Influence of Surface Treatment of Polyimide Film on Adhesion Enhancement between Polyimide and Metal Films

Soo-Jin Park,[†,*] Eun-Jung Lee, and Soo-Han Kwon

[†]*Department of Chemistry, Inha University, Incheon 402-751, Korea.* [*]*E-mail: sjpark@inha.ac.kr*
Department of Chemistry, Chungbuk National University, Cheongju 361-763, Korea
Received October 27, 2006

In this work, the effects of chemical treatment of polyimide films were studied by FT-IR, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angles. The adhesion characteristics of the films were also investigated in the peel strengths of polyimide/aluminum films. The increases of surface functional groups of KOH-treated polyimide films were greatly correlated with the polar component of surface free energy. The peel strength of polyimides to metal substrate was also greatly enhanced by increasing the KOH treatment time, which can be attributed to the formation of polar functional groups on the polyimide surfaces, resulting in enhancement of the work of adhesion between polymer film and metal plate.

Key Words : Polyimide, Chemical treatment, Adhesion characteristics, T-peel test

Introduction

Metal-coated polymers are used in various technologies for a wide range of applications. Thin film metallized polymers are used extensively in radio and electronics, cryogenics engineering, computer technology, solar-energy converters, etc.[1,2] With the increase of the use of metallized polymers in the microelectronic industry, an understanding of the mechanism responsible for adhesion between metals and polymers has become of increasing importance. Among the polymers suitable for microelectronic applications, polyimide has received a great attention due to their thermal and chemical stability, low dielectric constant, high electrical resistivity, and relative ease of processing into coating and films.[3-6] For all these reasons, polyimides have been widely used in microelectronics as dielectric spacing layers, protective coatings and substrates for metal thin films, replacing traditional inorganic insulators such as SiO_2 in many applications.[7-10] In these and other applications good adhesion between polyimide and a metal substrate is required.

However, the adhesion of metals directly to the polyimides is usually poor due to the inertness of polyimide surfaces. Failure to activate a polyimide surface will normally cause the subsequent coatings to be poorly adhered and easily cracked, blistered, or otherwise removed.[11,12] Various surface treatments and modification methods have been used to enhance the metal to polyimide adhesion. These include the uses of ion beam, photografting, plasma, and sputtering. Most of these methods require high vacuum equipment and the productivity is low; thus they are not economically feasible. These methods may also introduce foreign materials and undesirable modified layers into the interfaces, resulting in possible reliability failure.[13-15]

Interests in wet-process surface modifications of polyimides have increased due to simplicity and low cost. Polyimide films are resistant to most solvents and chemicals, but they react with oxidizing or reducing agents. However, if the concentrations of the chemical reagents, reaction temperatures, and reaction time are well controlled, the reactions can be confined to the surface.[16]

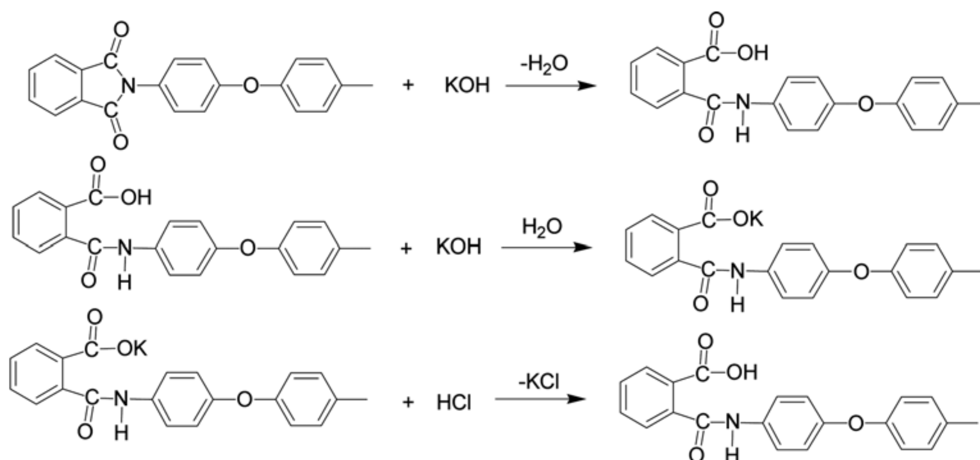

Figure 1. Imide ring opening in polyimide film by KOH treatment at room temperature.

