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Chemical structure and surface morphology of plasma polymerized-allylamine film

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Abstract−In this study, we conducted the plasma polymerization of allylamine using radio frequency (RF) glow discharge with continuous wave (CW) in order to make an organic thin film with an amine functional group retained. Allylamine as a monomer was deposited on a glass in a bell-jar type plasma reactor and polymerized to plasma-polymerized allylamine (PPAa). The parameter to control the property of plasma polymer was input power at other conditions remaining constant. The chemical structure and the surface morphology of plasma-polymerized allylamine (PPAa) film were characterized by contact angle measurement, Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM). The property of PPAa film was highly dependent upon the plasma input power. The input power, which determines the plasma density, results in a property of PPAa thin film such as hydrophilicity, high retention of functionality of PPAa's surface. Surface energy calculated by contact angle measurement indicated that increasing input power (from 30 W to 90 W) decreased the hydrophilic property of PPAa due to loss of amine functional group and high cross-linking. The increase of the energy causes the films to be harder. ATR-FTIR and XPS results showed that high input energy fragmented the amine group from monomer with increasing nitrogen atomic content and nitrile group. The high retention of amine groups seems mainly favored by low input power (<30 W). From thickness measurement using α-stepper, the deposition rates were 0.43, 0.83, 1.11, 1.37 nm/s at 30, 50, 70, 90 W, respectively. The change of surface morphology of plasma-polymerized thin films was investigated after soaking the PPAa film into ethanol. Due to weak adhesion with substrate and internal stress in plasma polymer film, the surface morphology of PPAa film revealed some irregular network pattern.

Key words: Plasma-polymerized-allylamine, Continuous Wave RF Discharge, Surface Chemical Property, Surface Morphology

INTRODUCTION

The synthesis of organic thin film has recently advanced due to their broad applications in mechanics, electronics and optics frields [Shi, 1996; Martinu, 2000; Poll and Schreiter, 1997; Retzko et al., 2001]. Plasma polymerization is a useful method to prepare ultra thin films [Favia and d'Agostino, 1998; Biederman and Slavínská, 2000; Shirtcliffe et al., 2001]. Plasma polymerization is a process in which monomers are polymerized in glow discharge of organic feed gases, where molecules become radicals, ions and electrons. These active species are deposited on a substrate in the form of thin film, powder or viscous liquid [Yasuda, 1985; Kurosawa et al., 2002; Anma et al., 2001; Ihara et al., 1997]. This process could modify the surface of various materials through coating their surfaces without changing bulk properties. Plasma-polymerized-polymer can have either hydrophobic or hydrophilic surfaces depending on the choice of monomer and present biocompatibility, permeability and anti-corrosion [Biederman et al., 1995; Bonizzoni and Vassallo, 2002; Bogaerts et al., 2002; Garrison et al., 1999]. Also, plasma polymer is inert, insoluble, strong and thermally stable because of high degree of cross linking, so it can be applied to biosensors, microelectronic devices, non-linear optics (NLO), and molecular devices [Shi, 1996; Chu et al., 2002; Muguruma and Karube, 1999].

