composed of a power unit, a discharging chamber (1 m × 1 m × 1 m rectangular, stainless steel), an exhaust unit, a vacuum gauge, and a gas supply unit. The substrate fixture and the plasma-discharging electrode (copper mesh grid-type) were installed in the chamber, sustaining a distance of 10 cm between the electrode and the sample substrate. The schematic of the plasma discharging system is shown in Fig. 1. The working pressure was 40 Pa. The flow rate was kept to be 700 sccm (std. cm³ min⁻¹) and 2100 sccm for acetylene (98.6%, Sin-Chang) and helium (99.99%, Sin-Chang), respectively, by using a mass flow controller (MFC). The glow discharge of acetylene/helium mixture gas was carried out at constant current of 1.5 A under variable voltage around 700 V. The discharge was sustained for 1 min, giving an estimated thickness of *ca.* 20 nm for the plasma polymer film on the aluminum substrate (100 mm × 100 mm × 0.1 mm; Sam-Ah). Then, the surface treatment with oxygen plasma was carried out under constant current of 1.2 A (*ca.* 700 V) for 10 sec to generate hydrophilic polar functional groups on the film surface. The flow rate of oxygen gas

(99.99%, Sin-Chang) was 1000 sccm. Finally, the plasma polymer films were rinsed with n-hexane and deionized water in an ultrasonic washer to remove low-molecular-weight species.^{12,13,18}

The aging condition was similar to the previous protocols employed for both hydrophilic and hydrophobic aging processes.¹² For hydrophobic aging, industrial field-oriented condition was simulated by blowing ambient air on a sample instead of keeping it inside nitrogen gas. Hydrophilic aging was simulated by dipping a sample in deionized water. One aging cycle is defined as one turn of both hydrophilic and hydrophobic aging procedures, for a duration of 10 min for each.

Surface contact-angle measurement was performed by using a dynamic Wilhelmy plate method (Sigma70, KSV Instruments). The surface tension of water was checked to be 72 (± 1) mN/m and the receding and advancing speeds of the sample plate were set to be 3 (± 0.01) mm/min. XPS spectra were obtained by using an instrument (Perkin-Elmer PHI 5400 ESCA) with a standard Mg K α X-ray source (1253.6 eV) at electron takeoff angle of 45°. All narrow scan data were obtained with an energy resolution of 1.1 eV at FWHM (full width at half maximum), as checked for the Ag 3d_{5/2} peak. The electron binding energy was calibrated against the peaks of Cu 2p_{3/2} (932.6 eV), Ag 3d_{5/2} (368.4 eV), and Au 4f_{7/2} (84.0 eV), and referenced to the C 1s peak of hydrocarbon at 285.0 eV. The chamber base pressure during the measurement was maintained below 3 × 10⁻⁷ Pa. The spectral data treatments included Shirley-type background subtraction and peak deconvolution. TOF-SIMS spectra were obtained with an instrument (TOF-SIMS IV, IonToF) using a Ga⁺ primary ion beam at 25 keV energy and ~ 0.7 pA ion current under the base pressure of 1 × 10⁻⁷ Pa. The total ion dose at the sample surface was ~ 4 × 10¹² ions cm⁻², which corresponded to the removal of less than one monolayer of the surface.^{30,31} The mass resolution, m/ Δ m, was determined to be greater than 9000 in FWHM for ²⁹Si⁺, and the pulse width was less than 700 ps for ¹H⁺ on a Si wafer. Surface morphology was observed by means of AFM (Dimension 3100, Veeco Digital Instruments) in a tapping mode with a tetrahedral silicon tip of 8 nm apex radius.

Results

We prepared acetylene plasma polymer films on an Al substrate from acetylene and He gases. Acetylene was chosen as a monomer gas owing to its advantages over ethylene and ethane during plasma polymerization. Acetylene is more susceptible to bond scission in plasma environment than the other gases.³ Also, acetylene can reduce the oxidative degradation of its plasma polymer films by hydrogen abstraction reaction because it generates a lower hydrogen content in the plasma polymers than the other gases.^{35,38} He gas in the plasma helps to remove the surface contaminants of the Al substrate, enhancing the adhesion properties of the plasma polymer to the substrate. He gas also stabilizes the polymer film layer by inducing cross-linking reactions.^{9,36} After preparation of the plasma polymer films, the surface was treated with oxygen

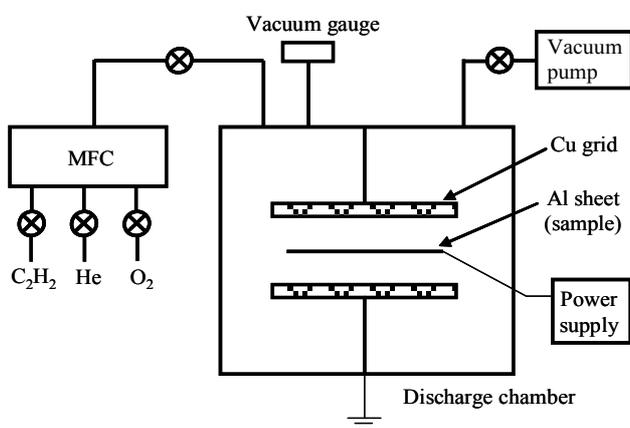


Figure 1. Schematic diagram of the plasma polymerization set-up.

