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Surface characterizations of potassium-hydroxide-modified Upilex-S® polyimide at an elevated temperature

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Abstract

Interests in wet-process surface modifications of polyimides have increased because of simplicity and low costs. In this study, Upilex-S®-50 [poly(biphenyl dianhydride-*p*-phenylene diamine)] polyimide films were initially modified with an aqueous potassium hydroxide (KOH) solution at a relatively high temperature to yield a potassium polyamate surface, followed by acidification to yield a polyamic acid surface. The hydrolysis reaction was confirmed by the Fourier transform infrared attenuated total reflection spectroscopy and X-ray photoelectron spectroscopy (XPS). XPS spectra revealed that potassium polyamate structure could be obtained only by washing the KOH-modified surface with 2-propanol. When the treated surface was rinsed with water, the surface would be partly converted into polyamic acid due to protonation of the carboxylate groups. Atomic force microscopic (AFM) images and AFM cross-sectional analyses revealed large amounts of pinholes on the modified surfaces that might be attributed to the stronger dissolutions of the amorphous regions in the polyimide surfaces.

Keywords: Polyimide; Upilex-S®; Potassium hydroxide; Surface modifications; Polyamic acid; Potassium polyamate

1. Introduction

Polyimides are used as dielectric layers in a variety of microelectronic applications since they have good processability, low dielectric constant, high thermal stability, low moisture absorption, and good mechanical properties. Electroless copper plating on polyimides is widely used in printed circuit board and multichip module thin-film package technology. 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. 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, particle beam, and sputtering [1]. 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/or undesirable modified layers into the interfaces, resulting in possible reliability failure.

Recently, interests in wet-process surface modifications of polyimides have increased due to simplicity and low cost. Polyimide films, such as poly(pyromellitic dianhydride-oxydianiline) (PMDA-ODA), poly(biphenyl dianhydride-*p*-phenylenediamine) (BPDA-PDA), and poly(hexafluoroisopropylidene biphenyl dianhydride-oxydianiline) (6FDA-ODA), are resistant to most solvents and chemicals, but they react with strong oxidizing

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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 surfaces. The depth of modifications can be easily controlled by these reaction conditions. Lee et al. studied extensively the wet treatments of spin-cast and thermally cured PMDA-PDA [2], BPDA-PDA [3,4], and 6FDA-ODA [5] thin films by potassium hydroxide (KOH) solutions. The modified surfaces were characterized with X-ray photoelectron spectroscopy (XPS), and external reflectance infrared spectroscopy and ellipsometry were applied to measure the absorbance–thickness relationship. They further used this modification method to improve the polyimide-to-polyimide joints. Stoffel [6] studied the effects of reaction time and temperatures to modification depths of several commercial polyimide films by using Rutherford backscattering spectroscopy. More recently, Kim and Shen [7] studied the NaOH-modified polyimide surfaces by sum-frequency vibrational spectroscopy.

In this study, Upilex-S® (BPDA-PDA) polyimide films were initially modified with aqueous KOH solutions at a comparatively high temperature of 80°C to first yield potassium polyamate surfaces and then reacted with dilute HCl solutions to yield polyamic acid surfaces (Fig. 1). Both surface chemistry and morphological changes with respect to reaction time were analyzed in detail by XPS, Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR), and atomic force spectroscopy (AFM).

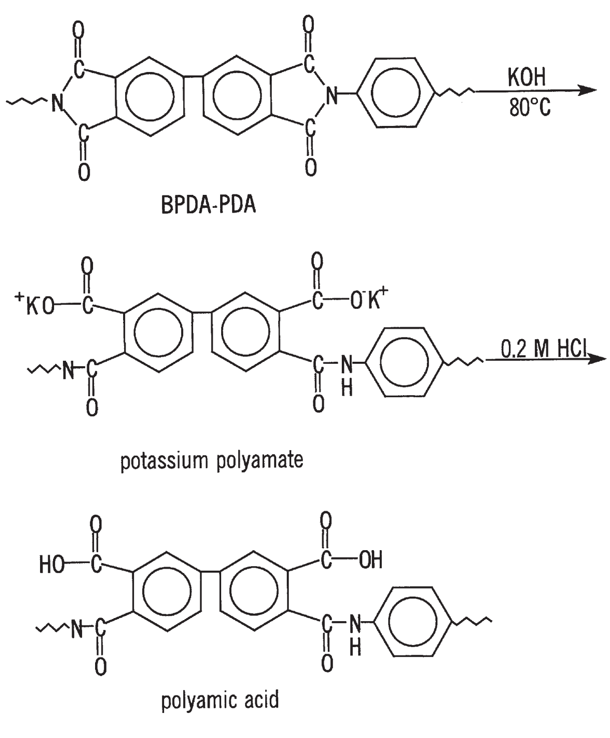


Fig. 1. Surface hydrolysis of BPDA-PDA polyimide.