In this work, polyimide films were initially modified with KOH solution as a function of KOH treatment time and then reacted with HCl solutions to polyamic acid surfaces (Figure 1). We attempt to investigate the effect of mechanical properties of the PI films and the influences of surface properties on the adhesion strength and mechanical properties of polyimide films are also studied by a peel test with a metal layer.

Experiments

Materials and sample preparation. Pyromellitic dianhydride-oxdianiline (PMDA-ODA) polyimide type 2545 (DuPont) is spun onto aluminum plate (Fukuda, >99.5%, 50 μm) and is then cured by following a standard recipe. Polyimide films were treated with 10 wt.% KOH aqueous solution at room temperature in the range of 0 to 80 min in order to give the corresponding potassium polyamate. The excess of KOH was removed by washing with water (2 × 3 min). Then, the polyimides were treated with 10 wt.% HCl aqueous solution at room temperature for 5 min. The modified surfaces would be polyamic acids, and the polymides were dried under vacuum for another 12 h.

Surface properties. FT-IR spectra of chemical treated polyimide were obtained using a MIDAC M2000. The scans were shown from 400 to 4000 cm^{-1} and required 40 s to complete.

The X-ray photoelectron spectroscopy (XPS) measurement of polyimide surfaces was performed using a VG Scientific ESCA LAB MK-II spectrometer equipped with a Mg-Kα X-ray source. The base pressure in the sample chamber was controlled in the range fixed the C_{1s} peak at 284.6 eV considering the neutralization.

Surface morpology. The surface free energy of the KOH-treated polyimide film was determined at 20 ± 1 °C using a sessile drop method on a Surface & Electro-Optic Co. SEO 300A. Four different wetting liquids, distilled water, diiodomethane, ethlyene glycol, and ethylene glycerol were selected. For each sample, every calculated contact angle was an average of 10 measurements with a standard deviation below 1°. For this work, the surface tension and its components for the wetting liquids are shown in Table 1.

The surface morphologies of the chemical treated polyimide were studied by atomic force microscopy (AFM), suing a Digital Instruments Inc. Nanoscope III microscope. In each case, an area of 10 × 10 μm was scanned using the tapping mode. The AFM observation was carried out at ambient pressure and room temperature. The surface roughness of the polyimides was evaluated in terms of the arithmetic-mean of the roughness (*R*a) and the rootmean-square (RMS) of the roughness.

Table 1. Surface free energy characteristics of the testing liquids, measured at 20 °C

	γ_L^L (mJ·m^{-2})	γ_L^{SP} (mJ·m^{-2})	γ_L (mJ·m^{-2})
Water	21.8	51.0	72.8
Diiodomethane	50.42	0.38	50.8
Ethylene glycol	31.0	16.7	47.7
Glycerol	33.9	29.8	63.7

Adhesion characteristics. The adhesion strength of the KOH-treated polyimides/aluminum was determined by measuring the T-peel adhesion strength. The aluminum foil used as a metal layer for the T-peel test was supplied by Fukuda with a thickness of 50 μm, and the epoxy resin was the diglycidyl ether of bisphenol A (YD-128, supplied from Kukdo Chem. Co.). The curing agent was diaminodiphenyl methane (DDM, 1:1 of equivalence ratio) purchased from Aldrich Chem. Each sample was cured for 2 h at 120 °C. The T-peel test (ASTM 1876-72) was measured at a peel rate of 254 mm/min using Lloyd LR5K.

