Fine Characterization of Plasma-Polymerized Films from a Methane/Air Mixture

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ABSTRACT: The plasma polymerization of methane/air mixtures was performed to produce a hydrophilic film on a substrate, and the obtained films were characterized with ellipsometry, elemental analysis, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and contact-angle measurements. Fourier transform infrared revealed that the structure of the plasma-polymerized films changed with increasing film thickness; that is, an increase in the film thickness led to an increase in the absorbance ratio of the carbonyl band at 1664 cm^{-1} to the methyl band at 1385 cm^{-1}. Although the contents of nitrogen and oxygen measured by elemental analysis changed with the film thickness, the contact angle and X-ray photoelectron spectroscopy atomic ratio of the films were independent of it. Nitrogen and oxygen were contained in the bulk more than on the surface of the films. Nitrogen and oxygen were copolymerized with methane, and the properties of the obtained films were similar to those of an amide compound. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3408–3414, 2006

Key words: ESCA/XPS; FTIR; modification; plasma polymerization

INTRODUCTION

Polymer films produced by a glow discharge often possess chemical and physical properties that are superior to those of conventionally polymerized materials. They are prepared by a dry-vapor phase-deposition process and may be uniformly coated onto virtually any substrate. Plasma polymerization provides a unique and powerful method for surface modifications without changes in the bulk properties of the coated substrates. These techniques are attractive for applications in which the surface properties are important for end use, such as membranes,[1,2] biomedical polymers,[3–5] fibers,[6] and sensors.[7] The effects of plasma treatment for polymers in nondepositing gases are not permanent as a result of the overturn and migration of the polar functional groups introduced into the surface.[8–11] Coatings with plasma polymers can be made to present a stable surface because of the highly crosslinked structure. A wide range of monomers are available for use in plasma polymerization, including saturated hydrocarbon, unsaturated hydrocarbon, halocarbon, and nitrogen-containing mono-

mers, whereas oxygen-containing monomers are scarcely employed.

Usually oxygen or nitrogen is incorporated into the plasma polymer to produce a hydrophilic polymer. Nitrogen can be readily incorporated into a plasma polymer when nitrogen is already present in the monomers, such as acrylonitrile,[12] allylamine,[13,14] pyridine,[15,16] and N-vinyl-2-pyrrolidone.[17,18] Oxygen, on the other hand, is difficult to directly incorporate into plasma polymers. Although oxygen-containing polymers were expected to display significant hydrophilic properties, plasma polymerization with ordinary alcohols, aldehydes, and esters did not produce hydrophilic films. The reason was thought to be that these oxygen-containing structures favor the decomposition of the monomer in plasma.[15] Hozumi and coworkers[19,20] performed the preparation of hydrophilic plasma polymers from liquid monomers involving hydroxyl, carboxyl, carbonyl, and ether groups. They reported that alcohols having triple bonds were the most profitable monomers among the oxygen-containing compounds for the preparation of hydrophilic polymer films by the plasma-polymerization technique.

As mentioned previously, many investigators have reported the plasma polymerization of nitrogen- or oxygen-containing hydrocarbons. However, only a few articles have reported plasma polymerization for

mixtures of hydrocarbons with simple oxygen- or nitrogen-containing gases. Yasuda et al.[21,22] investigated the plasma polymerization of some unsaturated organic compounds with N_2 and H_2O. The monomers used there were acetylene, allene, and ethylene. They found that nitrogen and oxygen atoms were incorporated into plasma polymers. Kim et al.[23] reported plasma polymer from ethylene/N_2 gas mixtures, with IR analysis indicating the presence of double- and triple-bonded CN and a trace of NH. One of the advantages of these processes is that harmful amide, amine, or carboxylic compounds and so on are not used as monomers of plasma polymerization to produce hydrophilic coatings. However, the complexity of the reactions in the plasma gas phase does not allow the prediction and control of the chemical effects of plasmas with sufficient accuracy. Moreover, there are few reports on the relationship between the structure of a plasma-polymerized film and its thickness. For the application of a plasma-polymerized film to the coating of materials, the structure of the film needs to be analyzed definitely.