2. Experimental

2.1. Sample preparation

Upilex-S®-50 Polyimide (BPDA-PDA) was obtained from UBE Industries (Tokyo, Japan) and cut into small pieces (1″ × 1″). 2-propanol (99%, Fisher Scientific), KOH (99.8%, Aldrich), and other reagents were used as-received. First, the polyimide slices were ultrasonically cleaned in 2-propanol for 20 min at room temperature, followed by thoroughly washed with deionized water, and then air-dried. Second, the polyimide samples were immersed in 1 M KOH aqueous solution at 80°C for 20 min; the resulting modified surfaces were potassium polyamate. Third, the excess KOH remained on the modified surfaces was then removed by two different methods: (1) washing with 2-propanol only for 15 min to yield potassium polyamate A, and (2) washing thoroughly with water (2 × 3 min) and followed by washing with 2-propanol (2 × 3 min) to yield potassium polyamate B. The samples were dried under vacuum for 12 h at room temperature. Finally, the potassium polyamate samples were then treated with 0.2 M HCl aqueous solution at room temperature for 5 min, followed by washing with water (2 × 3 min) and 2-propanol (2 × 3 min). The modified surfaces would be polyamic acids, and the samples were dried under vacuum for another 12 h.

2.2. Characterizations

FTIR-ATR spectra of the films were obtained by a Bio-Rad FTS-135 spectrophotometer (Cambridge, Massachusetts, USA) with a 45° single-reflection ZnSe ATR element PLC-11M (Harrick Scientific, New York, USA). The samples were scanned from 2000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. Two hundred scans were averaged for each spectrum.

XPS spectra were obtained with a Kratos Axis HSi (Manchester, UK), employing a monochromatic excitation radiation of AlK_{α} at 1486.6 eV. The photoelectron take-off angle with respect to the polymer surface was set at 45°. A pass energy of 150 eV was used for the survey spectra and 40 eV for the high resolution scans. All spectra recorded were referenced to the C_{1s} peak with an assigned value of 284.6 eV. Elemental spectra were deconvoluted by curve fitting with Gaussian functions. The areas under the peaks were divided by the atomic sensitivity factors of the respective elements (C: 0.278, O: 0.780, N: 0.477, and K: 1.466) for the calculations of the elemental concentrations.

AFM images were obtained by Nanoscope II (Digital Instruments, Santa Barbara, California, USA), using the tapping mode in air at room temperature.

3. Results and discussion

3.1. Fourier transform infrared attenuated total reflection spectroscopy

The polyimide surface was reacted with aqueous KOH solution to yield potassium polyamate, which was subsequently acidified by 0.2 M HCl to polyamic acid. Fig. 2 shows the FTIR-ATR spectra of (a) the polyimide surface treated by KOH solution at 80°C for 20 min, (b,c) the two kinds of potassium polyamates formed on the surfaces due to the different washing methods, and (d) the polyamic acid surface formed after HCl acidification. The key features of the FTIR-ATR spectrum of the virgin Upilex-S® (BPDA-PDA) film are listed in Table 1. In Fig. 2, the 1510 cm^{-1} peaks of the four samples were scaled to a constant since the aromatic skeletons remained unaltered after the chemical treatments, the changes to the other FTIR peaks of the modified polyimide surfaces were thus clearly revealed.

After treatment in KOH solution, the intensities of the imide structures at 1769 and 1697 cm^{-1} peaks were reduced. The shifting and broadening of the peaks from 1339 to 1332 cm^{-1} indicate that the imide structures of the original polyimide were hydrolyzed into the amide structures in potassium polyamates and polyamic acids after washing and acidification. 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 broadening of the peak at 1418 cm^{-1} is due to the vibrations of –OH in –COOH and C=O in $–COO^-$. Fig. 2(b) and (c) show characteristic peaks at 1560 cm^{-1} due to the presence of the carboxylate ions, $–COO^-$. However, the intensity of this peak in potassium polyamate A (Fig. 2(b)), which was washed by 2-propanol only, is different from that of potassium polyamate B (Fig. 2(c)), obtained by washing with water (2×3 min) followed by washing with 2-propanol (2×3 min). In the latter case, after rinsing with water, part of the potassium polyamate was acidified into polyamic acid. As a result, the 1560 cm^{-1} peak is much smaller in Fig. 2(c) and it disappears totally in Fig. 2(d). According to Stoffel [6], the modification depth of Upilex-S® by KOH for 20 min at 80°C was approximately 2000 Å, which is much smaller than the probing depth of FTIR-ATR. Therefore, in both potassium polyamate and polyamic acid spectra, the intensities of the imide structures at 1769, 1697 and 1339 cm^{-1} peaks were reduced but not completely eliminated, suggesting that only the uppermost layers of the polyimides were hydrolyzed.