Amine and carboxyl groups increase the adhesion of proteins and/or cells and subsequently provide many reactive sites for covalent bond between biomaterial and graft polymer. Plasma polymerization of monomer such as allylamine, allylalcohol and acrylic acid, provides wettability to hydrophobic surface in the form of thin film [Schõnherr et al., 2000; van Os et al., 1999; Rinsch et al., 1996]. To make high functional group retention, continuous-wave (CW) plasma with a low ratio of power to monomer flow rate or pulsed plasma with the ratio of rf 'on' to 'off' time have been used. Kuhn et al. [2001] reported pulsed plasma adhesion-promoting polymers with OH, COOH, NH_2, epoxy and CN groups. Kettle et al. [1997] showed that the introduction of allylamine, allylalcohol and acrylic acid to fiber surface improved the adhesion for composites. Hemerli et al. [2003] enhanced cell adhesion and viability by coating plasma-polymerized-allylamine on the surface of membrane. Gancarz et al. [2003] studied the enzyme immobilization through depositing plasma-polymerized-allylalcohol on polysulfone film. Other researchers have also studied plasma polymerization to understand the fundamental phenomena. Beck et al. [1998, 2001] showed the mechanism of plasma polymerization through a mass spectral investigation of the plasma-phase reactions in plasma deposition. They found that ion contribution to the deposit growth is very important at low power (<15 W). The cationic oligomerization in the gas phase illustrated the chemistry of the plasma deposition. Up to now, however, it has been difficult to expect both the chemical and the physical structure of film, because plasma polymer depends on parameters such as power, reactor shape and electrode [Russell and Weinkauf, 2001; Hynes, 1996]. The process parameters are highly system-dependent. Optimal parameters found for one system may not be commonly adopted for another system.

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In this study, we investigated the effect of plasma input power on the formation of thin films through plasma-polymerization and studied the structural and chemical characteristics of plasma-polymerized-allylamine (PPAa) film. Thin functionalized plasma polymer films have received a great deal of interest, but the protocol for the plasma polymerization process as yet is not well defined. To apply thin functionalized plasma polymer films to sensors or biochips, the protocol of fabrication on a qualified surface as substrate for binding the biomolecules must be established. We are trying to develop thin functionalized plasma polymer film for the application of biochip construction. For this application, the allylamine plasma polymer is required to have a high proportion of amines functional groups (so that it becomes positively charged in aqueous media) and hydrophilicity (used in aqueous media).

EXPERIMENTAL

1. Plasma Reactor

A schematic diagram of the reactor system is shown in Fig. 1. The plasma reactor system used in this study for the deposition consisted of four main components. The components are as follows: (1) a reaction chamber where the excitation of gases and molecules as well as deposition of plasma polymer occurs; (2) a vacuum system used to maintain a pressure inside the reactor; (3) a power supply coupled to the reactor to generate the power necessary for depositions, and (4) a flow regulation system used to control the gas flows of the excitation gas and the polymer precursors. The equipment is a bell-jar type reactor with radio frequency of 13.56 MHz (Model EPPS 2000, PLASMART Inc. Korea), with an output impedance of 50 ohms. The pressure of the vacuum chamber was monitored by vacuum gauge (Model 801, Varian). A mass flow controller (MFC, Model 5850E, Brooks, Japan) was used to input argon gas. Monomer vapor was introduced into the vacuum chamber from the reservoir by controlling the needle valve.

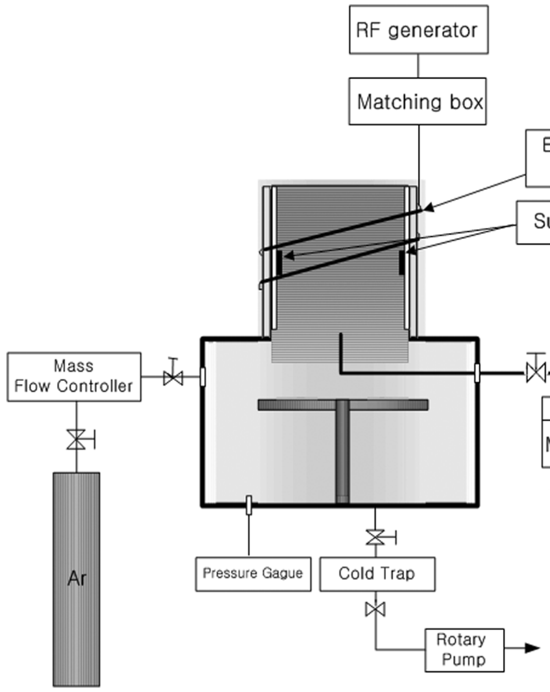

Fig. 1. Schematic diagram of the plasma reactor.

