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Characterization of Interphases Between PMDA/4-BDAF Polyimides and Silver and Graphite Substrates Using X-Ray Photoelectron Spectroscopy

by

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Charcterization of Interphases Between PMDA/4-BDAF Polyimides and Silver and Graphite Substrates Using X-Ray Photoelectron Spectroscopy

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Abstract

Interfaces formed by curing the polyamic acid (PAA) of pyromellitic dianhydride (PMDA)/2,2-bis[4-(4-aminophenoxy)-phenyl]-hexa-fluoropropane (4-BDAF) polyimide against silver substrates were characterized by x-ray photoelectron spectroscopy (XPS). The C(1s) multiplex spectra of PAA films cured against thick silver films were more similar to those obtained before curing than to those for the bulk PMDA/4-BDAF polyimide, indicating that curing of the polymer was inhibited by interaction of the PAA with the silver substrate. This was evidenced by observing a peak shifted upward by 3.2 eV from the main carbon peak near 284.6 eV which consisted of two overlapping peaks characteristic of the amide and carboxylate groups. Moreover, the main peak observed near 400.4 eV in the N(1s) spectra was attributed to the amides. The XPS results obtained from fracture surfaces of specimens prepared by curing thick PAA films against polished silver substrates indicated that the silver fracture surface was characteristic of a silver/PAA complex, while the polymer fracture surface was likely a PMDA/4-BDAF polyimide film. It was thus considered that a thin interfacial layer was formed between the silver surface and the cured polymer coating and that failure occurred at the interface of this interfacial layer and the bulk polyimide

film. Peaks characteristic of the imides appeared in spectra of a PAA film cured against a highly criented pyrolytic graphite (HOPG) substrate, indicating that the PAA was fully imidized at the HOPG surface. This was expected since no strong interaction of the PAA with HOPG was observed. Thus, the thermal curing of PAA at the substrate surfaces was strongly dependent on the nature of the substrates.

I. Introduction

Polyimides have attracted widespread interest for use in microelectronic devices and composite materials due to their unusual properties such as good thermal stability, low dielectric constant, high mechanical strength, and chemical inertness. As a result, numerous investigations have been directed toward elucidating the mechanisms by which polyimides interact with inorganic substrates. Most of the studies have focused on determining the molecular structures of interfaces between polyimides and metals.

Several experimental and theoretical investigations of interfaces created by evaporation of thin metal films onto the surfaces of cured polyimides and their model compounds have been reported (1-12). It was generally found that aluminum and chromium preferentially formed complexes with polyimides via the carbonyl oxygen atoms, while copper and silver interacted weakly with polyimides and tended to diffuse into the polymers during deposition at room temperature.

Several investigations of interfaces formed by spin-coating the polyamic acids from solutions or by codepositing monomers of the polyimides onto supported substrates and then curing them to form polyimides were also carried out.

A recent review of progress in polyimide/metal and polyimide/ceramic adhesion has been published (13).

Investigation of pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) monomers vapor-deposited onto polycrystalline silver surfaces was reported by Grunze and Lamb (14, 15). It was found that PMDA and ODA were both chemisorbed on the silver surface through the oxygen atoms in the PMDA and ODA fragments. Co-deposition of PMDA and ODA followed by thermal treatment of the films resulted in formation of thermally stable polyimide films. A peak observed near 286.2 eV in the C(1s) spectra of the co-deposited PMDA/ODA films having a thickness of about 11 A was assigned to aromatic carbon not bound to nitrogen or oxygen in ODA. The peak attributed to carbon in the PMDA ring and to carbon bound to nitrogen or oxygen in ODA was observed near 286.9 eV, and the peak due to imide carbon was observed near 290.0 eV in the C(1s) spectra. The calculated intensity ratio of these peaks was 4:9.5:9.6, while the intensity ratio for a stoichiometric PMDA/ODA polyimide was 4:10:8. The relatively higher intensity of the C(1s) peak near 286.2 eV was explained by the presence of fragmented PMDA and ODA in the polyimide/silver interface. This was also evidenced by observing a peak identified as the oxygen bonded directly to the silver surface near 531.5 eV in the

O(1s) spectra. It was thus concluded that the adhesion of polyimide films to silver surfaces involved bonding of fragments of PMDA and ODA which were chemisorbed on the silver surface.

Kim et al investigated interfaces created by thermal curing of polyamic acid (PAA) precursors of PMDA/ODA polyimides spin-coated onto copper and nickel substrates by using cross-section transmission electron microscopy (TEM) (16, 17). Results obtained from cross-section TEM showed that very fine Cu- and Ni-rich particles were precipitated in the polyimides. However, particles were not found closer than 80-200 nm from the metal surfaces. It was suggested that PAA films interacted preferentially with Cu and Ni to form PAA complexes which decomposed during subsequent thermal curing, leading to the formation of Cu- and Ni-rich particles in the polyimides.

Burrell et al (18) utilized x-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy to investigate thin PAA films of PMDA/ODA polyimides spin-coated onto copper and aluminum substrates, followed by thermal treatment to cure the films. XPS and IR measurements showed that PAA films deposited on Al substrates were completely cured during the heat treatment. After thermal curing, the peaks near 284.6 and 286 eV in the

C(1s) spectra of polyamic acids which were assigned to C-C or C-H, and C-N or C-O bonds, respectively, appeared sharper. The peaks near 287.9 and 289.0 eV due to the carbonyl carbon in amide and acid groups merged into a single component due to imide carbonyls near 288.6 eV upon curing. A decrease in intensity of the C-O component relative to the C=O component was also observed in the O(1s) spectra. Moreover, the imide nitrogen peak was observed near 400.6 eV and the amide nitrogen peak near 399.9 eV disappeared in the N(1s) spectra after the heat treament. These observations indicated that PAA films spin-coated onto Al substrates were fully imidized upon thermal treament. Grazing angle reflectance IR spectra were also obtained to further confirm the conclusions made from the XPS investigation. These spectra were characterized by the appearance of bands near 1780 and 1737 cm^{-1} due to imide groups and by the disappearance of a band near 1540 cm^{-1} which was assigned to the amide group.

After curing thin PAA films spin-coated onto Cu substrates, several carbonyl components which were not related to the cured polyimide were observed in the C(1s) spectra. Moreover, the amide nitrogen peak was still observed near 399.9 eV in the N(1s) spectra. Peaks due to Cu(I) and Cu(II) were both present in the Cu(2p) photoelectron and Cu(LMM) Auger spectra. In the IR spectra of PAA films cured against copper substrates, the bands characteristic of imide functionality near 1780 and 1737 cm^{-1} were weakly observed. However, a broad band centered at 1650 cm^{-1} which was attributed to the superposition of the amide carbonyl band and one or more bands due to new chemical species, appeared in the spectra. Cuprous oxide formation was also evidenced by observing a new band near 640 cm^{-1} in the spectra. As a result, it was suggested that copper carboxylates were formed when polyamic acids were deposited onto Cu substrates. Copper carboxylates could then react with the amide groups to yield imides plus oxides during thermal curing. However, imidization of PAA films deposited onto Cu substrates was inhibited by the formation of copper carboxylates during thermal treatment.

Iacona et al used XPS to investigate the effect of substrate on the thermal curing of polyamic acid (PAA) of 3,4,3',4'-benzophenone-tetracarboxylic dianhydride (BTDA)/4,4'-oxydi-aniline (ODA) type polyimide (19). It was found that the C(1s) spectra obtained from thin films of PAA spin-coated onto silicon (Si) wafers were similar to those obtained from neat PAA and were characterized by peaks near 285.0, 286.0, 288.1, and 289.4 eV which were assigned to aromatic ring carbon, C-N or C-O, C=O of amide groups or benzophenone linkage, and COOH functionality, respectively. The shake-up peak due to the $\pi \rightarrow \pi^*$ transitions in the phenyl rings was also observed.

However, there were new features revealed in the C(1s) spectra of thin PAA films spin-coated onto chromium and nickel surfaces. For example, the intensity of the COOH peak near 289.4 eV decreased about 50% and that of the C=O peak increased correspondingly. The position of this C=O peak also shifted from about 288.1 eV to near 288.5 eV. In fact, the peak near 288.5 eV consisted of two overlapping peaks characteristic of the C=O and COO^- functionalities. This was confirmed by obtaining the C(1s) spectrum of a PAA film after reaction with an aqueous solution of $NaHCO_3$. Another feature was that a new component near 287.0 eV due to a change in the charge density of the aromatic rings after the salification of the COOH groups was observed in the spectra. It was suggested that acid-base interaction occurred between the COOH groups of polymer and the oxides and hydroxides that covered the Ni and Cr surfaces but did not occur on the Si surfaces.

XPS spectra were then obtained from ultra-thin PAA films cured against the substrates at 200°C for 2 hours and at 300°C for 30 minutes. The C(1s) spectrum of a PAA film cured against a Si wafer was very similar to that of a polyimide film and was characterized by the merging of the amide and acid peaks into a single peak near 288.7 eV which was assigned to C=O of the imide groups. The peak near 286.0 eV was partially related to the aromatic carbon atoms of the BTDA moieties which underwent electron withdrawal due to the conjugated carbonyl groups, increasing its relative intensity. However, decomposition of the polymer was observed in the cases of thin PAA films cured against Cr and Ni substrates. In particular, a component near 284.0 eV due to amorphous carbon appeared but the COOH and C=O components were completely depleted in the C(1s) spectrum of PAA cured against Ni, indicating that the complete destruction of the polymer occurred at the Ni surface.

This substrate-dependent curing process was also confirmed by a close analysis of the related XPS N(1s) spectra. The main peak near 400.8 eV due to imide nitrogen and a low binding energy peak near 399.2 eV (about 10% of the total nitrogen) were observed in the N(1s) spectra of bulk polyimide as well as PAA cured on Si. This low binding energy peak was assigned to a C=N linkage which might be due to the isoimide species or a linear group which arose from the degradation of the imide. The intensity of the C=N peak for the PAA cured on Cr was found to increase up to about 34% of the total nitrogen. The situation was very complex for the Ni substrates. The N(1s) spectrum could be resolved in at least four peaks but none of these was related to amide or imide nitrogen. These results again indicated that complete destruction of the polymeric structure occurred at the Ni surface. The substrate-dependent effect observed above were explained in terms of acid-base interaction between the polymer and the substrate. However, the heavy decomposition shown by the Ni surface with PAA was further promoted by a redox reaction between the oxidized Ni species and the polymer chains.