Table 1
Key FTIR-ATR peaks for pristine BPDA-PDA polyimide

Wave numbers (cm^{-1})	Groups
1769, 1697	C=O in imide structure
1612, 1510, 1463	Aromatic ring
1224, 1116, 973, 828, 691	C–H in 1,4-substituted phenyl ring
1214, 886, 938, 762	C–H in 1,2,4-substituted phenyl ring

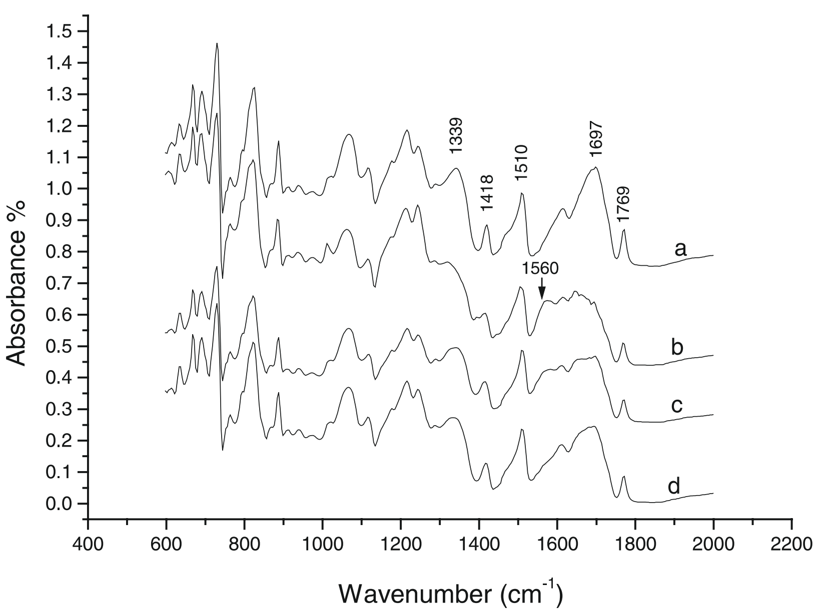


Fig. 2. FTIR-ATR spectra of (a) virgin Upilex-S®, (b) potassium polyamate A, (c) potassium polyamate B, and (d) polyamic acid.

3.2. X-ray photoelectron spectroscopic spectra

XPS survey spectra provide some details of the hydrolysis reactions on the polyimide surfaces. For the virgin Upilex-S® polyimide surfaces, only C, O, and N peaks are observed. After KOH treatment, two additional peaks for K are observed at around 295 eV. However, these two peaks disappear after HCl acidification treatment but the C and O peaks are substantially altered. Fig. 3 shows the XPS C_{1s} and K_{2p} peaks of the virgin Upilex-S® polyimide and the modified surfaces. In Fig. 3(a), the broad peak at 285.5 eV is attributed to the C-2 atoms bonded to the N-atoms; the sharp C-3 peak at 288.0 eV corresponds to the carbonyl carbons in the imide structure. In addition, the broad C-5 peak at 291.1 eV is due to the $\pi \rightarrow \pi^*$ transitions of the phenyl groups. There is only one carbonyl peak since all of the polyimide carbonyls have similar nuclear environments. However, the XPS spectra of the potassium polyamate surfaces (Fig. 3(b) and (c)) exhibit broad peaks at 287.8 eV since the binding energies of carboxylate carbons and amide carbons are slightly different. The polyamate surface also displays new peaks at 292.9 and 295.6 eV, corresponding to $K_{2p3/2}$ and $K_{2p1/2}$, respectively, which suggest the incorporation of potassium in the polyamate. These two peaks disappear in the XPS spectrum of polyamic acid (Fig. 3(d)). The two carbonyl peaks at 287.9 eV (carboxylate carbon) and 289 eV (amide carbon) are well separated in polyamic acid. Furthermore, the intensity of $K_{2p3/2}$ peak in potassium polyamate B (Fig. 3(c)), which was washed by water and 2-propanol, is higher than that in potassium polyamate A (Fig. 3(b)), which was washed by 2-propanol only. This indicates that the potassium ions were partially removed from the polyamates during washing.

The hydrolysis reactions can be further proven by the O_{1s} XPS spectra. The virgin Upilex-S® polyimide contains only carbonyl O-atoms, and thus only one O_{1s} peak would have been expected. However, peak asymmetry in Fig. 4(a) suggests the presence of an additional contribution with a higher binding energy. This is evident by curve fitting of the main O_{1s} envelope, which yields two peaks with binding energies of 531.3 and 533.0 eV. The high-energy oxygen peak contains approximately 10%