2. Plasma Polymerization

In the previous test, we realized that the deposition of PPAa film mostly occurred on an inner reactor wall wound with external copper coil. The formation of plasma polymer in the location was very sensitive to reaction conditions such as power, pressure and flow rate. Thus, a slide glass was attached on the inner reactor wall as plasma active zone. Initially, the pressure of the reactor was pumped down to 6.66 Pa by vacuum pump. After flowing of argon gas, it retained 33.33 Pa. To activate and clean the surface of substrate, argon plasma was generated with 100 W for 1 min. For polymerization, allylamine monomer vapor was fed to the vacuum chamber through a needle valve in order to make a mixture of monomer and argon. The pressure of the system was controlled in the range of 53.33-66.66 Pa and the power supplied to external electrode was set at 30, 50, 70, and 90 W, respectively. Plasma polymerization was carried out for 10 minutes. The mixture of argon gas and allylamine vapor became plasma state after absorbing electromagnetic energy. Electrons accelerated within the applied electric field impacted gas molecules to generate ions, electrons, free radicals and excited-state molecules. Energetic particles out of the plasma diffused toward the reactor walls, or the substrate surface, dissipating their energy. Fragments of monomers and gases can form oligomers and clusters which diffuse to the surface of substrate (and reactor walls) and cover. As plasma polymerization time increases, the thickness of the deposition layer increases. The color of allylamine plasma polymer film on the glass surface was dark yellow and became darker with increasing power.

3. Analytical Method

ATR-FTIR (Travel-IR made by Micro-ART) was used to identify the chemical structure of PPAa films and XPS (MK II, V.G Scientific LTD) to analyze the surface chemical composition of film. The morphology of PPAa deposited on glass slides was observed by SEM (SM-500, TOPCON). An α-step (Alpha-STEP 500, Tencor) was used to measure film thickness. The thickness of a given film was measured at three different positions. The hydrophilicity of film was investigated by a contact angle measurement (Contact-Angle (CA-A), Kyowa Interface Science Co. Ltd., FACE, Japan). Deionized water and diiodomethane used as polar and dispersion components, respectively, were dropped onto the surface of sample with 3 μl. The angles were read through the lens. In this experiment, eight point measurements on each sample were randomly performed, and the average value of the eight point measurements was regarded as the contact angle of the sample. The surface free energy of thin film after plasma treatment was calculated from the results of contact angle test by using Owen's method [Zenkiewicz, 2001]. The surface free energy (λ_s) of a solid is equal to the sum of both dispersion (λ_s^d) and polar (λ_s^p) components; $\lambda_s=\lambda_s^d+\lambda_s^p$

RESULTS AND DISCUSSION

1. Contact Angle Measurement

The surface hydrophilicity of PPAa thin film was measured by the contact angle of water and diiodomethane at each power. The contact angle provides the property of top surface on 0.5-1 nm less than 5-6 nm by XPS. Fig. 2 shows the surface free energy of each thin

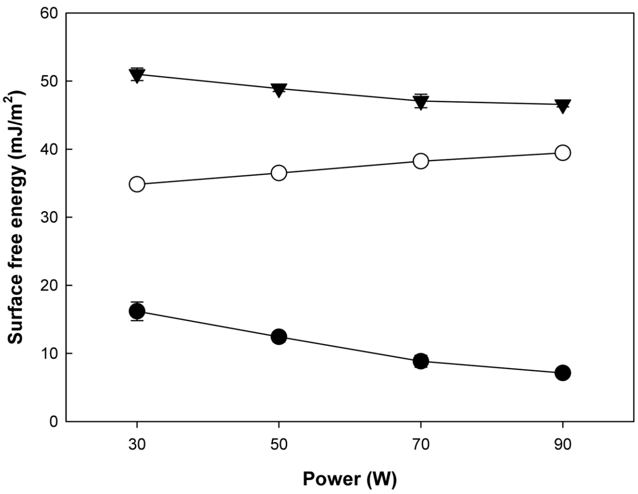

Fig. 2. Surface free energy with respect to power (▼ total, ○ dispersion, ● polar).