We have recently utilized surface-enhanced Raman scattering (SERS) and reflection-absorption infrared (RAIR) spectroscopy to determine the molecular structure of the interface between polyimides derived from pyromellitic dianhydride (PMDA) and 2,2-bis[4-(4-aminophenoxy)-phenyl]-hexa-fluoropropane (4-BDAF) and silver substrates (20). The SERS spectrum of the polymer cured against a silver island film was more similar to the SERS spectrum of the polyamic acid (PAA) than to the normal Raman spectrum of the polyimide, indicating that imidization of the polymer was inhibited by interaction of the PAA with the substrate. These conclusions were further confirmed by the RAIR spectra from various thickness PAA films of PMDA/4-BDAF polyimides cured against silver substrates. RAIR spectra obtained from relatively thick films of PAA cured against silver substrates were similar to transmission infrared spectra of neat polyimide. However, weak bands characteristic of imides and bands due to amide and carboxylate groups were present in the RAIR spectra of relatively thin PAA films cured against the silver substrates, verifying that imidization of PAA films deposited onto the silver surfaces was inhibited by the formation of silver carboxylates during thermal treatment.

The purpose of this paper is to report XPS results obtained from the PAA films of PMDA/4-BDAF polyimides cured against the silver and highly oriented pyrolytic graphite (HOPG) substrates. The results obtained show that imidization is inhibited by interaction of the PAA with the silver substrate and are consistent with those obtained using SERS and RAIR. A thin PAA film of a PMDA/4-BDAF polyimide deposited onto a HOPG substrate, however, was completely imidized upon thermal treatment.

II. Experimental

Substrates were prepared for XPS investigations as described below. Glass slides were cleaned by immersion in a 0.1N NaOH solution, removed, rinsed in a 0.1N HCl solution, rinsed in distilled water in ultrasonic cleaner several times and blown dry in a stream of nitrogen. Thick silver films (several hundred angstroms) were then evaporated onto the glass slides in a vacuum chamber. HOPG substrates obtained from Union Carbide Corporation were cleaned ultrasonically in acetone and then blown dry with nitrogen.

The polyamic acid of pyromellitic dianhydride (PMDA) and 2,2-bis[4-(4-aminophenoxy)-phenyl]-hexafluoropropane(4-BDAF) was supplied as a 24% (by weight) solution in N-methyl pyrrolidone (NMP) by Ethyl Corporation. Thin films of polyamic acid (PAA) were deposited onto thick silver films by spin-coating from a 0.2% solution in NMP. Thin PAA films were deposited by placing a few drops of a 0.04% solution in NMP onto the cleaned HOPG substrates. The thickness of thin PAA films deposited onto the silver and HOPG substrates was about 36 and 58 angstroms, respectively, as determined by ellipsometry. The films were cured at 107°C for 15 minutes and at 200°C for an additional 15 minutes in an oven purged with argon. XPS spectra of thick PAA films applied to the surface of the KBr pellet before and after thermal curing were also obtained to use as reference spectra.

In some cases, polished silver substrates were used to perform a series of delamination experiments. Small pieces of silver, about 1.0 cm x 1.5 cm, were cut from a 2.0 mm thick silver foil obtained from Aldrich Chemical Co. The substrate was metallographically polished, rinsed in distilled deionized water, and blown dry with a stream of nitrogen gas to obtain a mirror-like surface with a minimum of contamination. A thick film of PAA was applied to the cleaned silver substrate and cured under the conditions described above. The cured specimen was then immersed in liquid nitrogen, causing delamination to occur near the polymer/silver interface. The resulting fracture surfaces were examined by XPS. The thickness of the polymer films on the silver fracture surface was estimated by means of angle-resolved XPS measurements. The value of the reduced thickness (the thickness of the polymer divided by the electron mean free path) was about 0.46.

XPS spectra were obtained using a Physical Electronics Model 5300 X-ray photoelectron spectrometer with Mg K_α radiation at a power of 300 W. The pass energy was 44.75 (0.5 eV/step) and 17.90 eV (0.05 eV/step) for the survey and multiplex spectra, respectively. The pressure was kept at 10^{-8} to 10^{-9} Torr. A take-off angle of 45^o was used to obtain most of the spectra. However, take-off angles of 15^o, 30^o, and 75^o were also used to determine composition profiles in the near interface region. The XPS spectra were corrected for charging by referencing the C(1s) peak for C-C and C-H bands to 284.6 eV.

The thickness of the films was measured using a Rudolph Research Model 436 ellipsometer to examine the silver and HOPG substrates before and after deposition of the PAA films.

III. Results and Discussion

XPS survey spectra were obtained from the polyamic acid of PMDA/4-BDAF before and after curing. Bands characteristic of carbon, oxygen, nitrogen, and fluorine were observed in the spectra. Experimental atomic concentrations summarized in Table I were close to their theoretical concentrations with the exception of excess fluorine.

XPS multiplex spectra of the C(1s) core level for the PAA of PMDA/4-BDAF before and after curing are shown in Figures 1A and 1B, respectively. The C(1s) spectra of PAA (see Figure 1A) consisted of eight components. The first component near 284.6 eV was related to aromatic carbons not linked to nitrogen or oxygen. Components shifted upward by about 1.0 and 1.5 eV were assigned to aromatic carbons making single bonds with nitrogen and oxygen, respectively. The component located at a 2.4 eV separation was attributed to the alpha carbon linking the CF_3 groups. Assignments for the components positioned at separations of 3.3 and 4.2 eV were the amide and carboxylic acid groups, respectively. The shake-up component due to the $\pi \rightarrow \pi^*$ transitions in the phenyl rings was located at a separation of 6.3 eV. The last component observed at a 8.0 eV separation was related to the CF_3 group.

The overall line shapes of the C(1s) multiplex spectra for the PAA of PMDA/4-BDAF before and after curing were significantly different (see Figure 1). For example, the C(1s) spectra of cured PAA showed that the amide and acid components merged into a single component due to the imide carbonyl groups (see Figure 1B) which was shifted upward by 4.0 eV from the main peak near 284.6 eV. Moreover, the component attributed to the aromatic carbon atoms of the PMDA portion which undergo electron withdrawal due to the conjugated carbonyl groups superimposed upon the component due to C-N and thus increased its relative intensity. The relative intensity of this component was 20.3%, which was close to the theoretical value of 21.6% for the PMDA/4-BDAF polyimide. All the results observed indicated that imidization had occurred when the PAA of PMDA/4-BDAF was cured.

The relative areas under the CF_3 component were about 6.5% and 7.6% for the PAA and PMDA/4-BDAF polyimide, respectively, which were higher than the theoretical value of 5.4%. The higher CF_3 compositions in the C(1s) multiplex spectra (as opposed to theoretical one) were also reflected in the higher concentrations of fluorine shown in Table I. Similar observations have been reported by previous authors and explained by the strong electronegativity of fluorine and XPS being so surface sensitive (21).

PAA being imidized upon curing was also confirmed when the N(1s) multiplex spectra for the PAA of PMDA/4-BDAF before and after curing were compared (see Figure 2). The main peak near 400.3 eV in the N(1s) spectra of PAA before curing was assigned to the amide functionality (see Figure 2A). However, the intense peak due to the imide nitrogens appeared near 400.8 eV in the N(1s) spectra of PAA after curing (see Figure 2B).

XPS survey spectra were obtained before and after curing of thin PAA films spin-coated onto thick silver films from a 0.2% solution in NMP (see Figures 3A and 3B). In addition to observing the elements related to the polymer, peaks characteristic of silver were observed in the spectra. It was thus considered that the thickness of polymer films was thin enough to be characteristic of the "interface" region. Additional evidence was provided by using angle-resolved XPS to investigate the interaction of the thin PAA films with the silver substrate. As shown in Table II, the relative atomic concentration of the silver was found to increase with increasing take-off angle.

The C(1s) multiplex spectra of the thin films of PAA spin-coated onto the thick silver films before curing were taken at 15°, 45°, and 75° take-off angles (see Figure 4). Generally speaking, the overall line shapes for the C(1s) multiplex spectra were similar to those for neat PAA (see Figure 1A). However, the intensity ratio of the acid peak (shifted upward by 4.3 eV) relative to the amide peak (shifted upward by 3.2 eV) was different from that for neat PAA. The intensity ratio of the acid relative to amide components for the neat PAA was about 0.97, which was close to the theoretical ratio 1.00. The calculated intensity ratios for thin films of PAA spin-coated onto thick silver films obtained at 15°, 45°, and 75° were about 0.67, 0.50, and 0.47, respectively. In fact, the peak at a separation of 3.2 eV consisted of two overlapping peaks characteristic of the amide and carboxylate functionalities. As mentioned above, similar assignments have been confirmed by Iacona and co-workers (19). A decrease in intensity of the acid peak and an increase in intensity of the carboxylate peak were observed as the take-off angle was increased, indicating that the PAA interacted with silver to form carboxylates at the PAA/silver interfaces. In the N(1s) multiplex spectra of the PAA deposited onto the silver surface before curing, the main peak due to the amide groups was expected to observe near 400.3 eV. In fact, that is what was observed.

The C(1s) multiplex spectra of thin PAA films spin-coated onto thick silver films and then cured in an argon-purged oven at 107°C for 15 minutes and at 200°C for an additional 15 minutes were also obtained at take-off angles of 15°, 45°, and 75° (see Figure 5). The overall spectral features in the C(1s) spectra of the polymer cured against silver films were more similar to those of the PAA deposited onto silver films than to those of the bulk PMDA/4-BDAF polyimide (see Figures 1B, 4, and 5, respectively), indicating that curing of the polymer was inhibited by the interaction of the PAA with the silver substrate. This was substantiated by observing the peak located at a 3.2 eV separation from the main carbon peak near 284.6 eV which consisted of two overlapping components characteristic of the amide and carboxylate functionalities. However, partially imidized species were also observed in the C(1s) multiplex spectra (see Figure 5). The peak at a separation of 4.0 eV assigned to the imide groups was weakly observed in the spectra. The peak at a separation of 1.1 eV attributed to the aromatic carbon atoms of the PMDA portion which undergo electron withdrawal due to the conjugated carbonyl groups also increased in intensity.