We report here the preparation and characterization of hydrophilic polymer films derived from the plasma polymerization of methane/air gas mixtures. A detailed study of the plasma polymerization of methane/air gas mixtures has not been reported previously, although many investigators have studied the plasma polymerization of methane.[24–26] This article also presents the relationship between the structure of the film and the film thickness.

EXPERIMENTAL

Plasma polymerization

The plasma polymerization was conducted in a reactor system manufactured by Shinko Seiki Co., Ltd. (Kobe, Japan) Figure 1 shows the reactor chamber used here, a stainless steel bell jar with a diameter of 50 cm and a height of 50 cm. One pair of square titanium electrodes (18 cm wide) was placed in the bell jar, with a separation width of 10 cm. A glow discharge was created at the frequency of 15 kHz with magnetic enhancement, with bar magnets on a concentric iron ring.

A substrate was mounted on a moving stage, which was positioned 30 cm from a gas inlet. The substrate moved reversibly parallel to the electrode surface during plasma polymerization. The substrates employed in the plasma polymerization included a silicon wafer, a glass slide, and a KBr crystal. The silicon wafer was used for measurements such as ellipsometry, contact-angle measurements, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). The glass slide and KBr crystal were used for elemental analysis and Fourier transform infrared (FTIR) mea-
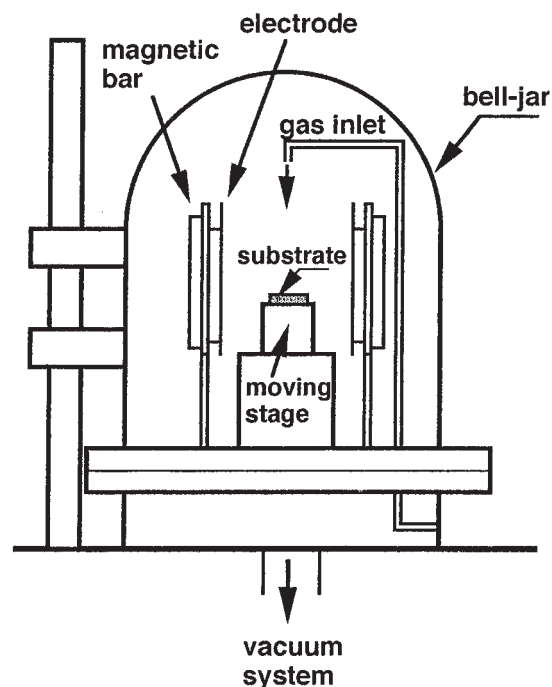

Figure 1 Schematic illustration of the reactor chamber.

surements, respectively. The reaction system was evacuated to less than 0.3 Pa. Then, nitrogen was introduced to the chamber by the opening of a needle valve to adjust the pressure at 130 Pa. After 5 min, nitrogen was stopped and evacuated to less than 0.2 Pa. Methane and dry air were introduced from the top of the chamber. The dry air used in this study was a mixed gas of oxygen (20%) and nitrogen (80%). The flow rates of methane, dry air, and nitrogen were controlled with a mass-flow controller. The mass-flow rate of methane was 2 sccm for all plasma polymerization processes in this study. The audio-frequency power was turned on, and the plasma polymerization was continued for a predetermined period of time. The reaction conditions were 4 Pa, 34 W, and a relative flow rate of 2/1 sccm (methane/air). During the plasma polymerization, the pressure of the system was measured with a Baratron MKS 600 series pressure controller (Wilmington, MA). Methane (pure-grade, >99.0%), dry air (zero-A grade), and nitrogen (99.999%) were purchased from Sumitomo Seika Chemicals Co., Ltd. (Osaka, Japan).

Film thickness

The film thickness of the polymers formed on the silicon wafers was determined on a Mizojiri Optical DVA-36L ellipsometer (Tokyo, Japan). The film thickness of the polymers formed on the glass slides and KBr crystals was measured with the following procedure. One end of the glass slide and KBr crystal was

wound with Scotch tape. After plasma polymerization, a sharp step formed by the tape being peeled off was measured with a KLA-Tencor Alpha-Step 200 (San Jose, CA). The silicon wafer was obtained from Newwingo Co., Ltd. (Osaka, Japan).

Elemental analysis

Samples for elemental analysis were deposited on glass slides and were collected via scraping with a razor blade. The elemental analysis was carried out with a Fasons EA 1108 (Milan, Italy).