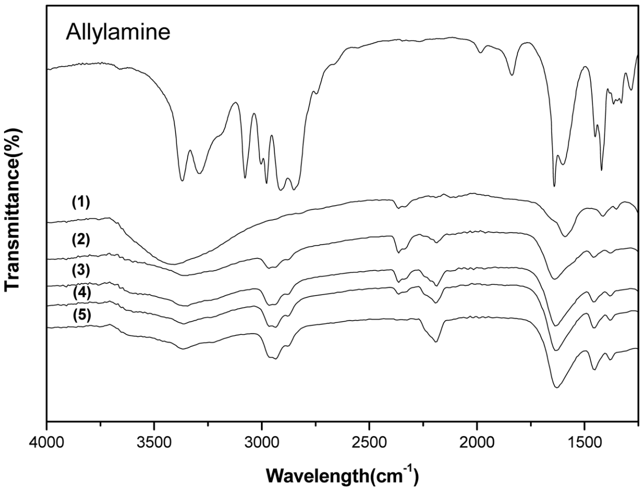

Fig. 3. ATR-FTIR transmission spectra of allylamine monomer and PPAa at various input power. (1) slide glass (2) polymer at 30 W (3) polymer at 50 W (4) polymer at 70 W (5) polymer at 90 W.

film prepared by plasma polymerization. The surface free energy was calculated with the contact angle. As shown in Fig. 2, the contribution of polar component was lager than the contribution of nonpolar component. Because the contact angle of water increases with increasing input power, the surface free energy decreases. So the hydrophilicity of PPAa decreased with increasing input power. Due to the change of the surface property related to physical and chemical structure, the hydrophobicity of plasma polymer increased. Aizawa et al. [2000] who fabricated the thin film of PPAa and studied the surface aging also indicated that the surface free energy decreased with increasing power. Polar contribution resulting from an increase of contact angle of water was smaller than the dispersion contribution resulted from a decrement of contact angle of diiodomethane. The main factors which resulted in the decrease of surface free energy were the loss of amine functional group and the formation of crosslinked structure due to more fragmentation of allylamine through increasing the input power. The physical property of PPAa becomes more rigid due to more dense packing and strong bonding. The plasma phase highly depends on the input power. High power results in an increase of electron density through the acceleration of consecutive activation-deactivation in plasma state. Ions and radicals resulting from the breakage of monomer increase the formation of more dense film at high power. Thus, the increase of the energy causes the films to be more rigid. Plasma with high energy (high electron density and subsequently accelerated plasma polymerization) influences the bulk structure of plasma polymer film. The change of bulk structure eventually affects the surface property of thin film. The amount of functional groups determines the surface free energy of plasma polymer. Polar effect comes from the functional groups like amine/imine and intermolecular forces like dipole-dipole moment. Surface free energy can also be the index of the surface functionality. The surface of high surface energy with functionality possesses high reactivity like covalent/ionic bonding ability.

2. ATR-FTIR Spectra

The chemical structure of PPAa film measured by ATR-FTIR is shown in Fig. 3. The ATR-FIIR spectra of the CW rf plasma deposited film, although only qualitative in nature, revealed progressive changes in film composition with varying input power. During plasma polymerization, the exited and broken monomers were crosslinked while forming new bonds through complex mechanism. Plasma polymers do not form long chains with repeat units, but construct irregular crosslinked networks [Russell and Weinkauf, 2001]. Allylamine monomer has double peaks of a primary amine N-H stretching vibration at 3,370 and 3,289 cm^{-1}, and shows multiple absorption peaks due to the stretching vibration of aliphatic C-H groups at 2,977, 2,913, and 2,850 cm^{-1}. The absorption peak of stretching vibration does not appear at 2,200 cm^{-1}, which represents the absence of nitrile ($C\equiv N$) groups in monomer. The monomer undergoes reorganization during plasma polymerization due to the breakage and the recombination of bonds. In case of PPAa, bands at 3,500-3,200 cm^{-1} and 2,900-2,800 cm^{-1} are significantly broadened because amine groups are partially transformed into amide, imine or nitrile functional groups. The peak at 1,640-1,560 cm^{-1} in the PPAa indicates the presence of alkene or imine groups. The peaks at 1,450 and 1,350 cm^{-1} indicate the CH_2 and CH_3 bending absorption peaks,