When the intensity ratios of the peaks characteristic of the imides (at the separations of 1.1 and 4.0 eV) relative to the amide peak (at a 3.2 eV separation) were measured, the ratios were found to decrease with increasing take-off angle. The ratios obtained at take-off angles of 15°, 45°, and 75° for the 4.0 eV separation peak relative to the 3.2 eV one were 3.9, 1.7, and 1.2, respectively. Those for the 1.1 eV separation peak relative to the 3.2 eV one also decreased from about 9.8 downward to about 3.3. A decrease in intensity of the imide peak and an increase in intensity of the carboxylate peak were also observed as a function of the take-off angle, further confirming that imidization was inhibited by the formation of carboxylates at the silver surface.

Additional evidence of imidization being inhibited by interaction of the PAA with the silver was provided when the N(1s) multiplex spectra of thin PAA films cured against thick silver films were obtained at 15°, 45°, and 75° take-off angles (see Figure 6). The N(1s) spectra were resolved into two components. The main peak near 400.4 eV was a somewhat low value for an imide but rather close to that of an amide. The peak at lower binding energy near 398.8 eV has been attributed to a C=N linkage which may be due to an isoimide species or a degradation product (22, 23). The relative intensity of this component was found to increase from about 15% to about 27% as the take-off angle increased from 15° to 75°. This will be discussed later.

In a series of experiments, samples were prepared by curing the thick PAA films of PMDA/4-BDAF against polished silver substrates and then delaminated. The XPS results obtained from the resulting fracture surfaces were used to complement those obtained from thin PAA films spin-coated onto thick silver films and then cured. XPS survey spectra obtained from the silver and polymer fracture surfaces of samples after delamination are shown in Figures 7A and 7B, respectively. The relative atomic concentrations of the polymer and silver fracture surfaces are summarized in Table III. In addition to the bands characteristic of silver, the elements characteristic of cured polymer such as carbon, oxygen, nitrogen, and fluorine were all observed in the survey spectra of the silver fracture surface (see Figure 7A). On the contrary, no bands characteristic of silver substrates were present in the survey spectra of the polymer fracture surface (see Figure 7B). As is evident from the data shown in Table III, the relative atomic concentrations of the polymer fracture surface were comparable to those observed for the bulk PMDA/4-BDAF polyimide in Table I.

Figure 8A shows the C(1s) multiplex spectra obtained from the silver fracture surface of a specimen prepared by curing the PAA of PMDA/4-BDAF against the substrate. The spectra were more similar to the C(1s) multiplex spectra of thin PAA films spin-coated onto thick silver films before and after curing (see Figures 4 and 5) than to those of the neat PMDA/4-BDAF polyimide (see Figure 1B), indicating that imidization was inhibited by the interaction of PAA with the silver substrate. This was evidenced by observation of weak bands located at 4.0 and 1.1 eV separations from the main carbon peak near 284.6 eV which were characteristic of the imides, and by observation of a relatively strong band (about 5% of the total carbon) at a 3.2 eV separation which consisted of two overlapping components characteristic of the amide and carboxylate groups. However, the C(1s) multiplex spectra of the polymer fracture surface shown in Figure 8B were more similar to those of the bulk PMDA/4-BDAF polyimide (see Figure 1B) and were characterized by the relatively strong bands characteristic of the imide groups located at the separations of 4.0 and 1.1 eV. Thus, it was concluded that the polymer fracture surface was characteristic of the PMDA/4-BDAF polyimide.

Consistent results were also observed in the N(1s) multiplex spectra of both the silver and polymer fracture surfaces. In the N(1s) spectra of the silver fracture surface, the main component was observed near 400.4 eV a value that was somewhat low for an imide but rather close to that expected for an amide (see Figure 9A). As mentioned above, the peak related to the amide group was also observed near 400.4 eV in the N(1s) spectra of thin PAA films cured against thick silver films (see Figure 6). Instead of an amide peak, a main peak due to the imide species was observed near 400.8 eV in the N(1s) spectra of the polymer fracture surface (see Figure 9B). Again, the results indicated that the silver fracture surface was characteristic of a silver/PAA complex, while the polymer fracture surface was likely a PMDA/4-BDAF polyimide film. Thus, it was considered that a thin interfacial layer was formed between the silver surface and the cured polymer film and that failure occurred at the interface of this interfacial layer and the bulk polyimide film.

Similar results were also obtained by Buchwalter and Greenblatt (24). When they used XPS to investigate the locus of failure between PMDA/ODA polyimide and SiO_2 surfaces, the elemental composition of the polymer fracture surface after the peeling of the polymer film was close to that for the neat PMDA/ODA polyimide. However, the atomic concentration collected for the SiO_2 fracture surface was different. Thus, the results suggestted a formation of a thin interfacial layer between the SiO_2 surface and the cured polymer coating. The failure occurred at the interface of this interfacial layer and the bulk polyimide film.

As mentioned above, the relative intensity of the low binding energy component near 398.8 eV in the N(1s) multiplex spectra of thin PAA films cured against thick silver films was found to increase as a function of the take-off angle (see Figure 6). This phenomenon was also related to the C/N atomic ratios summarized in Table II. The C/N ratios obtained at different take-off angles were generally constant in the case of thin PAA films deposited onto thick silver films before curing. Upon curing, the C/N ratios decreased dramatically as the take-off angle increased. The high nitrogen content can be rationalized in terms of the increase in concentration of this component near 398.8 eV in the interface region upon curing. Consistent results were also obtained from the silver fracture surface of a specimen prepared using the thick PAA films of PMDA/4-BDAF cured against the silver substrates (see Figure 9A). This low binding energy component also constituted about 26% of the total nitrogen on the silver fracture surface.

As mentioned above, this component has previously been attributed to either an isoimide species or a degradation product formed upon curing (22, 23). In our previous studies, a weak band near 1706 cm^{-1} due to isoimide moieties was observed in the SERS spectra of the PAA cured against a silver substrate (20). This band was assigned based on a comparison of the normal Raman spectra of the thermally and chemically cured polyimides. A strong band near 1704 cm^{-1} which did not appear in the spectra of thermally cured polyimide was observed in the spectra of chemically cured polyimide. A similar assignment for the isoimide species was also reported by Saini et al (25). Thus, the low binding energy component near 398.8 eV in the N(1s) spectra was tentatively assigned to the isoimide moieties.

It was also plausible that this component was associated with the amine moieties which derived from the hydrolysis of the isoimide species at the very surface of the metal oxide as proposed by Buchwalter (26). When she compared the bonding strength of 3-aminophenyl acetylene-terminated 3, 3′, 4, 4′ - benzophenone tetracarboxylic dianhydride (BTDA) /m-aminophenoxybenzene (APB) and PMDA/ODA polyimides to SiO_2 after thermal curing, better bonding of BTDA/APB was observed. This was interpreted in terms of the isoimide moieties of the BTDA/ODA being hydrolyzed to the amine and acid species in the near interface region. As a result, the acid part of the hydrolyzed BTDA/APB interacted with the SiO_2 to produce relatively strong bonds at the interface. Since the peak position of the amine species such as aniline was close to that of the low binding energy component in the N(1s) spectra, the possibility of observing the amine species here can not be ruled out.

An alternative interpretation based on the results of Iacona and his coworkers is possible (19). They proposed that a decomposition process generally started because the imidization was inhibited by the formation of carboxylates during the thermal treatment. As a result, the remaining system was essentially a polyamide which was well known to undergo thermal degradation at lower temperature than a polyimide. The degradation pathways of the polyamide systems were thus used to address several possible decomposition mechanisms. The low binding energy component near 398.8 eV in the N(1s) spectra was possibly related to a linear C=N group produced by the thermal degradation of amide species at the surface. One of possible degradation products suggested by Ehlers et al. was the carbodiimide (27).

XPS results obtained from the PAA of PMDA/4-BDAF polyimide cured against the silver can be summarized as follows. Imidization was inhibited by the formation of carboxylates at the PAA/silver interfaces, consistent with the previous results obtained using SERS and RAIR (20). The peak near 398.8 eV in the N(1s) multiplex spectra was related to a C=N linkage which arose from either an isoimide species or a thermal degradation product.

In another series of experiments, XPS was used to investigate the curing of thin PAA films deposited onto the HOPG substrates. XPS survey spectra were obtained before and after curing of thin PAA films deposited onto HOPG substrates from a 0.05% solution in NMP (see Figures 10A and 10B, respectively). Carbon, oxygen, nitrogen, and fluorine were identifed in the spectra. Figure 11A shows the C(1s) multiplex spectra of the thin PAA films deposited onto the HOPG substrate before curing. Generally speaking, the overall line shapes and the fitting of the C(1s) multiplex spectra were similar to those for the neat PAA (see Figure 1A) with the exception of the component near 283.6 eV due to HOPG. The intensity ratio of the acid peak (shifted upward by 4.2 eV) relative to the amide peak (shifted upward by 3.2 eV) was about 1.00, which was close to that (about 0.97) observed for neat PAA.

This was different from the case of silver substrates. As mentioned above, the intensity of the acid peak was relatively weak compared to that of the amide peak because of the formation of silver/PAA complex. Moreover, the main peak due to the amide groups was observed near 400.3 eV in the N(1s) multiplex spectra of the PAA deposited onto the HOPG surface before curing (see Figure 12A). The position of this nitrogen peak was exactly the same as that observed for the neat PAA (see Figure 2A). Thus, these results indicated that no strong interaction of the PAA with the HOPG substrate occurred upon PAA deposition.