Contact-angle measurements

Static contact angles of water droplets on the plasma-polymerized film were measured with a Kyowa Interface Science CA-X150 contact-angle meter (Saitama, Japan).

FTIR

FTIR spectra were obtained with a Thermo Nicolet 20 DXB spectrometer (Madison, WI). FTIR analyses of the plasma-polymerized film were performed with transmission spectra of the polymer deposited on a KBr crystal.

XPS

XPS was performed on an Ulvac-Phi 5500 MT X-ray photoelectron spectrometer (Kanagawa, Japan). The spectra were taken with a Mg Kα X-ray source exciting radiation (1253.6 eV) at 15 kV, 200 W, and an analyzer pass energy of 23.5 eV. The takeoff angle of an electron from the sample was fixed at 45° with respect to the specimen surface. Binding energies were referenced to the saturated hydrocarbon C_{1s} core-level peak at 285.0 eV. The relative atomic concentration of each element at the film surface was estimated from peak areas with atomic sensitivity factors specified for the Ulvac-Phi 5500 MT. The C_{1s} core-level spectra were decomposed into three Gaussian functions with a computer program supplied by Ulvac-Phi. In peak synthesis, a full width at half-maximum of 1.7 eV was used for each Gaussian peak.

AFM

A Digital Instruments Nanoscope IIIa atomic force microscope (Santa Barbara, CA) was used to examine the surface topography of the film on a silicon wafer. The AFM images were acquired under ambient conditions with the tapping mode. The value of the mean roughness (R_a) was calculated with a computer program supplied by Digital Instruments.
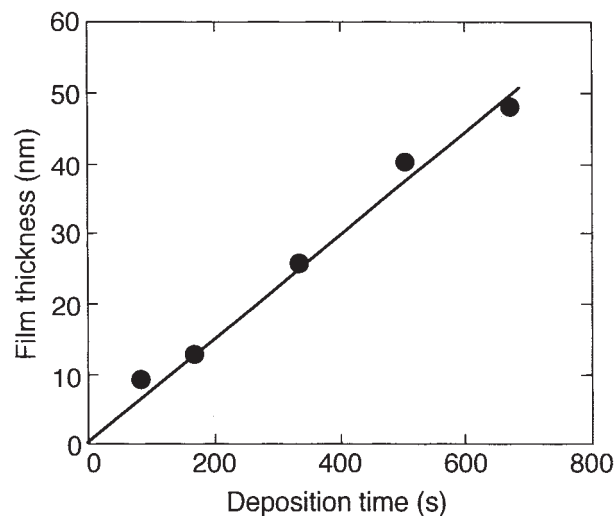

Figure 2 Film thickness as a function of the deposition time for plasma-polymerized films.

RESULTS AND DISCUSSION

Ellipsometry was used to measure the thickness of plasma-polymerized films that were deposited for different times under the same reactor conditions [4 Pa, 34 W, and a relative flow rate of 2/1 sccm (methane/air)]. As shown in Figure 2, the film thickness varied almost linearly with the deposition time.

The chemical characterization of the plasma-polymerized films was evaluated with elemental analysis, FTIR, and XPS. These three techniques were complementary to one another. Elemental analysis provided the overall film stoichiometry. It was especially important for the determination of the hydrogen content, which could not be obtained from XPS. FTIR indicated the functional groups contained in the bulk of the film. XPS provided information on the structure and composition of the outermost layer (<5 nm) of the film.

The results of elemental analysis are summarized in Table I. The oxygen content was the difference between the sample weight and the sum of the C, H, and N contents determined. Because the samples for elemental analysis were prepared by the deposition of the polymers on glass slides and the collection of the polymers via the scraping of the deposits with a razor blade, we could not measure the thin film. The C and H contents were almost independent of the film thickness.

The H/C atomic ratios were 1.21–1.31, which were smaller than that of methane. The N/C and O/C atomic ratios were 0.20–0.26 and 0.27–0.31, respectively. A highly branched structure was expected from these results. The N/O atomic ratio increased with increasing film thickness.