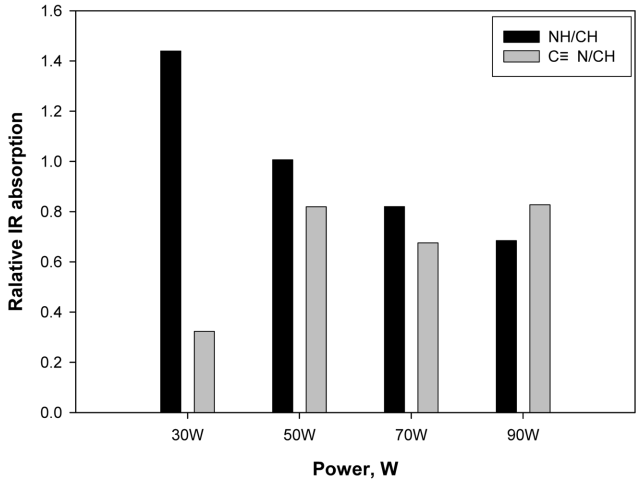

Fig. 4. Relative IR absorption at different power.

respectively. And a new peak appears at 2,185 cm^{-1}, which is associated with nitrile (C≡N) stretching vibration. Fig. 4 shows the relative IR absorption peak ratios of NH to CH and C≡N to CH. High-power plasma leads to a higher ratio of C≡N to CH than the ratio of NH to CH, thus to a recombination of amine functionalities into nitrile (C≡N) groups [Schönherr et al., 2000; van Os et al., 1999; Rinsch, 1996; Hamerli, 2003]. Plasma constituents such as photons, metastables, electrons, dissociated chemical bonds lead to serious removal of hydrogen (dehydrogenation) in amine group. Relative high IR absorption ratio of NH to CH than the ratio C≡N to CH resulted from high amine functional group on the surface of PPAa. As shown from FTIR results, ions largely fragment from monomer at high power and so plasma obtained at different powers contains different compositions of ion species. More fragmented species existed in high plasma density. Fragmentation is limited at low power. At high power, however, fragmentation is accelerated and this acceleration is related to the dissociation yield of monomer in plasma phase and the increase of CN content in polymer. Thus, it results in the formation of imine groups and at high power, nitrile groups [Alexander et al., 2004]. Thus, the high retention of amine groups seems to mainly favor low power (<30 W) operation.