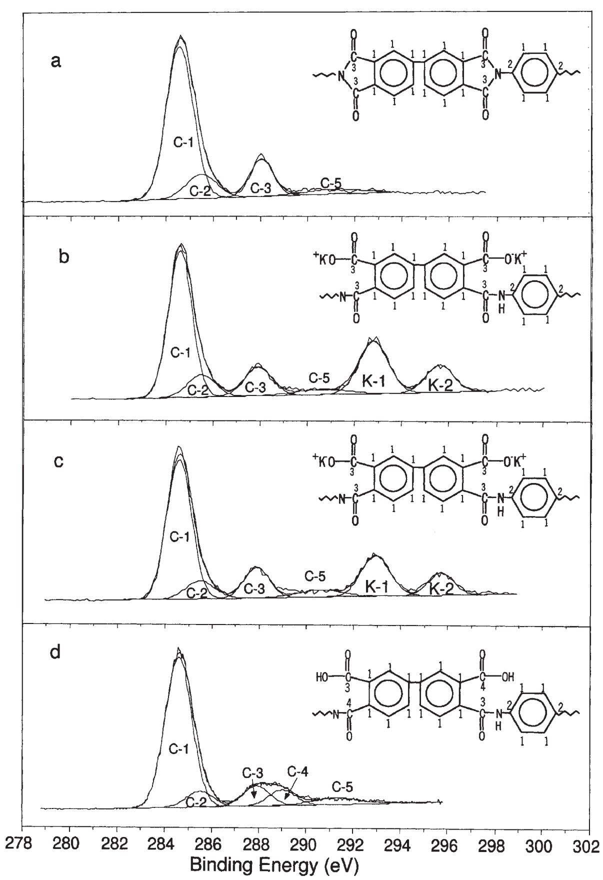


Fig. 3. XPS C_{1s} spectra for (a) virgin Upilex-S®, (b) potassium polyamate A, (c) potassium polyamate B, and (d) polyamic acid.

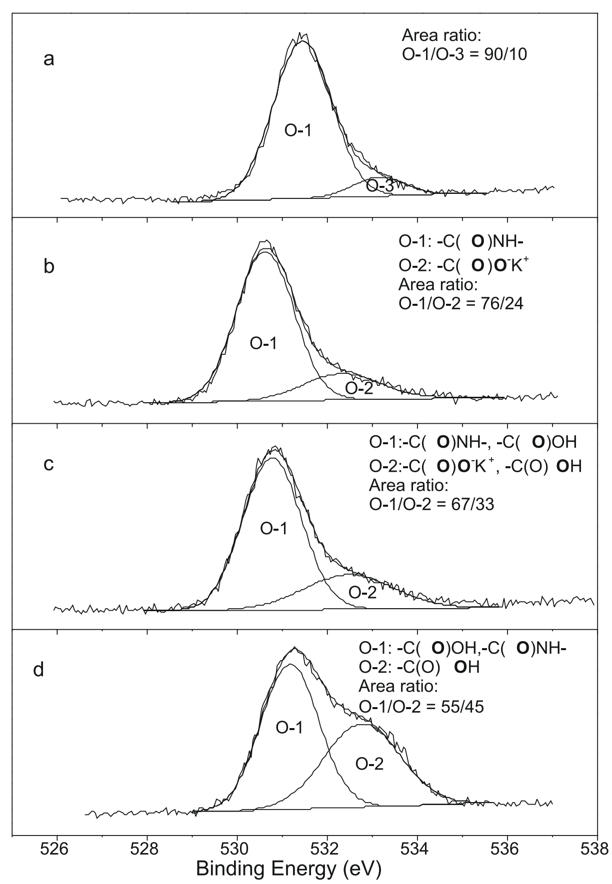


Fig. 4. XPS O_{1s} spectra for (a) virgin Upilex-S®, (b) potassium polyamate A, (c) potassium polyamate B, and (d) polyamic acid.

of the total area of the O_{1s} peak. The presence of this peak has been reported for the Upilex-S® film samples [9] and other thermally cured polyimides [10], which is probably due to oxygen contaminations during production.

Potassium polyamates had two different oxygen environments; thus two peaks are observed in the O_{1s} spectrum in Fig. 4(b) and (c). The two O-atoms in –COOK have the same binding energy at 532.4 eV. The lower-binding-energy peak at 530.7 eV is attributed to the carbonyl oxygen in the amide structure [–C(O)NH]. The non-proportionality of the two peaks is probably due to the relatively high surface oxidation rates during storage that contribute significantly to the peak at 532.4 eV. In Fig. 4(c), the O-1/O-2 area ratio is relatively smaller than that in Fig. 4(b), which is probably due to the protonation effect of water and partial conversion of the potassium polyamate into polyamic acid.

In a previous study, Lee [4] attributed the higher-binding-energy peak to the negatively charged carboxylate oxygen [–C(O)O^-K^+] and the lower-binding-energy peak to both of the carbonyl oxygen [–C(O)O^-K^+] and amide oxygen [–C(O)NH–]. Lee claimed that the XPS area ratio of these two peaks, 1:2, was in good agreement with the calculation from the two different oxygen environments (i.e. $[–C(O)O^-K^+]/\{[–C(O)O^-K^+] + [–C(O)NH–]\} = 1/2$). However, the two oxygen atoms in the carboxylate group [–C(O)O^- K^+] would have the same physical and chemical properties due to the effect of charge delocalizations; thus they would have the same binding energy. This was proved by the use of a model compound, sodium benzoate (C_6H_5COONa), which displayed only one peak at the binding energy of 531.2 eV for the two oxygen atoms in the O_{1s} spectrum [11]. In addition, the high-binding-energy peak in Lee's work [4] would probably be partially contributed by the hydroxyl oxygen in –C(O)OH because water was used to wash the extra KOH on the modified polyimide to obtain the potassium polyamate and part of the polyamate would have been converted into polyamic acid [4,12,13].