Results and Discussion

Surface properties. The polyimide surface was reacted with aqueous KOH solution to yield potassium polyamate, which was subsequently acidified by 10 wt.% HCl to polyamic acid. Figure 2 shows the FT-IR spectra of pure polyimide, KOH-treated polyimide, and HCl-treated polyimide. The key features of the FT-IR spectrum of the polyimide film are listed in Table 2.[17] In Figure 2, the 1513 cm^{-1} peaks of the polyimide were scaled to a constant since the aromatic skeletons remained unaltered after the chemical treatments. The changes to the other FT-IR peaks of the modified polyimide surfaces were thus clearly revealed.

In Figure 2(a), the characteristic absorption bands of the pure polyimide appear near 1780 (C=O in phase), 1720 (C=O out of phase), 1513 (C=C in C_6H_6), 1370 (C=O in imide), 1100 ($(OC)_2NC$ in imide), and 720 cm^{-1} (imide ring deformation). After treatment in KOH solution, in Figure 2(b), the intensities of the imide structures at 1780 and 1720 cm^{-1} peak were reduced. The shifting of the peak 1370 cm^{-1} indicate that the imide structures of the pure polyimide were hydrolyzed into the amide structures in potassium polyamates and polyamic acids after washing and acidification. The characteristic absorption bands of the polyamic acid

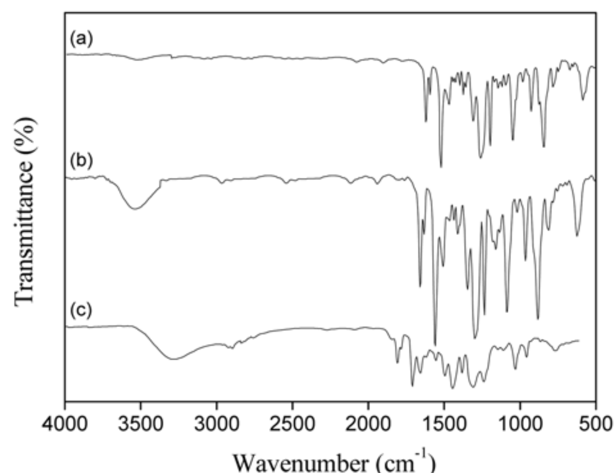

Figure 2. FT-IR spectra of polyimide films; (a) pure poltimide, (b) 10 wt.% KOH treatment, and (c) 10 wt.% HCl treatment.

Table 2. FT-IR peak assignment of the surface treated polyimide films

Peak position (cm^{-1})	Peak assignment
3600-2500	(N-H) and (O-H) reduplication
3500-3100	(N-H) in amide
1780	(C=O) in phase
1720	(C=O) out-of-phase
1650	(C=O) in amide
1595	(COO^{-1})
1513	(C=C) in C_6H_5)
1370	(C-N) in imide
1100	$(OC)_2NC$ in imide
720	imide deformation

Table 3. Normalized areas and atomic compositions obtained by XPS high resolution spectra for the Al metal-polyimide interface as a function of treatment time

Treatment time (min)	Total area (%)			O_{1s}/C_{1s}
	C_{1s} (285 eV)	O_{1s} (533 eV)	N_{1s} (398 eV)	
0	25.4	36.8	37.8	1.448
20	22.3	46.5	30.6	2.085
40	21.2	51.9	25.7	2.448
60	20.5	58.3	21.2	2.843
80	21.2	57.6	20.7	2.716

appear near 3400-2400 (O-H in carboxylic), 3500-3100 (N-H in amide), 1650 (C=O in amide), 1535 (C=O in amide), and 1513 cm^{-1} (C=C in C_6H_5) and the 1595 cm^{-1} peak disappears. The hydrolysis reactions can be further confirmed by the appearance of the peaks for carboxylate ions in potassium polyamates and carboxyl acids in polyamic acids. The peak at 1418 cm^{-1} is due to the vibrations of -OH in -COOH and C=O in -COO-. In both Figure 2(b) and (c), the intensities of the imide structures at 1780, 1720, and 1370 cm^{-1} peaks were reduced but not completely eliminated, suggesting that only the uppermost layers of the polyimide were hydrolyzed.