3. X-Ray Photoelectron Spectroscopy

The chemical composition of the PPAa film was investigated through XPS analysis. Table 1 represents the elemental compositions of carbon (C), nitrogen (N) and oxygen (O) with respect to the plasma input power. The ratio of N to C at 30 W was higher than that at high power due to the low loss of amine groups. Low-energetic plasma below 30 W could protect the amine functionality of plasma polymer. The fragment of monomer caused hemolytic cleavage of the C-NH_2 bond to give a relatively stable allyl radical and NH_2 under plasma action over critical 50 W as high energy [Beck et al., 1998]. High power plasma increased the ratio of N to C while removing hydrogen atom from amine groups. Incensement of N/C ratio over 50 W derived from nitrogen-containing fragments such as HCN and C≡N. Thin film made from microwave-polymerized-allylamine represented that the ratio of N to C was 0.29-0.35 at 400 W, and 0.39-0.47 at 1,200 W [Hamerli et al., 2003]. In microwave plasma, the enrichment of nitrogen occurred as a result of high-energetic plasma, whereas the N/C ratio for polymers produced by low-energetic plasma was lower than that of the monomer (the ratio of N/C of allylamine monomer is 0.33). The authors explained that the ion density at high energy in the post-discharge region was similar to that at low energy in glow-discharge plasma; thus less fragmentation occurred. In case of CW RF discharge, however, the ratio of N to C at 50 W was <0.25 [Schönherr, 2000], and in low-duty cycle pulsed conditions, the ratio of N to C was rather <0.30 [van Os et al., 1999]. The low power of CW or pulsed plasma resulted in increasing the ratio of N to C because the low energetic plasma made less fragmentation of monomer. In our plasma system, the ratio of N to C at 30-90 W was <0.14 (Table 1). This reflects that the loss of amine groups is significant as increasing plasma power. One reason is because argon gas was added. So argon plasma greatly affects bond breakage in monomer structure or the surface of PPAa. However, the presence of argon could stabilize plasma state [Schönherr et al., 2000]. The other reason is that monomer was mainly deposited on the high-energy glow region near the wall of the external coil. In this region, high energy plasma can make more fragmentation of monomer or PPAa. Low power and pulsed plasma have received great interest due to the improvement of wettability while reducing the bond breakage of functional groups [Russell and Weinkauf, 2001; Hynes et al., 1996; Wang et al., 1996; Han et al., 1997]. The nitrile (C≡N) group is an adhesion-promoting group. It could be achieved by using acrylonitrile-plasma polymerization [Kuhn et al., 2001]. O1s peak represented 5.7-15.2% in Table 1. More amine groups which reacted with oxygen in air existed on the surface of PPAa at 30 W. Thus, it contained more oxygen. Because other PPAa over 50 W retained a little amine group, oxygen content was low. Other literature also reported the concentration of oxygen as minimum 4-7%, and maximum 18% [Beck et al., 2001]. According to ATR-FTIR and XPS results, the continuous RF plasma at low power could fabricate plasma polymer having such high functional group retention.

Table 1. Elemental composition of PPAa films prepared at different power

Power	C	N	O	N/C
30 W	76.7	8.1	15.2	0.11
50 W	85.3	7.2	7.5	0.08
70 W	81.3	10.4	8.3	0.13
90 W	82.7	11.6	5.7	0.14

Fig. 5 shows the peak fitted C1s core line of the spectrum for PPAa prepared at every power. C1s spectrum of PPAa thin film was

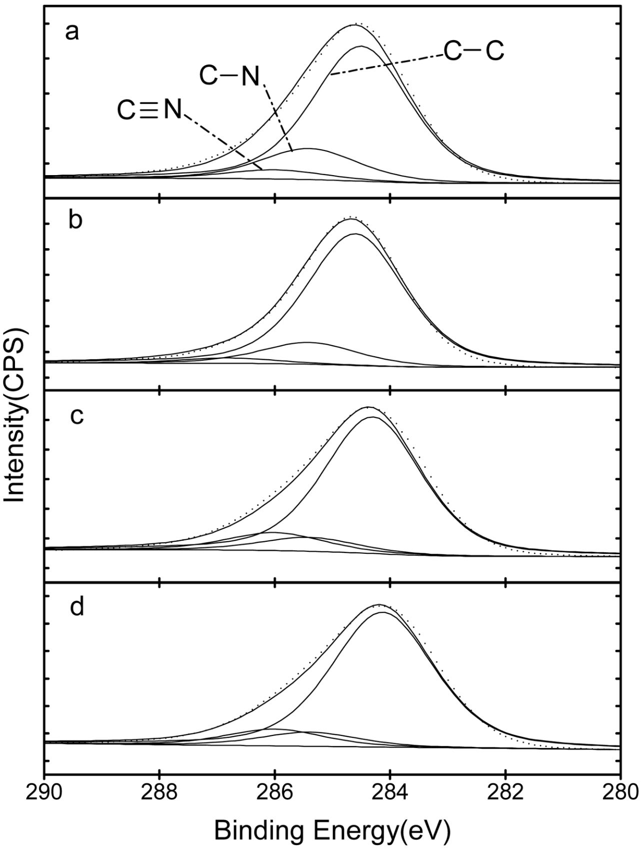

Fig. 5. XPS C1s core level scan spectra of (a) polymer at 30 W, (b) polymer at 50 W, (c) polymer at 70 W, and (d) polymer at 90 W.