Figure 3 shows FTIR spectra of plasma-polymerized films with various thicknesses. The band assignments are listed in Table II.[21,22,27–29] The bands

TABLE I
Elemental Analysis of Films Prepared from Methane/Air (2/1) by Plasma Polymerization

Film thickness (nm)	Elemental composition (wt %)				Empirical formula of polymer	Atomic ratios			
	C	H	N	O		H/C	N/C	O/C	N/O
100	56.91	5.77	13.74	23.58	$C_1H_{1.21}N_{0.21}O_{0.31}$	1.21	0.21	0.31	0.67
300	57.68	6.05	13.22	23.05	$C_1H_{1.25}N_{0.20}O_{0.30}$	1.25	0.20	0.30	0.66
400	58.92	6.51	13.53	21.03	$C_1H_{1.31}N_{0.20}O_{0.27}$	1.31	0.20	0.27	0.73
600	56.14	5.84	17.25	20.77	$C_1H_{1.24}N_{0.26}O_{0.28}$	1.24	0.26	0.28	0.95
1000	56.33	5.86	17.01	20.80	$C_1H_{1.24}N_{0.26}O_{0.28}$	1.24	0.26	0.28	0.93

at 2300–2400 cm^{-1} were assigned to CO_2 in the air. Typical bands characteristic of hydrocarbons were found at 2965 (CH_3 asymmetric stretching), 2934 (CH_2 asymmetric stretching), 2875 (CH_3 symmetric stretching), 1457 (CH_2 bending), and 1385 cm^{-1} (CH_3 bending). The broad band around 3300 cm^{-1} was assigned to O—H stretching or N—H stretching. The strong band at 1664 cm^{-1} was assigned to C=O stretching of amide groups.[21,22] The band at 1119 cm^{-1} was assigned to C—O stretching in a secondary alcohol or C—N stretching in a secondary amine. The spectra of these films were similar, except for the absorption bands of 2242 and 2188 cm^{-1}. A weak band appearing at 2242 cm^{-1} was assigned to C≡N stretching of nitrile. Another weak band at 2188 cm^{-1} suggested isonitrile.[21] These spectra resembled those of plasma-polymerized films of acetylene/N_2/H_2O.[21,22] Yasuda et al.[21,22] called this polymer amide-like from the IR spectrum and the fairly equal incorporation of nitrogen and oxygen from elemental analysis. Also, in our experiment, the plasma-polymerized films from methane/air seemed to be an amide-like polymer. There were no bands around 720 cm^{-1}, and this

indicated the presence of a linear chain of four or more methylene sequences. The luck of the absorption of these bands in the FTIR spectrum and the deficiencies of hydrogen in the elemental analysis suggested a highly branched structure.

Figure 4 shows the absorbance ratios of the absorption band at 1664 cm^{-1} to that at 1385 cm^{-1} as a function of the film thickness. As the film thickness increased, the absorbance ratio of the band at 1664 cm^{-1} (C=O in amide) increased with respect to the band at 1385 cm^{-1} (C—H in methyl). This suggested that functional groups from methane were dominant when the film thickness was thin. Furthermore, it can be seen from the elemental analysis in Table I that the C and H contents were almost independent of the film thickness, whereas the N/O atomic ratio increased with increasing film thickness. From these results and FTIR analysis, it is suggested that the oxygen-containing functional groups were converted to amide groups with increasing film thickness.

The XPS results and water contact angles of plasma-polymerized films on silicon wafers are summarized in Table III. C, N, O, and a small amount (<1%) of Ti were detected in the XPS spectra of the films. It seems that a Ti electrode was etched by
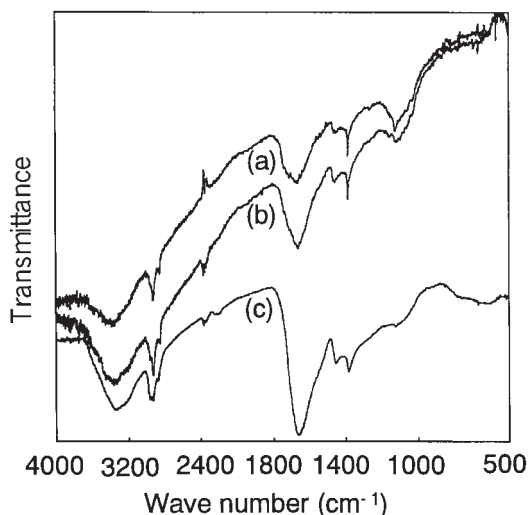

Figure 3 FTIR spectra of plasma-polymerized films with different thicknesses: (a) 10, (b) 20, and (c) 600 nm.