Table 3 shows the normalized area and atomic composition obtained by XPS for the polyimides as a function of treatment time. XPS result of polyimide shows carbon, nitrogen, and oxygen (binding energy 285, 404, and 532 eV, respectively). And it represents the O_{1S}/C_{1S} ratios of the polyimides before and after KOH treatment. As a result, the O_{1S}/C_{1S} ratios of the polyimide increased with the treatment times, which can be attributed to the increase of carbon-oxygen functional groups of polyimide surfaces by the treatment.[18]

Surface morpology. The concept of surface free energy, γ, for physical interactions which can be resolved into a London dispersive component (*L*) and specific (*SP*) component is[19,20]

$$\gamma = \gamma^L + \gamma^{SP} \tag{1}$$

The change in free energy of the interface is called the work of adhesion (W_A) and can be expressed as

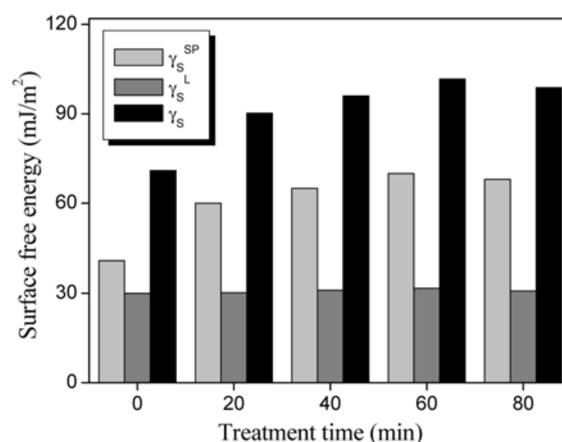

Figure 3. Surface free energies and their components of polyimide film as a function of KOH treatment time.

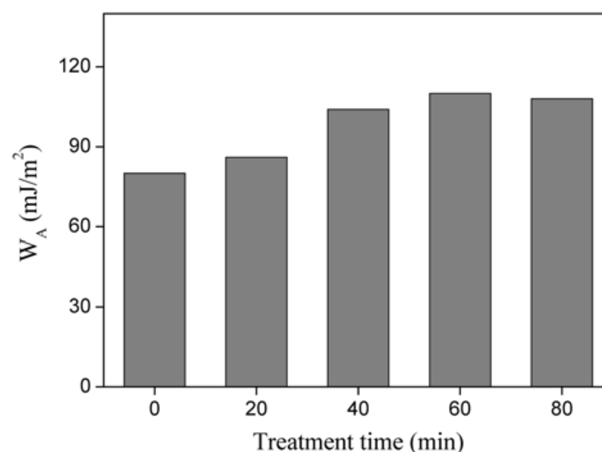

Figure 4. Work of adhesion of the aluminum metal plate-polyimide interface.

$$W_A = \gamma_{SV} + \gamma_{SL} - \gamma_{LV} \tag{2}$$

Combining equations (1) and (2) yields the following equation:

$$W_A = \gamma_{LV}(1 + \cos\theta) \tag{3}$$

Work of adhesion represents the energy of attraction between molecules across the interface. The wettability of a solid surface by a liquid is judged by the magnitude of contact angle; the lower the contact angle is, the more wettable the surface is.