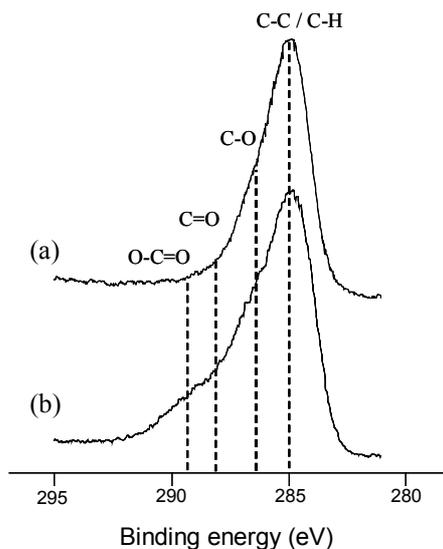


Figure 2. XPS spectra in C 1s region obtained from the plasma polymer films (a) before and (b) after the aging process.

plasma to generate oxygen-containing polar functional groups, which increased the surface hydrophilicity probably through hydration, hydrogen bonding, and other interactions. The sequential application of the plasma polymerization and the oxygen plasma treatment provided a better opportunity than one pot synthesis of the films in the gas mixture of helium, acetylene, and oxygen, in generating a tenacious hydrophilic film.³³

The wettability of the films prepared as described above was evaluated by measuring both advancing and receding angles for water. The measurements were made for plasma polymer films before and after the treatment with 300 aging cycles. The advancing contact angles increased from 31° to 64° after the aging process, while the receding angles remained at ~0° even after the aging. The advancing and receding angles reflect the more and less wettable parts, respectively, of polymer surfaces.³⁹ According to theoretical studies,⁴⁰ the increase in advancing angle is interpreted to indicate transformation of some hydrophilic surface regions to hydrophobic regions by the aging process. The receding angle remains almost unchanged at a low value. Therefore, the increase in the contact angle hysteresis in the present data indicates that the aging process increases the portion of the hydrophobic area on the surface.

The change in chemical composition of the surfaces after the aging process is examined by means of XPS and TOF-SIMS analyses. XPS measurements showed that the abun-

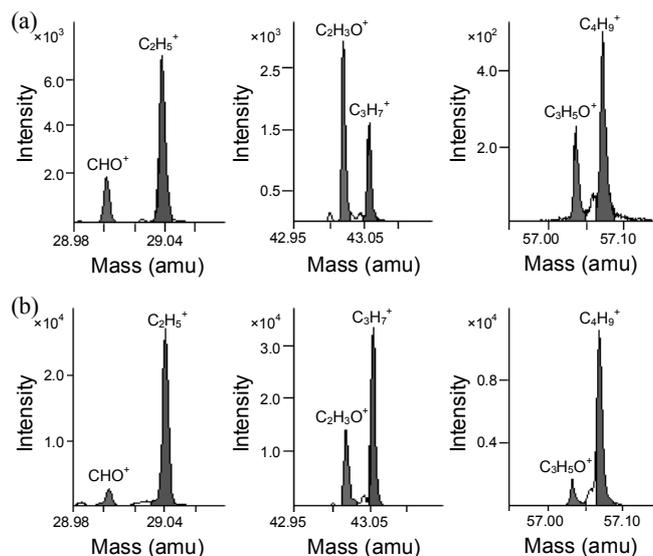


Figure 3. High resolution TOF-SIMS spectra of the plasma polymer films (a) before and (b) after aging.

dance ratio of oxygen to carbon increased from *ca.* 16% to *ca.* 26% after aging, indicating the uptake of oxygen on the surface.^{24,32} Fig. 2 shows the high resolution XPS spectra of C 1s peak obtained from the original and the aged samples. The C 1s binding energies of possible chemical species include C-C and C-H bonds at 285.0 eV, C-O bonds (hydroxyls or ethers) at 286.5 eV, C=O bonds (carbonyls) at 287.9 eV, and O-C=O bonds (carboxyls) at 289.3 eV.^{3,24} The C 1s peak has a broad envelope, which is typical for polymer films.^{11,15,19} The envelope is broadened toward a high-energy side after aging, which was observed in previous XPS studies also.^{12,23} The C 1s peak is deconvoluted into various possible components and their estimated fractions are summarized in Table 1. The analysis shows that the aging process increases the relative populations of oxygen-containing groups including carbonyl, carboxyl, hydroxyl, and ether groups. These functionalities may be originated from ketones, aldehydes and carboxylic acids, and carboxylates produced in the polymer surface region.