de-convoluted into three peaks. C1s1 at 284.6 eV was due to carbon atoms composing of CHx groups, C1s2 at 285.4 eV due to carbon atoms singly bonded with nitrogen (C-N might be primary, secondary, or tertiary amine groups), and C1s3 at 286 eV due to imine (C=N) groups [Beck et al., 1998]. The percentage contributions of $C\equiv N$ at C1s3 components of PPAa were increased, as verified by ATR-FTIR spectra. C1s2 and C1s3 also included C-O and C=O functionalities, respectively. The percentage contributions of C-O and C=O at C1s2 and C1s3 components were decreased, as verified in Table 1. With increasing input power, the percentage of C-N largely goes down. This trend resulted from the loss of C-N functionality by fragment. Higher percentage of $C\equiv N$ was obtained by high CW RF plasma.

4. Deposition Rate and Surface Morphology

The deposition by plasma polymerization was performed for 10 min at 53.33-66.66 Pa. The thickness of thin film measured from α-stepper is about 259 nm at 30 W, about 500 nm at 50 W, about 664 nm at 70 W, and about 826 nm at 90 W. The thickness of this film increased with increasing input power since high power generates high plasma density. The approximate deposition rate was about 0.43, 0.83, 1.11, 1.37 nm/s at 30, 50, 70, 90 W, respectively. From a view point of deposition efficiency, the high input power increases the deposition efficiency within the same polymerization period. Fig. 6 shows the surface morphology of the PPAa films observed with optical microscopy and SEM. Figs. 6(a1) and (a2) were taken after soaking in ethanol. The PPAs films were washed for the purpose of cleaning to dissolve weakly bonded molecules. SEM images in Fig. 6(b1) and (b2) were taken just after deposition. Some network patterns are found on the samples of Fig. 6(a1) and (a2). There is no such network observed by SEM in the samples without soaking except some coarse grains to form a somewhat rough surface in Fig. 6(b2). When thin film absorbs solvent, it is peeled off partially from substrate by weak adhesion. This kind of phenomenon was found in previous researches [da Silva et al., 2003; Zajickova et al., 2003; Zhang et al., 2003]. Plasma polymerized films with highly hydrophobic hexamethyldisilizane showed wrinkles in the film, indicating a great affinity to the solvents [da Silva et al., 2003]. Most likely peeling that occurred in the aging test is due to stresses present in the film [Zajickova et al., 2003]. 'Lightning' network and a valley of the pattern was found on surface morphology of plasma polymerized vinyl acetic acid [Zhang et al., 2003]. Generally, such irregular pattern due to inner stress as well as wet absorption characterizes the surface morphology of plasma-polymerized thin films irrespective of monomer type. Some problems like the above mentioned need to be overcome when thin functionalized plasma polymer would be applied to supporter for biological molecules. Recently, plasma polymerized films have been used to biosensor [Muguruma et al., 2000; Mar et al., 1999], protein chip [Kim et al., 2003; Szili et al., 2004], SPR [Zang et al., 2003].