Figure 3 shows the results of surface free energies of the KOH-treated polyimides as a function of KOH treatment times. As a result, it is observed that the polar component of surface free energy is largely increased with increasing KOH treatment times. These behaviors can be interpreted as the fact that the KOH treatment of the polyimide surfaces produces various oxygen complexes in hydrophobic face polarity and wettability, resulting in enhancing the total surface free energy. It is also found that dispersive components of the KOH-treated polyimides are not increased. This result indicated that KOH treatment can not cause the

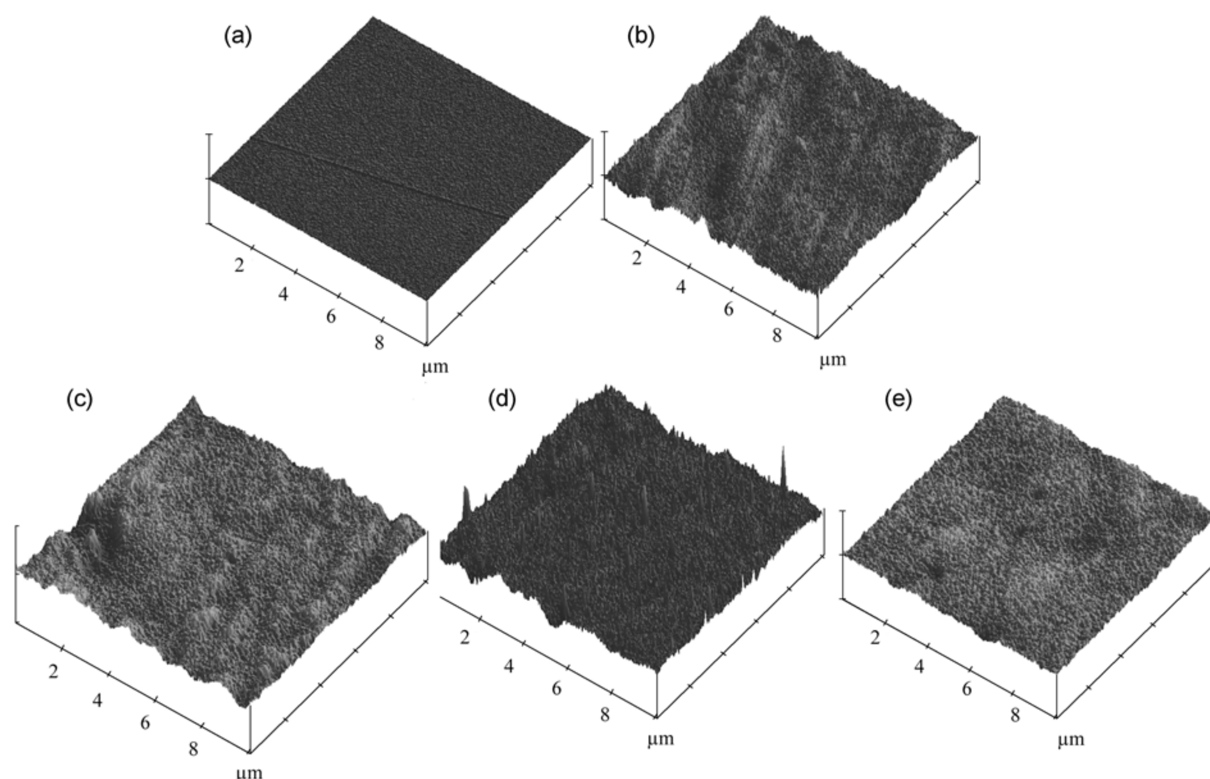

Figure 5. Three-dimensional AFM spectra of polyimide films as a function of treatment time; (a) 0, (b) 20, (c) 40, (d) 60, and (e) 80 min.

increase of the dispersive component.[21]

Figure 4 shows the results of work of adhesion of the KOH-treated polyimides. The work of adhesion of the pure polyimide is about 86 mJ/m^2 and the work of adhesion of the polyimide has increased as the time of treatment to KOH is increased. The maximum work of adhesion of the polyimide which is treated with KOH within 60 min is about 110 mJ/m^2.