The C(1s) multiplex spectra of thin PAA films deposited onto the HOPG substrate and then cured in an argon-purged oven at 107°C for 15 minutes and at 200°C for an additional 15 minutes were also obtained (see Figure 11B). The overall spectral shapes in the C(1s) spectra of the polymer cured against the HOPG substrate were quite similar to those of the bulk PMDA/4-BDAF polyimide (see Figures 1B and 11B, respectively) except that a component characteristic of HOPG was observed near 283.6 eV, indicating that the PAA was completely imidized at the HOPG surface during thermal treatment. The C(1s) spectrum of PAA cured against HOPG showed the merging of the amide and acid components into a single component due to the imide carbonyl groups which was shifted upward by 4.0 eV from the main peak near 284.6 eV (see Figure 11B). Moreover, the component attributed to the aromatic carbon atoms of the PMDA portion which undergo electron withdrawal due to the conjugated carbonyl groups superimposed upon the C-N component and thus increased its relative intensity.

That PAA was fully imidized during thermal treatment was also confirmed when the N(1s) multiplex spectra of the thin PAA films deposited onto the HOPG substrate before and after curing were compared (see Figure 12). The main peak due to the amide groups was observed near 400.3 eV in the N(1s) spectra obtained before curing (see Figure 12A), while the imide nitrogen appeared near 400.8 eV in the N(1s) spectra obtained upon curing. A similar shift of 0.5 eV to higher binding energy position from the amide peak for the neat polymer was also observed. Since no strong interaction of the PAA with the HOPG was observed, the PAA was thus expected to be fully imidized at the HOPG surface during thermal treatment. In fact, that is what was observed. On the contrary, imidization was inhibited by formation of carboxylates at the PAA/silver interface upon curing. It is clear that the thermal curing of PAA at the substrate surfaces was strongly dependent on the nature of the substrates. As mentioned above, Iacona and his coworkers have reported similar observations in the XPS studies of the

PAA for the BTDA/ODA polyimide cured against the various substrates (19).

IV. Conclusions

X-ray photoelectron spectra obtained from thin films of polyamic acid (PAA) of PMDA/4-BDAF cured against silver films were more similar to those of the bulk PAA than to those of the bulk PMDA/4-BDAF polyimide, indicating that curing of the polymer was inhibited by interaction of the PAA with the silver substrate. The results were consistent with those reported previously by using SERS and RAIR techniques (20).

XPS results obtained from fracture surfaces of specimens prepared using thick PAA films cured against polished silver substrates indicated that the silver fracture surface was characteristic of silver/PAA complex, while the polymer fracture surface was likely a PMDA/4-BDAF polyimide film. Thus, it was considered that a thin interfacial layer was formed between the silver surface and the cured polymer film and the locus of failure was at the interface of this interfacial layer and the bulk polyimide film.

A component near 398.8 eV was observed in the N(1s) spectra of the thin PAA films cured against the thick silver films and of the silver fracture surface. This low binding energy component was attributed to a C=N linkage which arose from either an isoimide species or a degradation product. However, the possibility of observing an amine species from the hydrolyzed isoimide could not be ruled out.

The overall spectral features in the XPS spectra of thin PAA films cured against HOPG were quite similar to those of the bulk PMDA/4-BDAF polyimide, indicating that the PAA was completely imidized at the HOPG surface during thermal treatment. No strong interaction of the PAA with the HOPG was observed and the PAA was thus expected to be fully imidized at the HOPG surface during thermal treatment. As mentioned above, imidization was inhibited by the formation of the carboxylates at the PAA/silver interface upon curing. It was clear that the thermal curing of PAA at the substrate surfaces was strongly dependent on the nature of the substrates.

V. Acknowledgements

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VI. References

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Table I. Atomic Concentrations of the polyamic acid and PMDA/4-BDAF. The take-off angle was 45°.

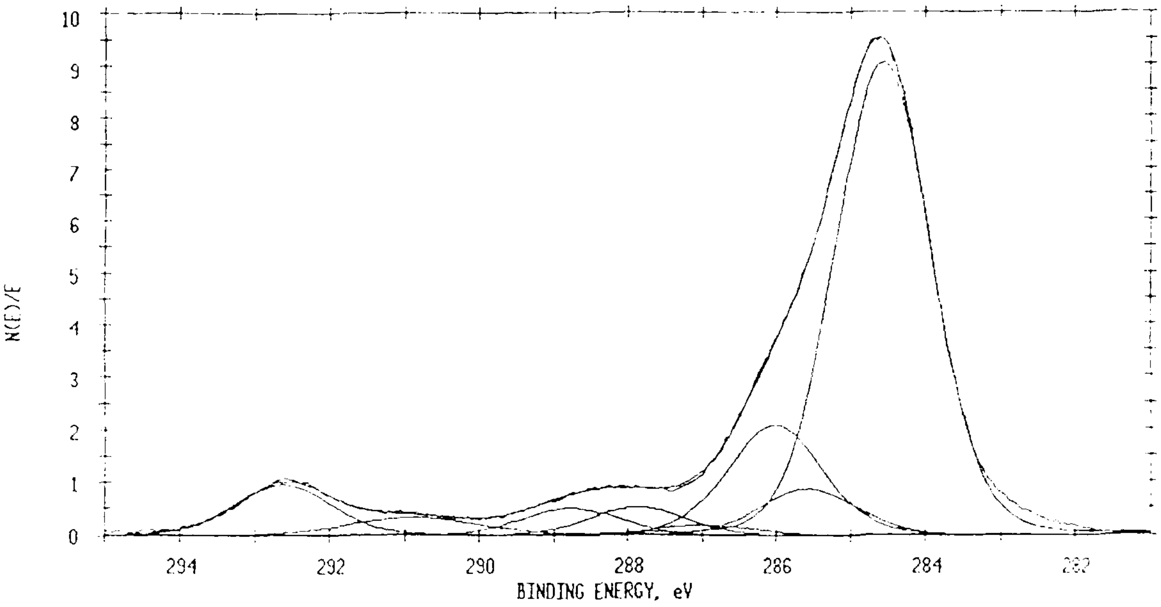
	Atomic Concentrations (%)			
	C(1s)	O(1s)	N(1s)	F(1s)
PAA of PMDA/4BDAF				
Experimental	71.2	13.3	3.7	11.8
Theoretical	69.8	15.1	3.8	11.3
PMDA/4-BDAF				
Experimental	68.3	11.3	3.5	16.9
Theoretical	72.5	11.8	3.9	11.8

Table II. Atomic Concentrations for thin polyamic acid films of PMDA/4-BDAF deposited onto thick silver films before and after curing.

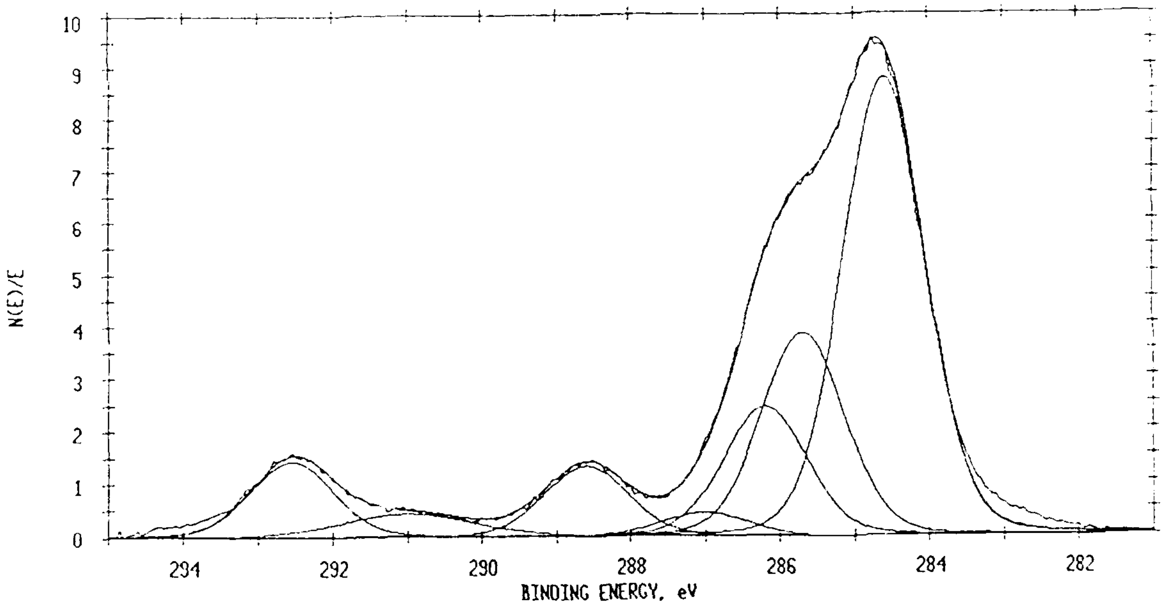
Take-off Angle(^{o})	Atomic Concentrations (%)					
	C(1s)	O(1s)	N(1s)	F(1s)	Ag(3d)	C/N
Before Curing:						
15	63.5	12.0	3.2	10.2	11.1	19.8
45	57.0	13.1	2.9	8.0	19.0	19.7
75	52.6	12.8	2.7	7.2	24.7	19.5
After Curing:						
15	73.0	10.8	2.7	8.4	5.1	27.0
45	66.6	11.8	3.0	7.8	10.8	22.2
75	63.8	10.6	3.6	7.1	14.9	17.5

Table III. Atomic Concentrations of fracture surfaces of specimens prepared using the polyamic acid of PMDA/4-BDAF cured against polished silver substrates. The take-off angle was 45°.