TABLE II
Assignment of FTIR Absorption Bands for Films Prepared from Methane/Air (2/1) by Plasma Polymerization

| Absorption band (cm^{-1})	Assignment
3332	N—H stretching, O—H stretching
2965	C—H asymmetric stretching in methyl
2934	C—H asymmetric stretching in methylene
2875	C—H symmetric stretching in methyl
2242	C≡N stretching in nitrile
2188	N=C stretching in isonitrile
1664	C=O stretching in amide
1457	C—H asymmetric bending in methylene
1385	C—H symmetric bending in methyl
1119	C—O stretching in —C—OH (secondary alcohol), C—N stretching in C—NH (secondary amine)
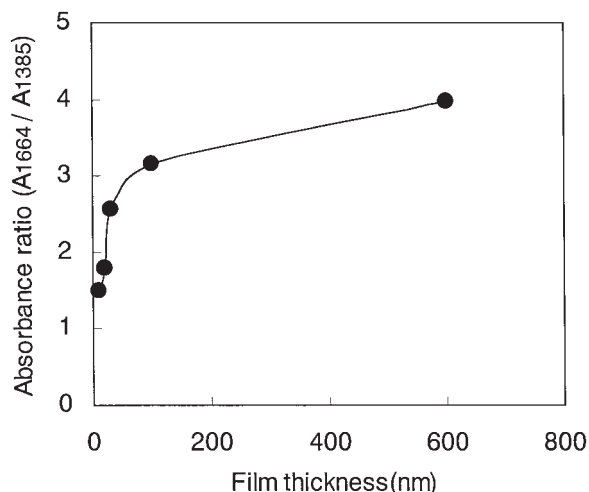
Figure 4 Changes in the absorbance ratio of the band at 1664 cm^{-1} to the band at 1385 cm^{-1} as a function of the film thickness.
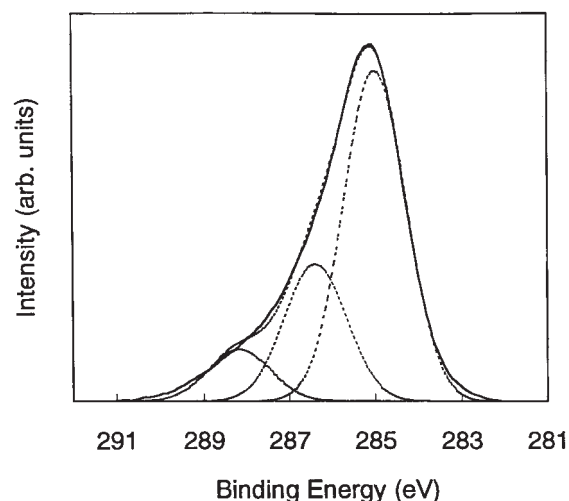

Figure 5 XPS C$_{1s}$ core-level spectrum of a plasma-polymerized film (film thickness = 40 nm).

plasma and deposited on the polymerized film. When the film thickness was thin, silicon of the substrate was detected. The atomic concentrations of C, O, and N were 77–81, 10–12, and 10–11, respectively. The atomic ratios of the films were almost independent of the film thickness.

Figure 5 shows the XPS C$_{1s}$ core-level spectrum of a plasma-polymerized film. It consists of a strong band at 285.0 eV due to C—C and C—H bonds and weak bands at 286.4 and 288.2 eV that are attributed to C—O and/or C—N bonds and to the N—C≡O bond, respectively.[18,30,31]

The water contact angles of the films were 59.8–63.5°, and they were also independent of the film thickness, as shown in Table III as well as XPS results. Figure 6 shows the typical change in the contact angle of a plasma-polymerized film from a methane/air mixture. The contact angle increased with the aging time until 7 days, and after that, the value became stable. This may be explained by the overturn and migration of the polar functional groups introduced into the surface. Yasuda et al.[8]

measured the contact angle of water on the plasma-polymerized methane subjected to an additional oxygen-plasma treatment to introduce the hydrophilic groups at the surface. They observed that the plasma-polymerized methane showed no significant decay of wettability even after 200 days. On the basis of this observation, they concluded that no rotation of the hydrophilic groups was possible because of the extremely high degree of crosslinking. In our study, a plasma-polymerized methane/air mixture formed a loosely crosslinked structure because of the introduction of nitrogen- and oxygen-containing groups.