The surface morphology is of great importance for the surface wettability of the polymer films. In this work, AFM was employed to examine the morphological changes induced on the KOH-treated polyimide. The differences in morphology after surface treatment further support variation in the relative of amounts of ablation, chain scission, and other functionalization. Figure 5 shows the three-dimensional AFM images of the KOH-treated polyimide as a function of the treatment time, and Figure 6 shows the arithmetic mean of the roughness (*R*a) and the root-mean-square (RMS) of the roughness. The *R*a and RMS roughness of the pure polyimide was about 0.548 and 0.742 nm, respectively. The *Ra* roughness values of the KOH-treated polyimide at the treatment time of 20, 40, 60, and 80 min were increased to 4.825, 5.367, 5.534, and 3.145 nm, respectively. Also, the RMS roughness values of the KOH-treated polyimide at the treatment time of 20, 40, 60, and 80 min were increased to 6.475, 6.787, 7.521, and 4.053 nm, respectively. We concluded that the treatment time controls the oxygen atom and as a result reactive etching of the polyimide surface leads to the surface morphological changes.

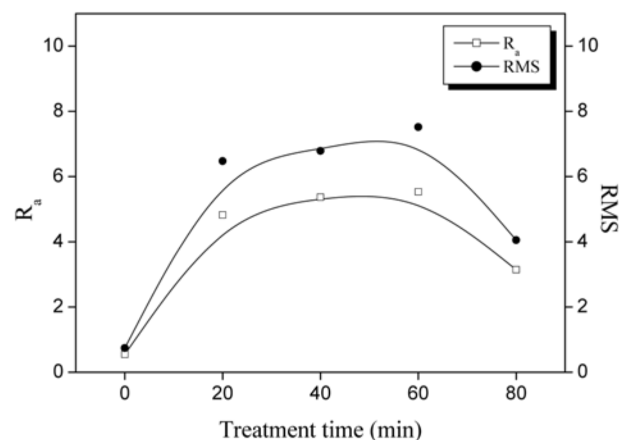

Figure 6. *Ra* and RMS of polyimide films as a function of treatment time.

Adhesion characteristics. A study on the influence of wet chemical treatments on the evolution of polymer surface roughness is important in order to evaluate the adhesion strength of plated metals atop of polymers. A good adhesion between the metal and the polymer is of prime importance for the reliability of the interconnection. By the chemical treatment of the surface, its characteristics (physical and chemical) can be changed into the increase of adhesion. It is obvious that the surface properties of the polymer are important for the adhesion of the metal to the polymer. Hence, there is an intense research recently on improving the adhesion of plated aluminum onto polymer surfaces. Figure 7 represents the peel strength values of polyimide/aluminum samples as a function of KOH-treatment times. These adhe-

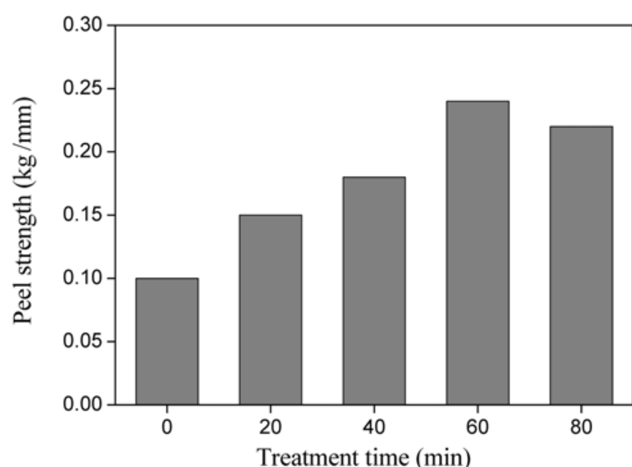

Figure 7. Peel strength of polyimide films as a function of treatment time.

sion strengths are much higher in KOH-treated polyimide/aluminum systems than that of the pristine polyimide/aluminum system. The present data indicate that the peel strength was increased from about 0.1 kg_f/mm for the pure polyimide to about 0.24 kg_f/mm for the KOH-treated polyimide. The increased formation of the functional groups identified as C=O and O-C-O bonds, as shown by the increase in the O_{1s}/C_{1s} in Table 3, may contribute to the enhanced chemical interactions between polyimide and aluminum surfaces resulting in an increase in the measured peel strengths.[22]