Fracture Surfaces	Atomic Concentrations (%)					
	C(1s)	O(1s)	N(1s)	F(1s)	Ag(3d)	Cl(2p)
Silver	54.5	12.1	2.8	8.0	20.1	2.5
Polymer	69.2	12.8	3.8	14.2	-	-

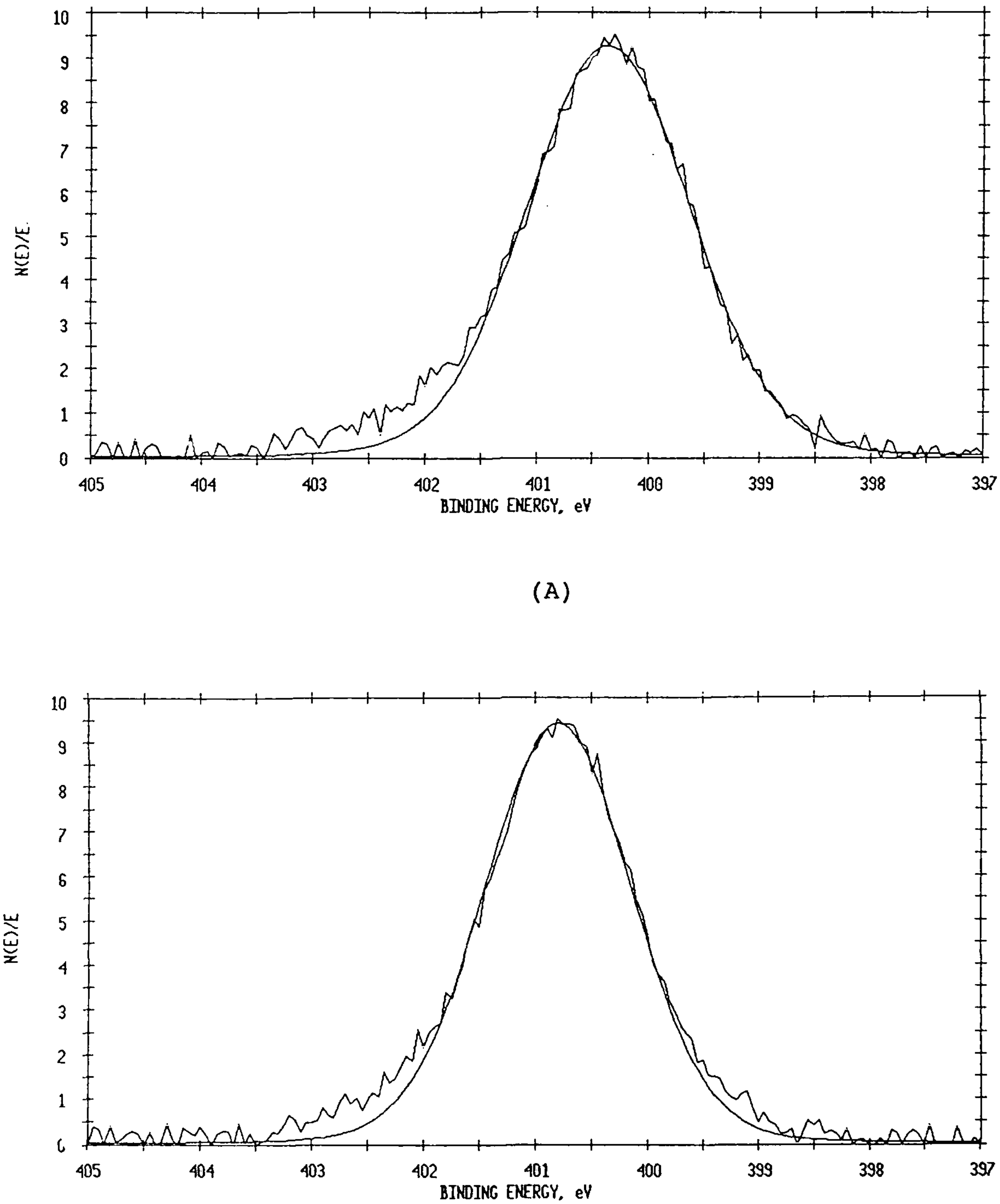


(A)



(B)

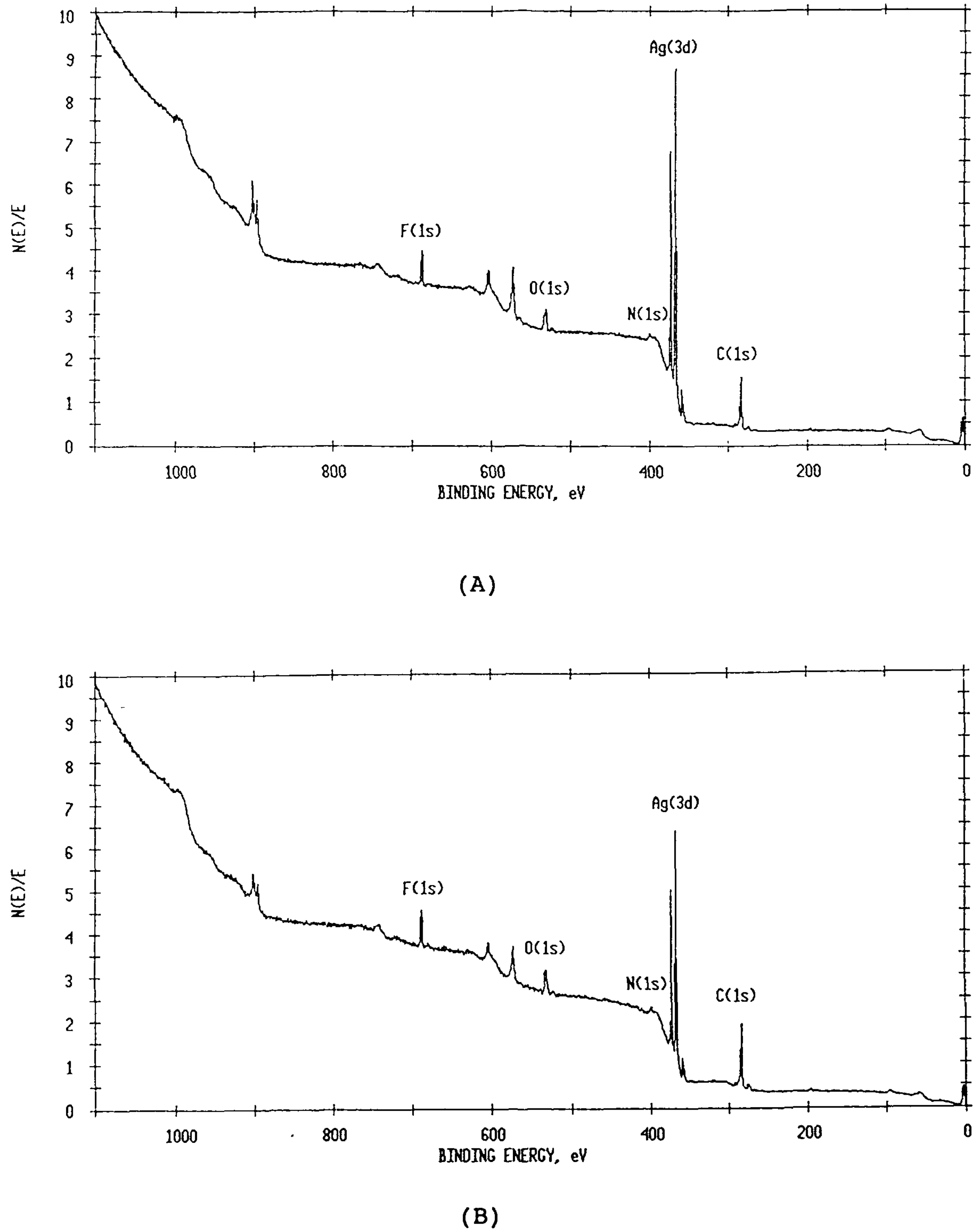
Figure 1. XPS multiplex spectra of the C(1s) core level obtained from the (A) - polyamic acid and (B) - PMDA/4-BDAF polyimide.



(A)

(B)

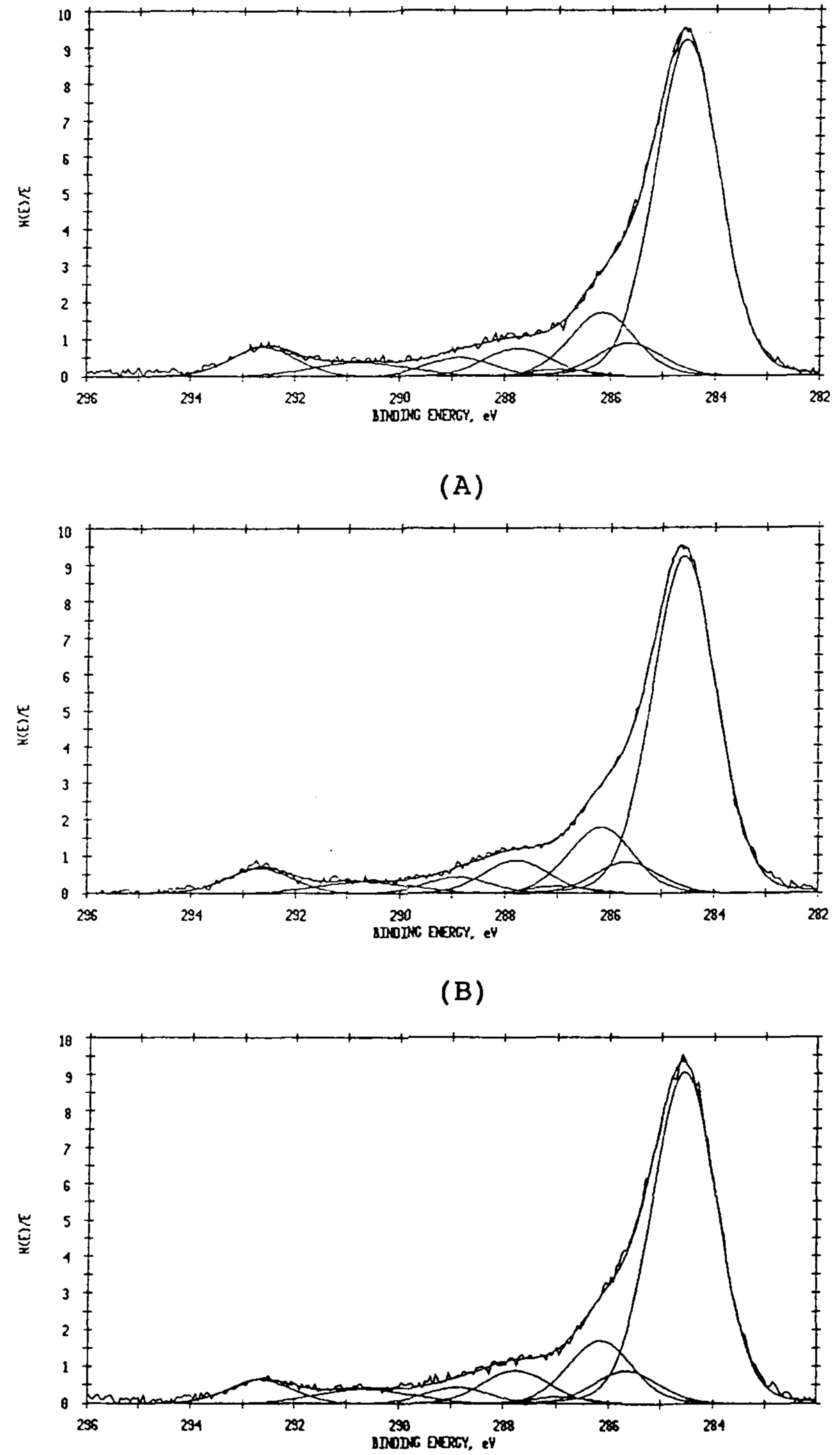
Figure 2. XPS multiplex spectra of the N(1s) core level obtained from the (A) - polyamic acid and (B) - PMDA/4-BDAF polyimide.