Figure 3 shows TOF-SIMS spectra for several representative molecular fragments emitted from the original and the aged sample surfaces. The high mass resolution ($m/\Delta m > 9000$) of TOF-SIMS enables us to compare the peak intensities of the oxygen-containing polar (C_xH_yO) species and the oxygen-absent non-polar (C_nH_{2n+1}) species that appear at very close masses. The former species are believed to originate from the polar hydrophilic parts of the surface, and the latter

Table 1. Water contact angles, components of C 1s peaks and secondary ion ratio before and after aging.

Sample	Contact angle ^a (°)		Components of C 1s peaks (%)				Secondary ion ratio		
	a.a.	r.a.	C-C	C-O	C=O	O-C=O	C ₂ H ₅ ⁺	C ₃ H ₅ ⁺	C ₄ H ₉ ⁺
Non-aged	31 ± 1	~ 0	69	12	4.4	0.02	4.0	0.53	2.0
Aged	64 ± 1	~ 0	41	43	8.6	7.9	13	2.4	7.1

^aAdvancing (a.a.) and receding (r.a.) contact angles.

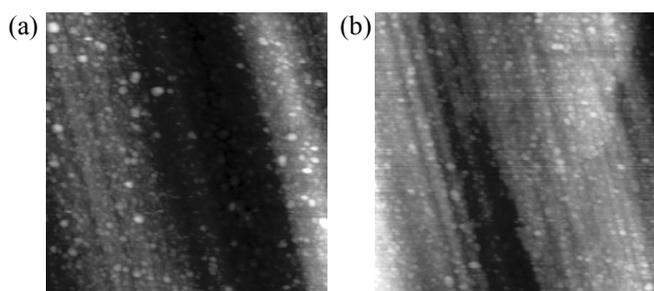


Figure 4. Tapping mode AFM scans ($2 \times 2 \mu\text{m}^2$) of plasma polymer films (a) before and (b) after aging.

from the non-polar hydrophobic parts.^{20,32,33} Note that such an analysis cannot be done with low mass-resolution (about unity) spectra obtained from ordinary static SIMS experiments.²⁹ As shown in Fig. 3, the intensities of the oxygen-absent non-polar species vividly increase relative to the oxygen-containing polar species after the aging, indicating that the hydrophobic area is increased on the aged surface. Quantitative changes in the ratio of $\text{C}_n\text{H}_{2n+1}$ to $\text{C}_x\text{H}_y\text{O}$ species are summarized in Table 1.

The surface morphology of the samples was investigated with AFM, and the images as shown in Fig. 4. No significant change in topographic shape was observed after the aging, and the surface roughness appeared not much changed either, the value of root mean square (RMS) roughness being 14.6 nm and 15.1 nm before and after the aging, respectively.

Discussion

Contact angle measurements show that the advancing contact angle increases by more than 30° after the aging, and this implies that the surface area of hydrophobic regions increases on the polymer films. However, the receding contact angle stays unchanged at $\sim 0^\circ$ after the aging, which suggests that hydrophilic polar functional groups still exist on the surface though its coverage is lowered. The polar groups may remain on the aged surfaces probably due to immobilization of molecular chains in the three-dimensionally cross-linked plasma polymer.^{9,10}

XPS spectra in Fig. 2 indicate that the aging process causes oxidation of the plasma polymer surface by the uptake of oxygen from ambient environments. This increases the population of hydrophilic polar functional groups, and the

generated polar functional groups may include hydroxyl, ether, carbonyl, and carboxyl species. Even though the XPS result indicates that the aged film has more polar functional groups in the surface region, hydrophobicity of the surface is increased by the aging process.

According to TOF-SIMS measurements, the relative intensities of the oxygen-containing hydrophilic species are decreased by the aging, and the hydrophobic species are increased. The observation is consistent with the contact angle measurement showing an increase in the advancing angle. However, there is apparent contradiction in the surface compositions measured by XPS and TOF-SIMS, the former indicating an increased population of hydrophilic functional groups after the aging, and the latter, a decreased population. The discrepancy may be explained by accounting for the different probing depths of two methods. The ion species emitted in TOF-SIMS experiments reflect physico-chemical information in the outermost surface layer, comparable to the contact angle measurement with a probing depth of ~ 0.5 nm.^{27,28} On the other hand, the sampling depth of XPS, which is determined by the electron escape length, is typically greater than a few nanometers from the surface. Therefore, XPS results reflect chemical composition averaged over a substantial depth from the surface. In this respect, we consider that the aging process causes oxidation of the films and increases the hydrophilic functional groups near the surface or in the bulk region, but their population is decreased right at the topmost surface.