Conclusions

In this work, it was found that KOH treatment introduced carbon-oxygen functional groups onto the polyimide surfaces. The O_{1S}/C_{1S} ratios of the KOH-treated polyimides increased as a function of the treatment time, resulting in enhancing the surface free energy. Also, the *Ra* and RMS of the film surfaces, confirmed by AFM observation, were greatly increased by KOH treatments. The adhesion strengths at interfaces between the treated polyimide film and the aluminum matrix showed the superior increments, which were attributed to the strong interaction between the oxygen-containing groups of polyimide and aluminum film. These results could be explained by the increment of the polarity and hydrophilicity of the polyimide surfaces and roughness, due to the increase of specific surface area by KOH treatment.

References

1. Tew, G. N. *J. Am. Chem. Soc.* **2006,** *128*, 3104.
2. Khongtong, S.; Ferguson, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 7254.
3. Liaw, D.-J.; Chang, F.-C.; Leung, M.; Chou, M.-Y.; Muellen, K. *Macromolecules* **2005**, *38*, 4024.
4. Park, S. J.; Kim, H. S.; Jin, F. L. *J. Colloid Interface Sci.* **2005**, *288*, 238.
5. Kim, Y.-H.; Kim, H.-S.; Kwon, S.-K. *Macromolecules* **2005**, *38*, 7950.
6. Tummala, R. R.; Rymaszewski, E. J. *Microelectronics Packaging Handbook*; Van Nostrand Reinhold: New York, U. S. A., 1989; p 54.
7. Ling, Q.-D.; Chang, F.-C.; Song, Y.; Zhu, C.-X.; Liaw, D.-J.; Chan, D. S.-H.; Kang, E.-T.; Neoh, K.-G. *J. Am. Chem. Soc.* **2006**, *128*, 8732.
8. Zhang, F.; Jia, Z.; Srinivasan, M. P. *Langmuir* **2005**, *21*, 3389.
9. Park, S. J.; Cho, K. S.; Kim, S. H. *J. Colloid Interface Sci.* **2004**, *272*, 384.
10. Manzione, T. L. *Plastic Packaging of Microelectronic Devices*; Van Nostrand Reinhold: New York, U. S. A., 1990; p 87.
11. Murdey, R.; Stuckless, J. T. *J. Am. Chem. Soc.* **2003**, *125*, 3995.
12. Honma, M.; Hirata, K.; Nose, T. *Appl. Phys. Lett.* **2006**, *88*, 33513.
13. Butoi, C. I.; Steen, M. L.; Peers, J. R. D.; Fisher, E. R. *J. Phys. Chem. B* **2001**, *105*, 5957.
14. Helt, J. M.; Drain, C. M.; Bazzan, G. *J. Am. Chem. Soc.* **2006**, *128*, 9371.
15. Ramos, M. D. *Vaccum* **2002**, *64*, 255.
16. Acevado, M.; Harris, F. W. *Polymer* **1994**, *35*, 4456.
17. Thanuja, J.; Srinivasan, M. *J. Polym. Sci. Polym. Chem.* **1988**, *26*, 1697.
18. Park, S. J.; Lee, H. Y. *J. Colloid Interface Sci.* **2005**, *285*, 267.
19. Fowkes, F. M. *J. Phys. Chem.* **1963**, *67*, 2538.
20. Park, S. J. *Interfacial Forces and Fields: Theory and Applications*; Hsu, J. P., Ed.; Marcel Dekker: New York, U. S. A., 1999; p 394.
21. Murakami, T.; Kuroda, S.; Osawa, Z. *J. Colloid Interface Sci.* **1998**, *202*, 37.
22. Shirahata, N.; Hozumi, A. *Chem. Mater.* **2005**, *17*, 20.