(A)

(B)

Figure 3. XPS survey spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF spin-coated onto thick silver films from a 0.2% solution in N-methylpyrrolidone (A) - before and (B) - after curing.

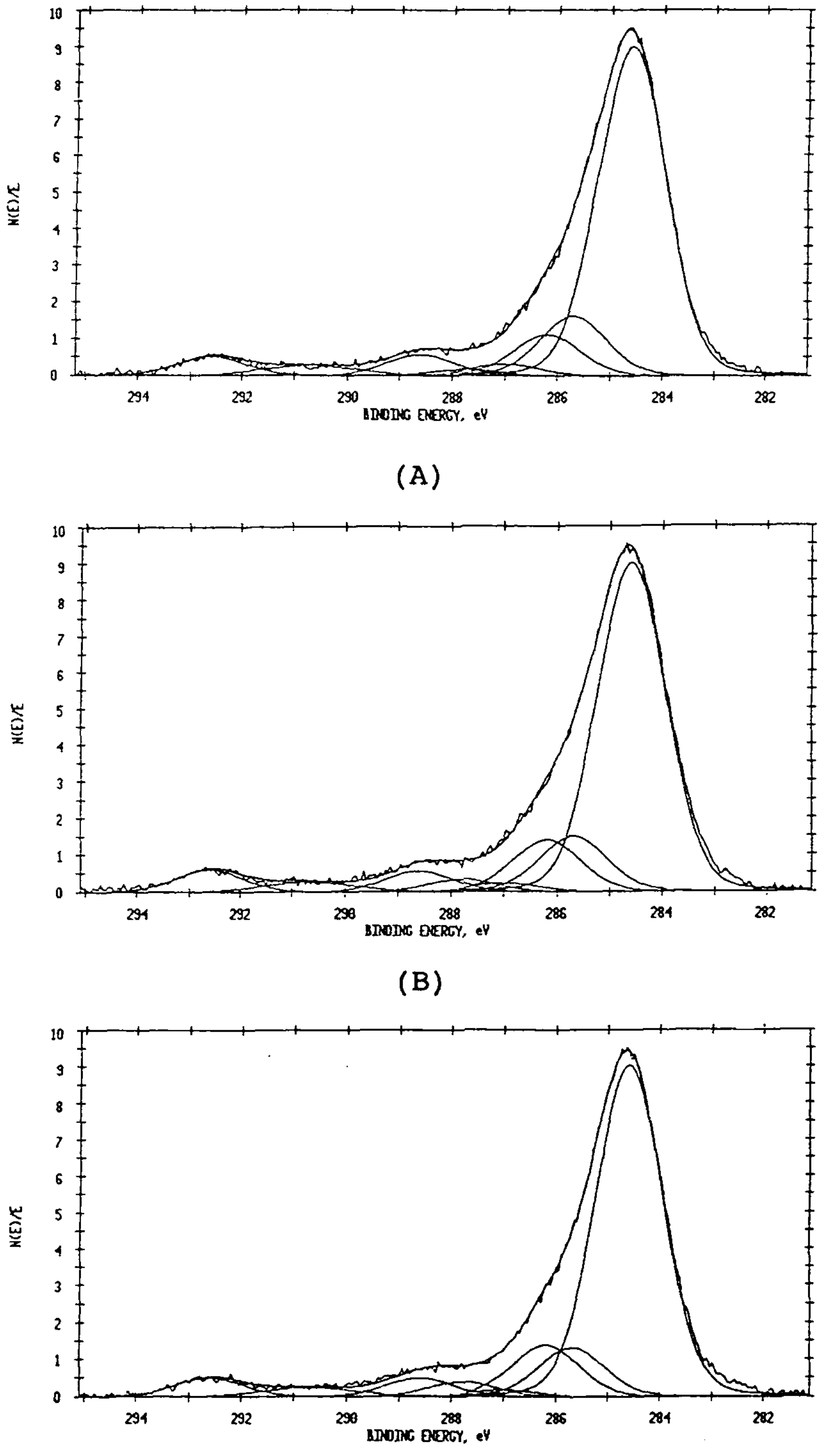


(A)

(B)

(C)

Figure 4. C(1s) multiplex spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF spin-coated onto thick silver films from a 0.2% solution in N-methylpyrrolidone before curing. The spectra were obtained at take-off angles of (A) - 15°, (B) - 45°, and (C) - 75°.



(A)

(B)

(C)

Figure 5. C(1s) multiplex spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF spin-coated onto thick silver films from a 0.2% solution in N-methylpyrrolidone after curing. The spectra were obtained at take-off angles of (A) - 15°, (B) - 45°, and (C) - 75°.

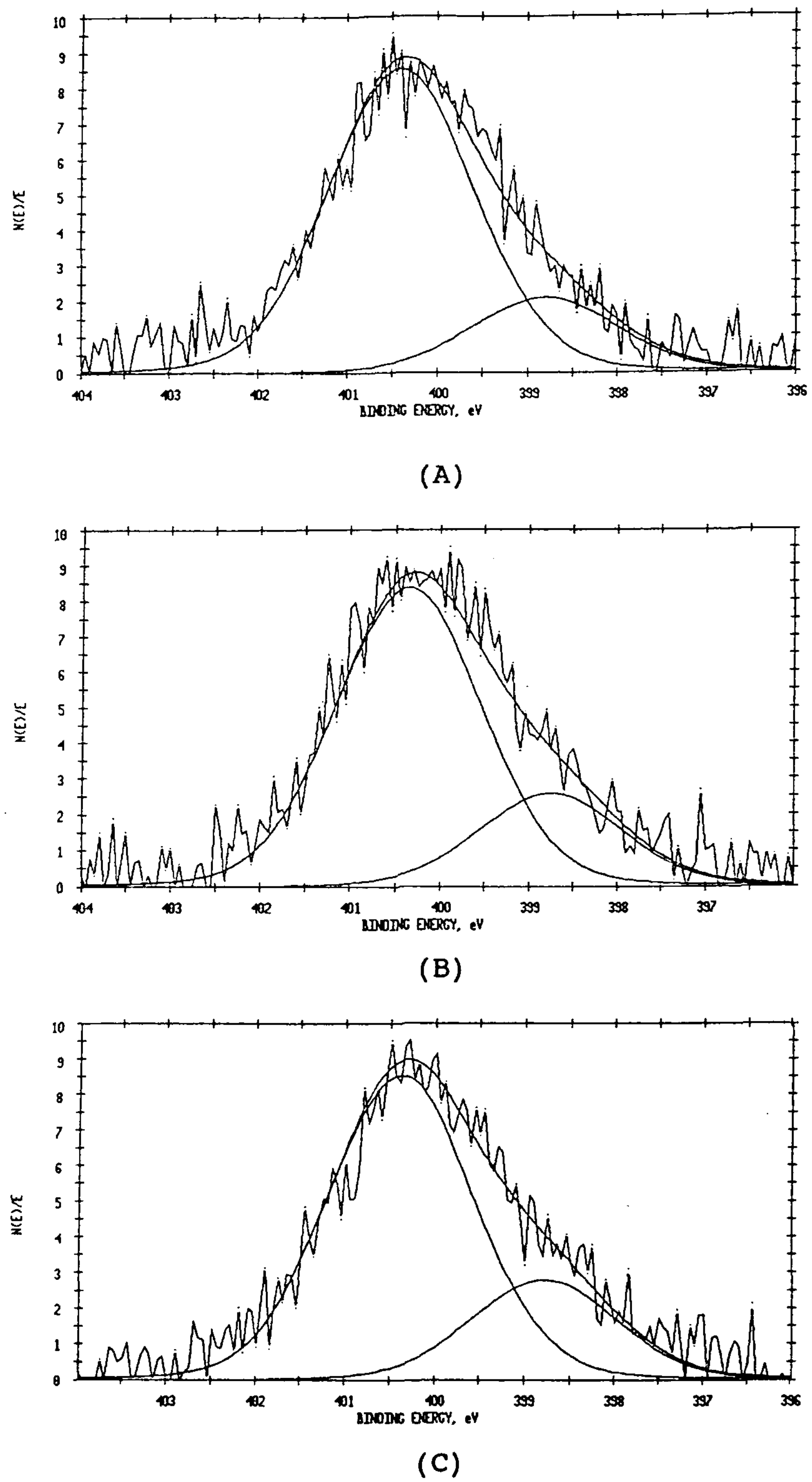
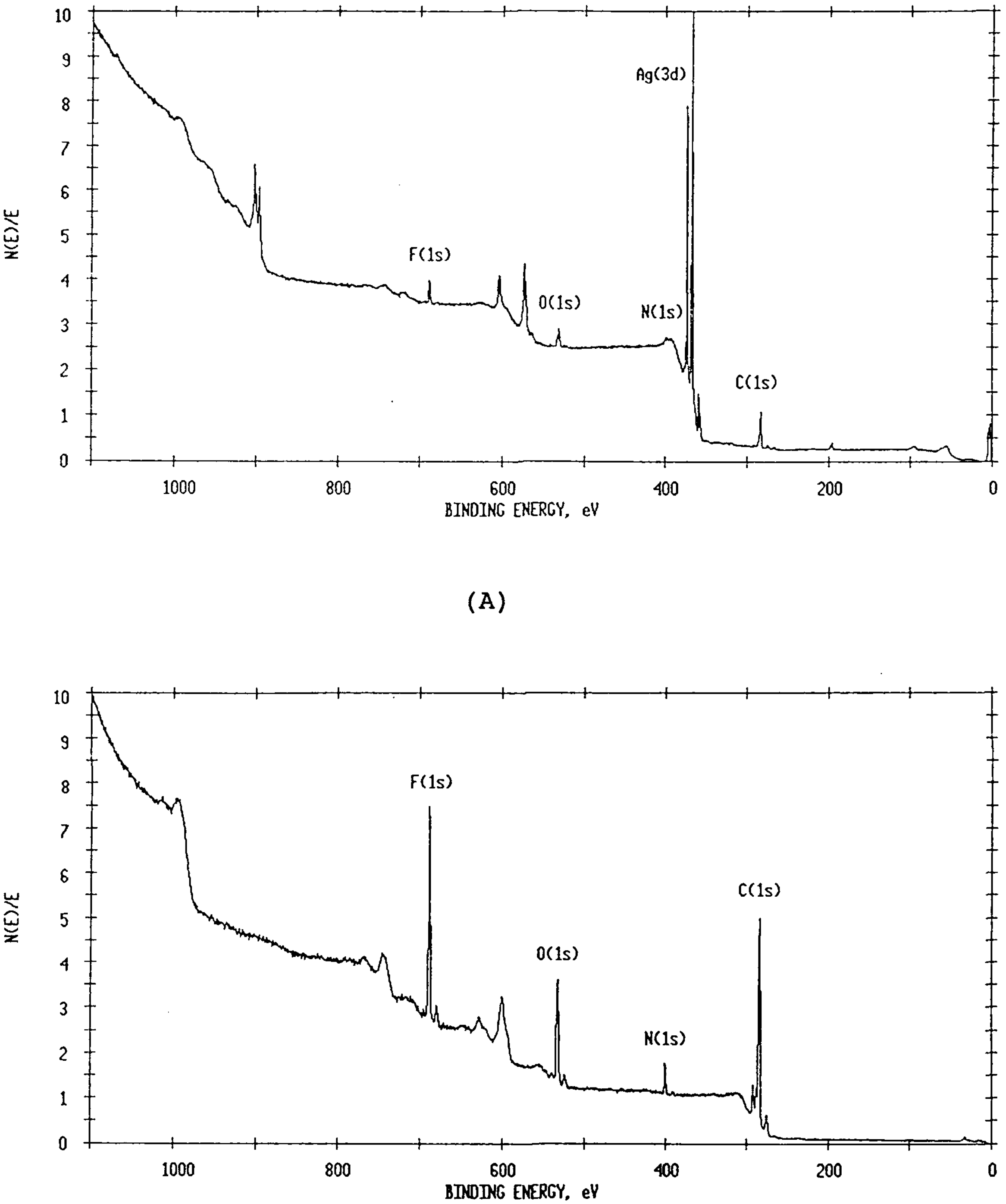