CONCLUSIONS

Continuous wave RF plasma polymerization was used to control the structure and property of the plasma-polymerized-allylamine thin film. The property of PPAa film was highly dependent upon the plasma input power. The input power was the most important

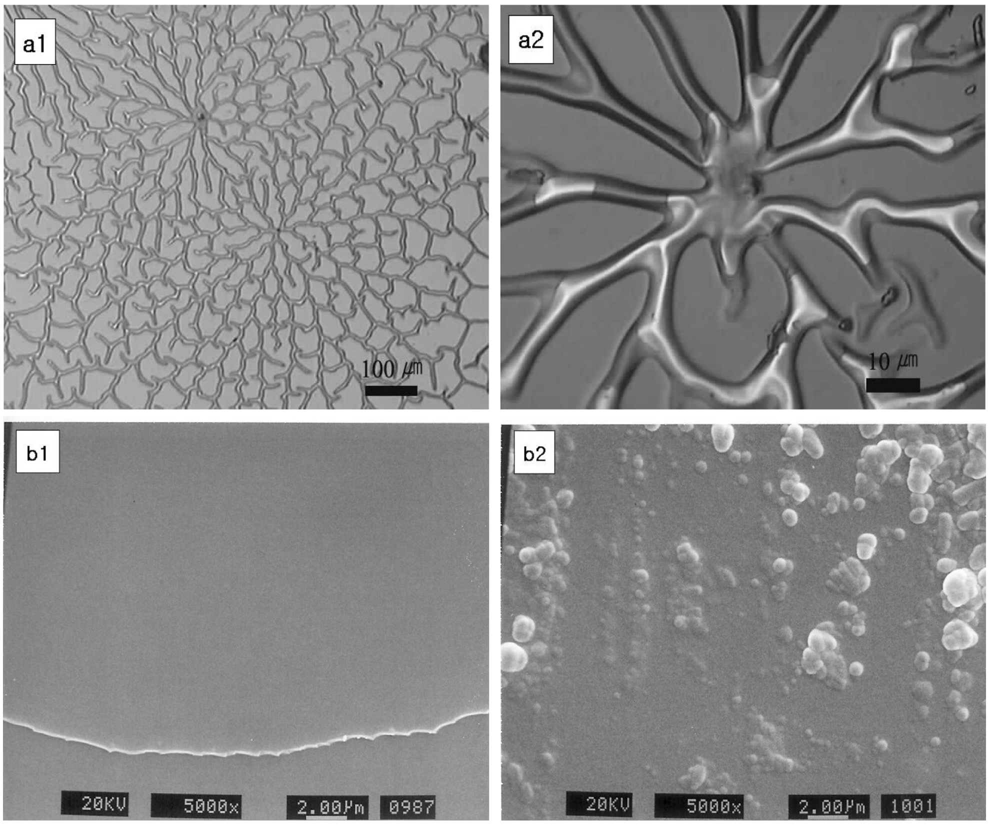

Fig. 6. Optical micrographs (a1, a2) and SEM images (b1, b2) of plasma-polymerized allylamine at 30 W.

factor to determine the kinetics and density of electrons in plasma. The surface of plasma polymers produced at lower wattage could contain more amine groups due to fewer fragments of precursor as represented in ATR-FTIR and XPS analysis. In our own system, an input power of less than 30 W must be selected to prepare the hydrophilic surface and introduce high retention functional group. Hydrophilicity and high retention amine functionality of plasma polymer are essential on the substrate of biochip for water base solution and the immobilization of biomolecular (protein, DNA). The deposition rate from the thickness of thin films gradually increased with increasing the input power. Because of the unstable and hydrophilic property of the PPAa in aqueous media, the surface morphology of PPAa is subjected to some irregular network patterns. A thin film of plasma polymer having a gradient layer could be obtained by varying the input power from high to low wattage during plasma polymerization.

ACKNOWLEDGMENTS

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NOMENCLATURE

RF : Radio Frequency
CW : Continuous Wave
PPAa : Plasma Polymerized Allylamine
ATR-FTIR : Attenuated Total Reflection Fourier Transform Infrared
XPS : X-ray Photoelectron Spectroscopy
SEM : Scanning Electron Microscopy
W : Watt
MFC : Mass Flow Controller

Greek Letters

λ_s : surface free energy
λ_s^d : dispersion component
λ_s^p : polar component

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