In Fig. 4(d), the O_{1s} XPS spectrum of polyamic acid is fitted with two peaks at 531.3 and 532.9 eV. The low-binding-energy peak is assigned to the carbonyl oxygens in both carboxylic acid [–C(O)OH] and amide [–C(O)NH–] groups. The high-binding-energy peak is assigned to the hydroxyl oxygen in the –C(O)OH groups. The increase of the relative amount of high-binding-energy peak in the polyamic acid is probably due to the change of the chemical environment of the oxygen atoms from carboxyl oxygen to hydroxyl oxygen. Furthermore, the shift of the carboxyl oxygen peak at 530.7 eV in potassium polyamate (Fig. 4(b) and (c)) to 531.3 eV is probably due to the formation of intermolecular hydrogen bonds between the carboxyl oxygen and the hydrogen from the neighboring hydroxyl group of the polyamic acid [HO–C=OL HO–C=O] [4,11].

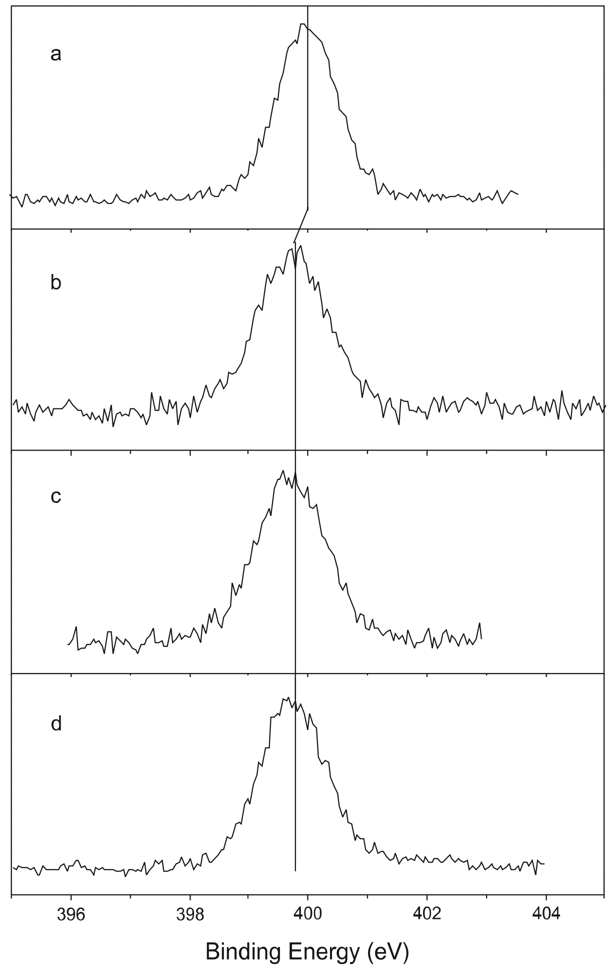


Fig. 5. XPS N_{1s} spectra for (a) virgin Upilex-S®, (b) potassium polyamate A, (c) potassium polyamate B, and (d) polyamic acid.

There is only one peak observed in the N_{1s} spectrum of the virgin Upilex-S® at 400.0 eV (Fig. 5(a)) which can be attributed to the nitrogen atoms in the imide structure [–C(O)NH–]. The N_{1s}-peak shifts to 399.7 eV in potassium polyamate (Fig. 5(b) and (c)) and then to 399.8 eV in polyamic acid (Fig. 5(d)), which corresponds to the hydrolysis reaction.

Table 2 is the XPS elemental analyses of the virgin Upilex-S® and the subsequently modified surfaces. There were small amounts of silicon contaminations in the untreated Upilex-S® polyimide surfaces, and 2-propanol was effective in removing these contaminations as revealed by XPS. The atomic ratio of N, O, and K in potassium polyamate A obtained by XPS was in good agreement with its molecular formula, suggesting a full conversion to potassium polyamate on the KOH-treated Upilex-S® surfaces within the detecting depth of XPS. In potassium polyamate B, the stoichiometric potassium obtained by XPS is lower than the theoretic amount due to the partial conversion of potassium polyamate into polyamic acid and the partial removal of potassium during the water-rinsing step. Finally, the atomic ratio of the N- and O-atoms in the polyamic acid is in good agreement with that calculated from the molecular formula, i.e. 1:3. No obvious degradations were observed on the modified polyimide surfaces as indicated from both XPS compositional analyses and elemental spectra.