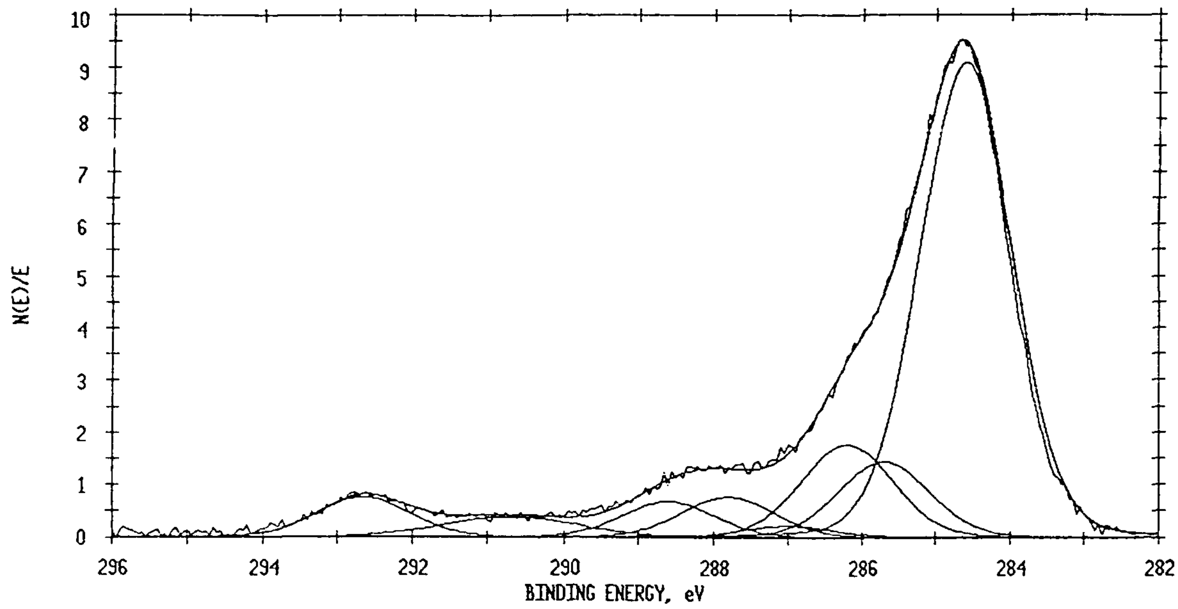
Figure 6. N(1s) multiplex spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF spin-coated onto thick silver films from a 0.2% solution in N-methylpyrrolidone after curing. The spectra were obtained at take-off angles of (A) - 15°, (B) - 45°, and (C) - 75°.



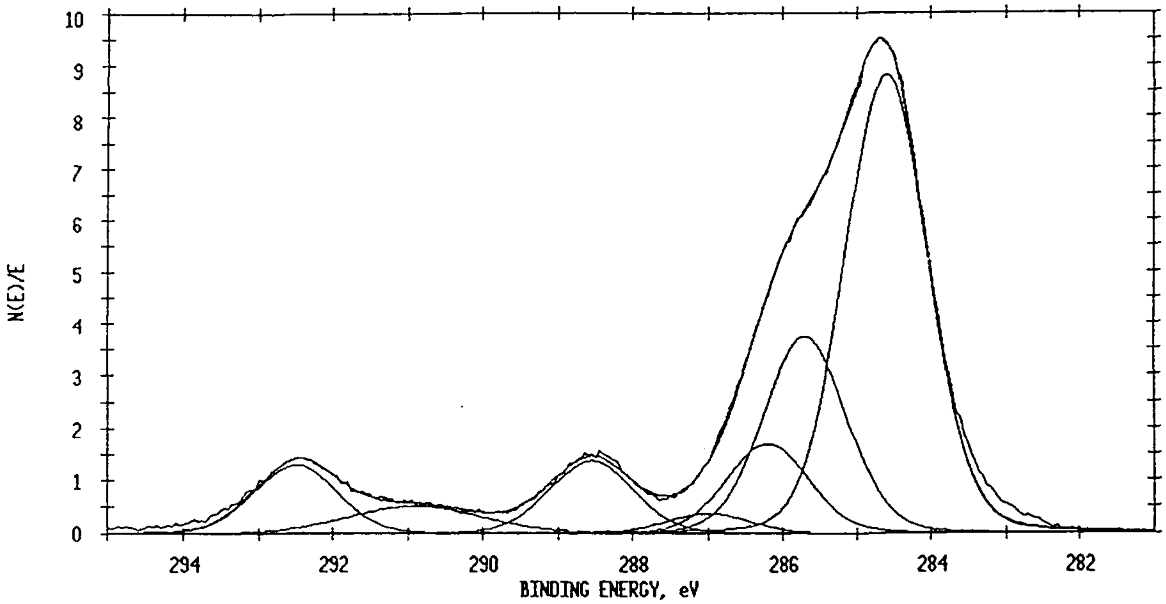
(A)

(B)

Figure 7. XPS survey spectra obtained from (A) - silver and (B) - polymer fracture surfaces of specimens prepared by curing the polyamic acid of PMDA/4-BDAF against polished silver substrates. The take-off angle was 45°.



(A)



(B)

Figure 8. C(1s) multiplex spectra obtained from (A) - silver and (B) - polymer fracture surfaces of specimens prepared by curing the polyamic acid of PMDA/4-BDAF against polished silver substrates. The take-off angle was 45°.