A comparison of the N/C and O/C atomic ratios obtained by elemental analysis with those obtained by XPS showed that nitrogen and oxygen existed in the bulk more than on the surface of the film independently of the film thickness. This indicated that the surface structure of the film differed from the bulk structure. The distribution of the functional groups of the plasma-polymerized acrylic acid film deposited on the polymer substrate was studied with an angle-

TABLE III
XPS Results and Contact Angles of Films Prepared from Methane/Air (2/1) by Plasma Polymerization

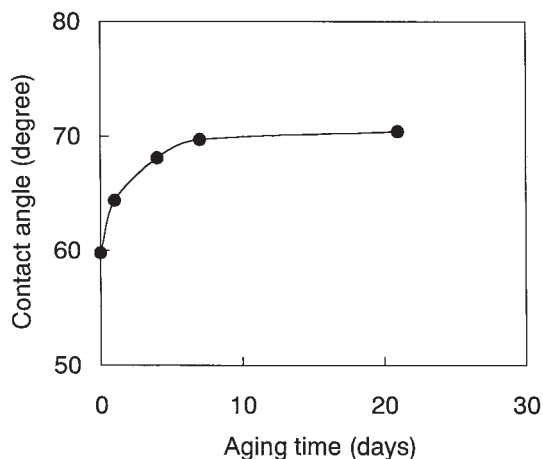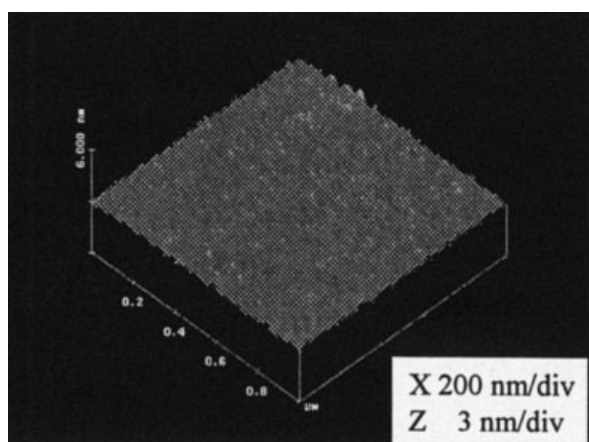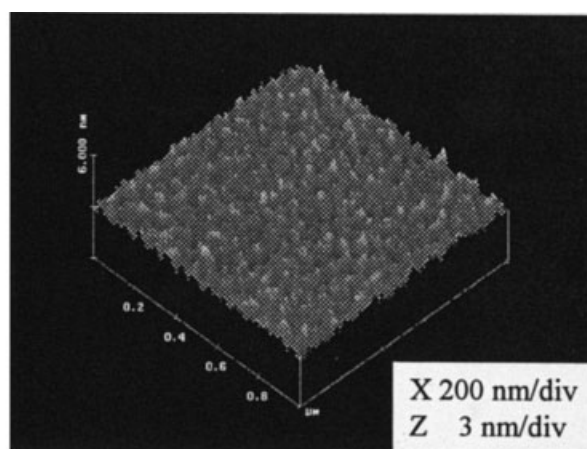| Film thickness (nm)	Atomic concentration (atom %)				Atomic ratio			Contact angle (°)
	C$_{1s}$	O$_{1s}$	N$_{1s}$	Si$_{2p}$	N/C	O/C	N/O	
10	72.7	12.6	11.9	2.8	0.15	0.17	0.88	59.8
33	78.3	10.7	11.0		0.14	0.14	1.03	62.1
40	79.7	9.8	10.5		0.13	0.12	1.08	60.8
48	80.6	9.8	9.6		0.12	0.12	0.98	63.5
60	78.7	10.7	10.6		0.13	0.14	0.98	62.3
100	77.5	11.8	10.7		0.13	0.15	0.90	60.2
400	77.8	11.4	10.8		0.14	0.14	0.95	61.2
600	77.3	12.3	10.4		0.13	0.16	0.85	62.6