Table 2
XPS elemental compositions of the virgin and modified Upilex-S® polyimide surfaces

Polyimide surface	Atomic concentration (%)					Stoichiometric formula	Molecular formula
	C	N	O	K	Si		
Virgin Upilex-S®	77.5	6.1	14.2	0	2.2	$C_{22}N_{1.73}O_{4.03}\ Si_{0.62}$	$C_{22}N_2O_4$
Degreased Upilex-S®	79.1	6.3	14.6	0	0	$C_{22}N_{1.75}O_{4.06}$	
Potassium polyamate A	70.7	6.0	17.3	6.0	0	$C_{22}N_{1.87}O_{5.38}K_{1.87}$	$C_{22}N_2O_6K_2$
Potassium polyamate B	75.7	4.9	16.1	3.3	0	$C_{22}N_{1.42}O_{4.68}K_{0.96}$	
Polyamic acid	71.9	6.4	21.7	0	0	$C_{22}N_{1.96}O_{6.64}$	$C_{22}N_2O_6$

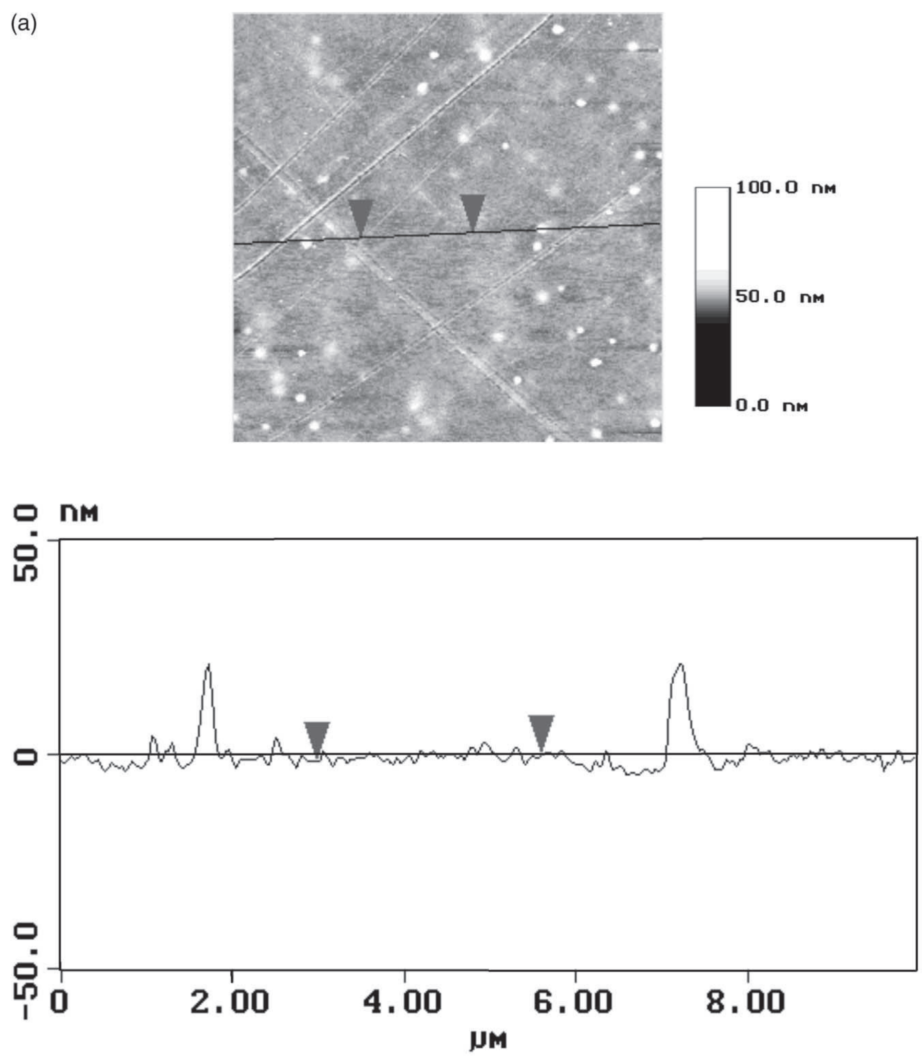


Fig. 6. AFM micrographic and cross-sectional analyses (10 × 10 μm^2 × 100 nm) of (a) virgin Upilex-S® surface, (b) Upilex-S® surface after treatment in KOH at 80°C for 5 min, (c) for 10 min, (d) for 20 min, and (e) for 40 min.