The increase in the surface population of hydrophobic groups can originate either from intrinsic restructuring of polymer chains and outward diffusion of nonpolar hydrocarbon segments, or from extrinsic contaminants accumulated on the surface during the aging. External species such as silicon oils, which are well known contaminants in polymer processing,^{20,30} are not observed in the SIMS measurement of the aged samples. Therefore, the observed hydrophobic recovery of the samples is considered to be intrinsic. The intrinsic surface restructuring may occur *via* reorientation of polymer chain segments at the surface in response to the interfacial forces caused by the surface free energy difference between the polymer surface and the contact medium.^{12,21} Diffusion of low molecular weight species^{12,13} to the surface may also occur, but this effect is expected to be small, because the plasma polymer films were washed with n-hexane after the plasma polymerization and O_2 plasma treatment to remove the low molecular species. The oxygen-containing low-

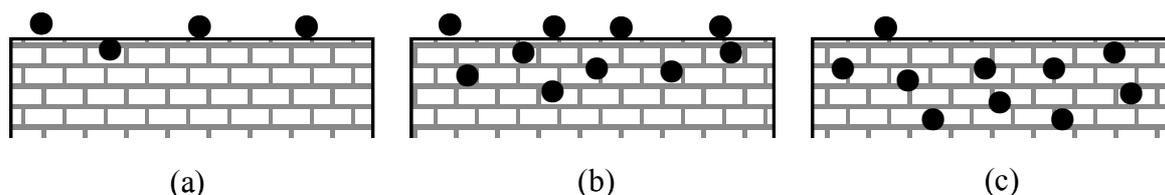


Figure 5. Schematic drawing of the surface region of plasma polymer films for three conditions: (a) non-aged, (b) oxidized in the aging environment, and (c) surface-restructured during the aging process. Oxygen-containing hydrophilic polar functional groups are denoted by \bullet , which were introduced by O_2 -plasma surface treatment and the aging process onto the random three-dimensional network of the plasma polymer film. Bulk parts of the plasma polymer films and the aluminum substrates are omitted for brevity.

molecular-weight species generated during the aging are also expected to be washed away during the dipping procedure in water.

The wettability of polymer films depends on surface roughness also.^{5,41} However, the effect of surface roughness is difficult to assess precisely, unless the surface roughness is independently controlled from the change of surface composition of the samples. The AFM image in Fig. 4 at least reveals no drastic change in surface topography due to the aging, although it is often difficult to extract quantitative information about surface roughness from the AFM image of polymer surfaces. Thus, the observed contact angle change is most likely attributed to the change of surface composition, rather than surface morphology.

Based on the present observations, the following mechanism of the aging process may be proposed. The aging process causes oxidative degradation of the polymer films through reactions with atmospheric oxygen or water, as noted in other reports.^{20,22} This increases the oxygen content near the surface of the film or in the bulk, as observed by XPS which measures the oxygen content integrated over a substantial depth from the surface. The oxidative degradation process is shown schematically in Fig. 5 (b). The polar functional segments protruded outward from the surface, however, may experience repulsive forces at the polymer/air interface and be reorientated inwards, as depicted in Fig. 5 (c). This surface restructuring process may occur simultaneously with oxidative degradation processes during the aging. As a result, functionality difference may appear between the outermost surface and the near-surface region of the aged polymer film, as revealed in the TOF-SIMS result which is sensitive to the top molecular layer of the surface.

Summary and Conclusions

A hydrophilic polymer film was prepared by using a plasma polymerization method from a gas mixture of acetylene and helium, and the film was modified to have a hydrophilic surface by oxygen plasma treatment. Aging of the plasma polymer film was examined by exposing the samples to water and air environments, and by analyzing the resulting surfaces with contact angle measurement, XPS, TOF-SIMS, and AFM.

The following mechanistic sequence of the aging events is suggested. The plasma polymers are degraded by the oxidation through incorporation of oxygen from air and water, increasing the content of the oxygen-containing polar functional groups near the film surface. At the same time, reorientation of the surface functionalities of the polymer chains and surface restructuring occur, which reduces the population of hydrophilic functionalities at the uppermost layer of the film and gradually increases hydrophobicity of the surface.

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