Figure 6 Typical change in the contact angle of water on a plasma-polymerized film as a function of the aging time (film thickness = 10 nm).

dependent XPS experiment.[4,5] It was suggested that the hydrophilic oxygen-containing functional groups diffused into the bulk of the material with time because the air/film interface was hydrophobic. Also, in our case, the bulk phase of these films was more hydrophilic than air, and so the hydrophilic nitrogen- and oxygen-containing groups were buried in the bulk of the film.
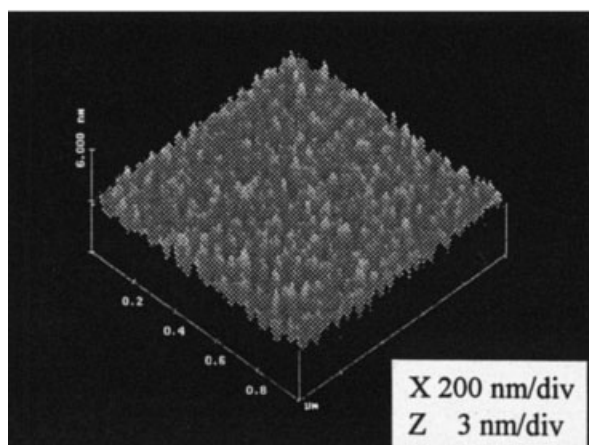
Figure 7 shows AFM images of plasma-polymerized films with different thicknesses on silicon wafers. An uncoated silicon wafer had a smooth surface [Fig 7(a)]. In contrast, plasma-polymerized surfaces had rough surfaces. The surface roughness increased with the film thickness. R_a was used for quantitative evaluation. This was the mean value of the surface with respect to the center plane. The film 600 nm thick [$R_a = 1.580$ nm; Fig. 7(d)] had a much rougher surface than that 40 nm thick [$R_a = 0.173$ nm; Fig. 7(b)]. It seems that the film 40 nm thick had
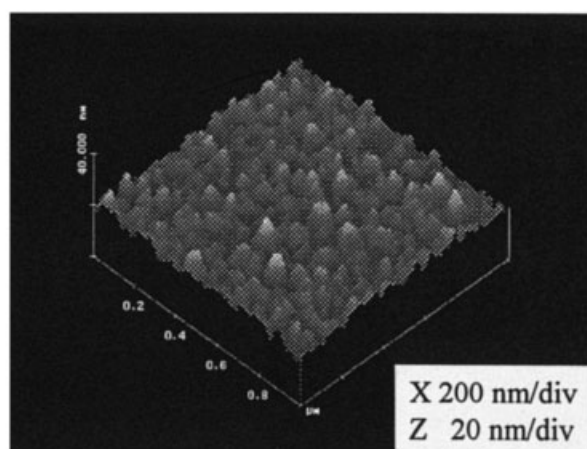

Figure 7 AFM micrographs of plasma-polymerized films on silicon wafers with different thicknesses: (a) uncoated ($R_a = 0.106$ nm), (b) 40 nm ($R_a = 0.173$ nm), (c) 100 nm ($R_a = 0.228$ nm), and (d) 600 nm ($R_a = 1.580$ nm). R_a values were evaluated from corresponding micrographs with a surface area of 1000 × 1000 nm.

a relatively flat but grainy surface. The small granules agglomerated and were incorporated into the film structure with an increase in the film thickness.

CONCLUSIONS

Plasma polymerizations of methane/air mixtures were investigated from the viewpoint of the structure of the bulk and surface:

1. Nitrogen and oxygen atoms were incorporated into the plasma-polymerized film.
2. The elemental composition obtained by XPS analysis and the water contact angles were independent of the film thickness. The fairly equal incorporation of nitrogen and oxygen was confirmed by XPS analysis.
3. The elemental composition obtained by elemental analysis changed according to the film thickness. Also, the composition of functional groups by FTIR changed with the film thickness.
4. The structure of the film was similar to that of an amide compound.

This is a safe process to produce hydrophilic coatings because harmful amide, amine, or carboxylic compounds and so on are not used as monomers of plasma polymerization. Moreover, this is a solvent-free process and so is environmentally clean. Applications of this film to the modification of polymer surfaces will be explored in the near future.

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