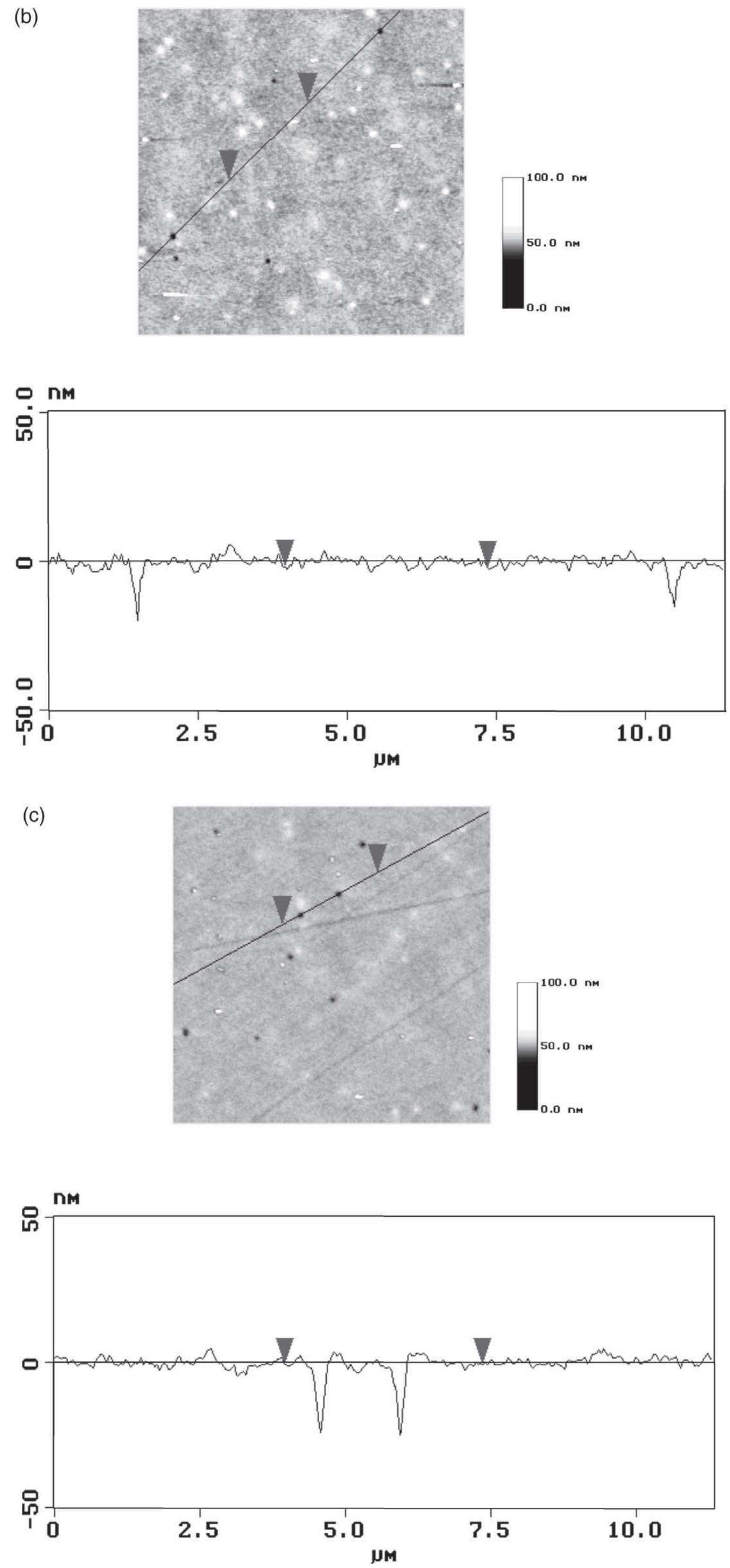
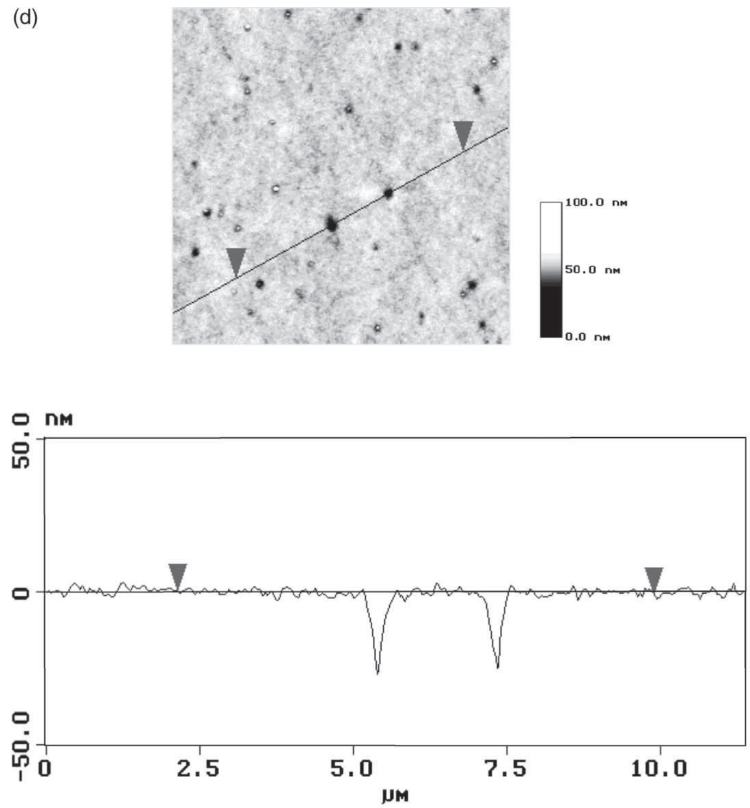


Fig. 6 (*continued*)

(d)



(e)

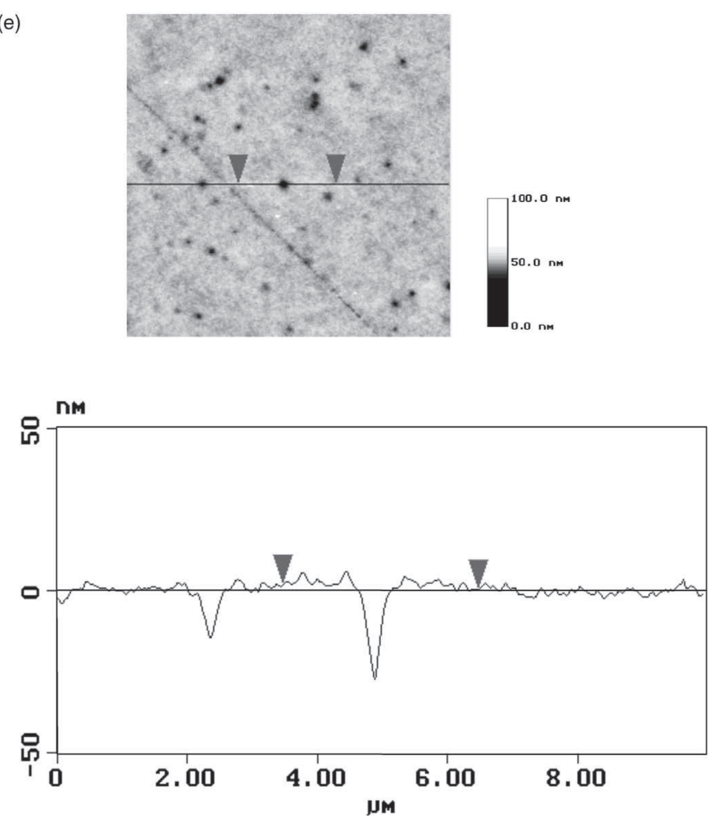


Fig. 6 (*Continued*)

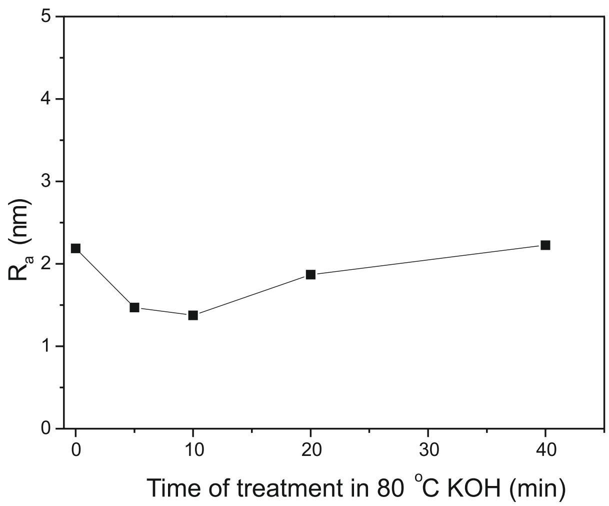


Fig. 7. Mean roughness (R_a) of KOH-modified Upilex-S® polyimide surfaces at 80°C for various time.

3.3. Atomic force spectroscopic studies

AFM images (Fig. 6) of all samples were carried out in air by tapping mode method. The mean roughness (R_a) was determined by scanning a surface area of 10×10 μm^2 of the sample. Virgin Upilex-S® polyimide surface (Fig. 6(a)) was generally smooth with a mean roughness slightly greater than 2.0 nm (Fig. 7). After KOH treatment at 80°C followed by acidification, the surface roughness decreased due to the removal of the surface protrusions as shown in the cross-sectional analyses of Fig. 6(b) and (c). However, pinholes were growing simultaneously due to the same chemical attack. As a result, the surface roughness increased as the treatment time increased (Fig. 6(d) and (e)). The density of the pinholes increased with treatment time while the depth and diameter remained unaltered. Cross-sectional analyses by AFM revealed that these pinholes had an average depth of 25–50 nm. However, no pinholes were observed on polyimide surfaces if they were treated at temperatures below 70°C in our previous experiments. When a basic solution is in contact with the polyimide, the imide rings will be opened and converted into amides, which then can be etched away easily. Recent studies found that the amorphous regions of the polyimide are much more easily etched away by the basic solutions than the crystalline regions [7,8]. Since no other kinds of degradations were found on the modified polyimide surfaces, the pinholes were probably due to the dissolution of the amorphous regions in the polyimide surfaces at the elevated reaction temperature.

4. Conclusions

Upilex-S®-50 polyimide films were initially modified with aqueous KOH solution at a relatively high temperature of 80°C to yield potassium polyamate surfaces, followed by HCl acidification to yield polyamic acid surfaces. The hydrolysis reaction was confirmed by FTIR-ATR and XPS. However, XPS results revealed that pure potassium polyamate structure could be obtained when the KOH-modified polyimide surfaces were washed with undiluted 2-propanol only. If the KOH-modified polyimide surfaces were rinsed with water, the carboxylate groups in the potassium polyamate would be partly protonated and converted into carboxylic acid groups to form polyamic acid. AFM micrographs and AFM cross-sectional analyses revealed that the pinholes formed on the modified surfaces had an average depth of 25–50 nm, which might be attributed to the dissolution of the amorphous regions in the polyimide surfaces.

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