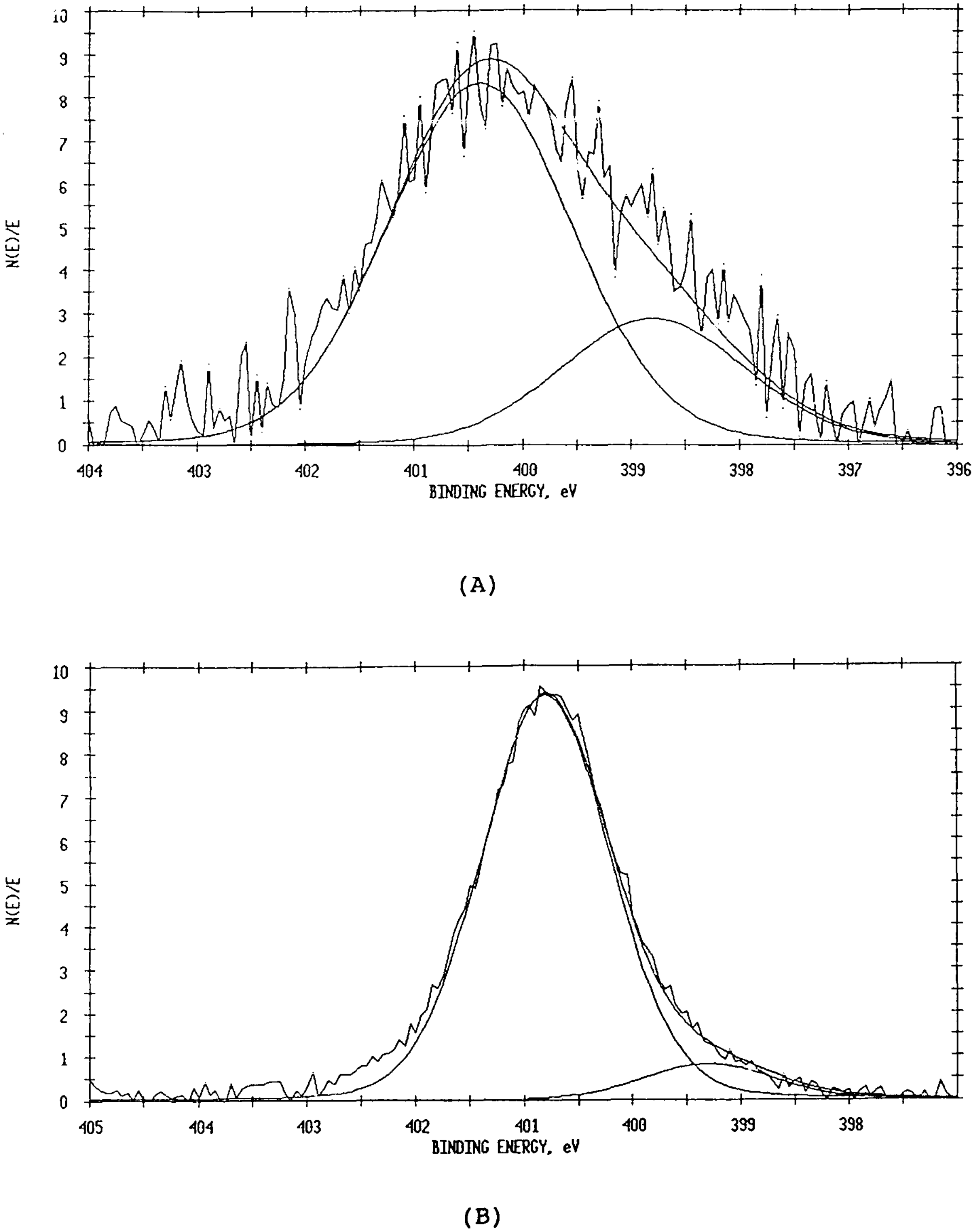
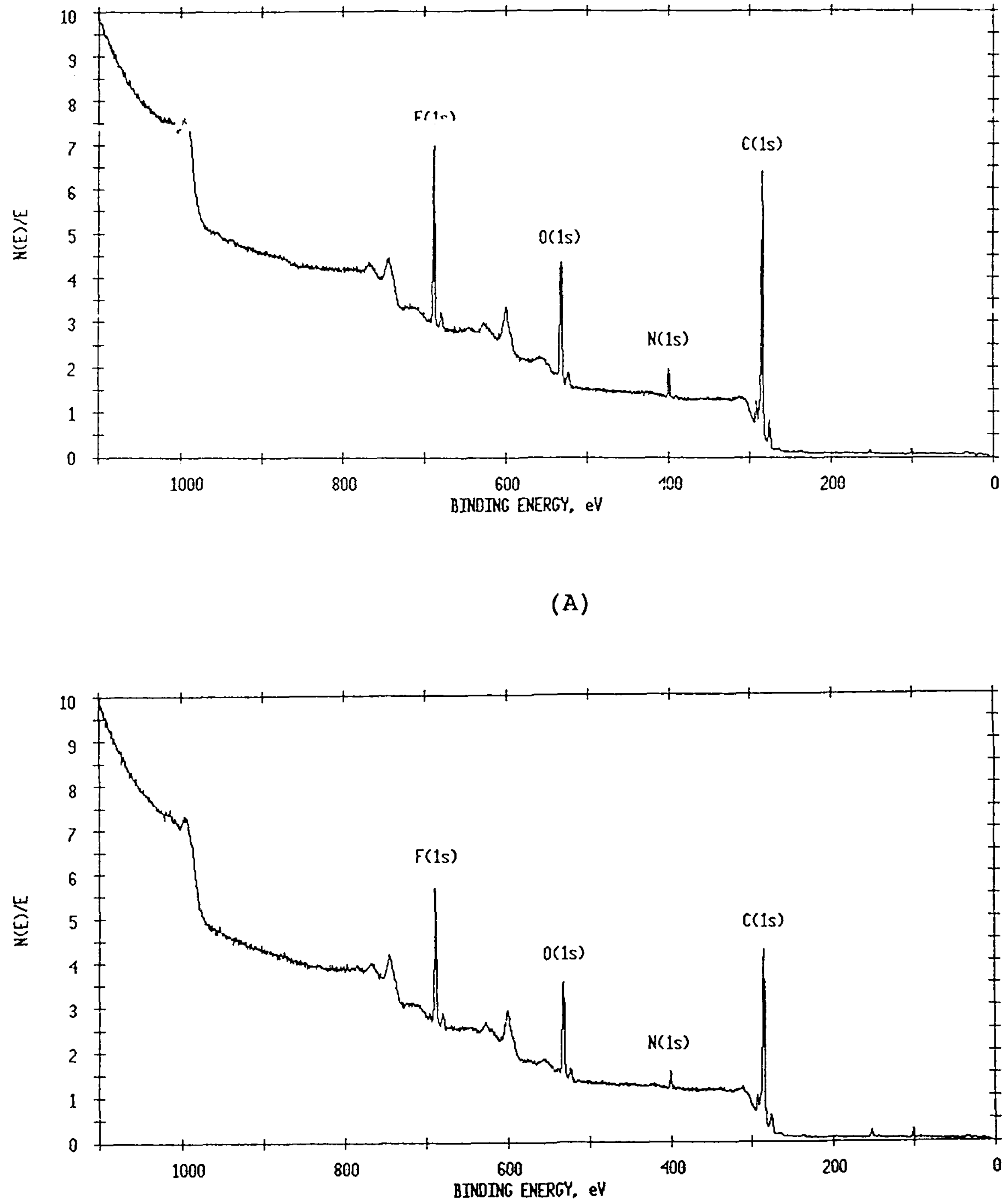


Figure 9. N(1s) multiplex spectra obtained from (A) - silver and (B) - polymer fracture surfaces of specimens prepared by curing the polyamic acid of PMDA/4-BDAF against polished silver substrates. The take-off angle was 45°.



(A)

(B)

Figure 10. XPS survey spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF deposited onto HOPG substrates from a 0.05% solution in N-methylpyrrolidone (A) - before and (B) - after curing. The take-off angle was 45°.

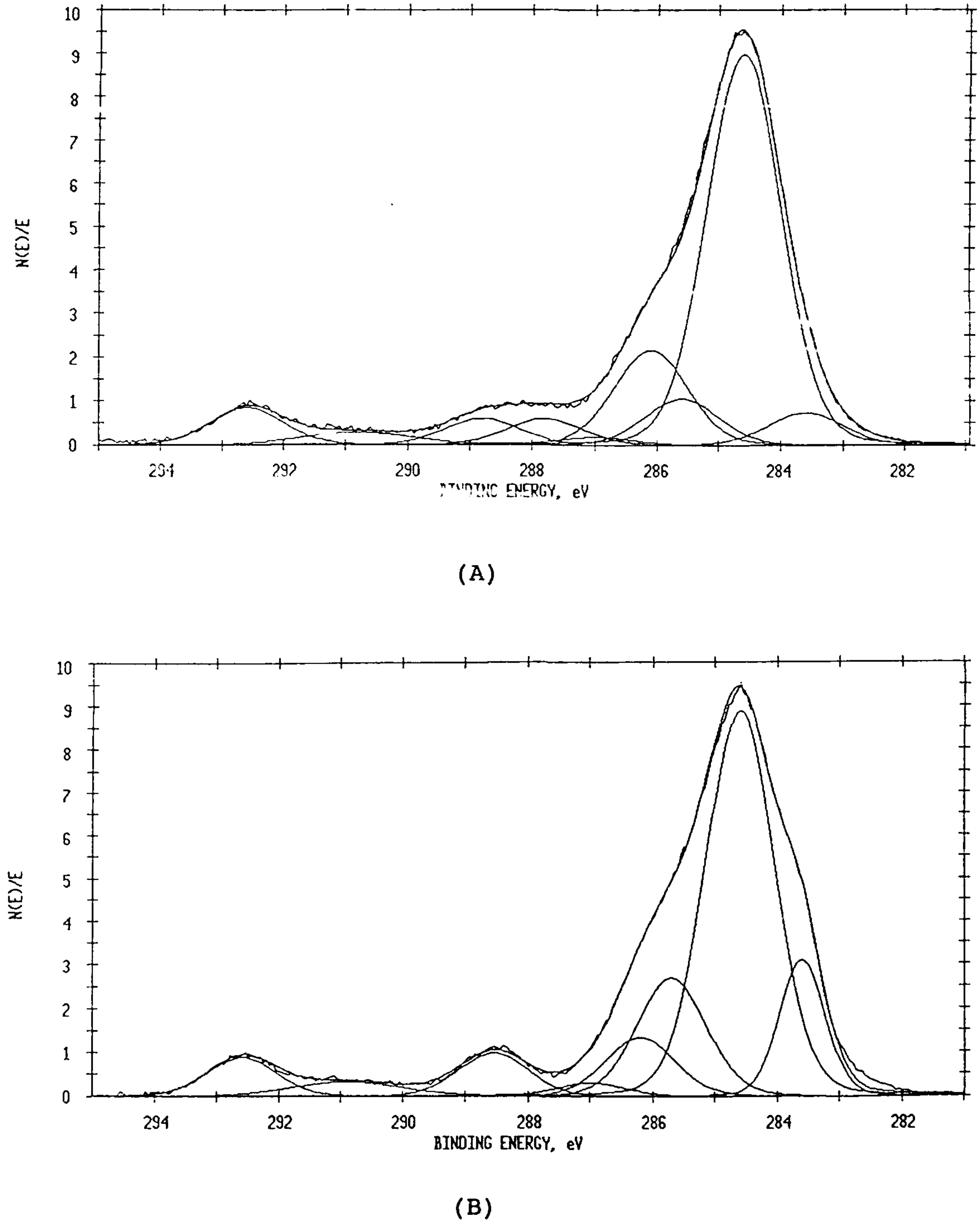
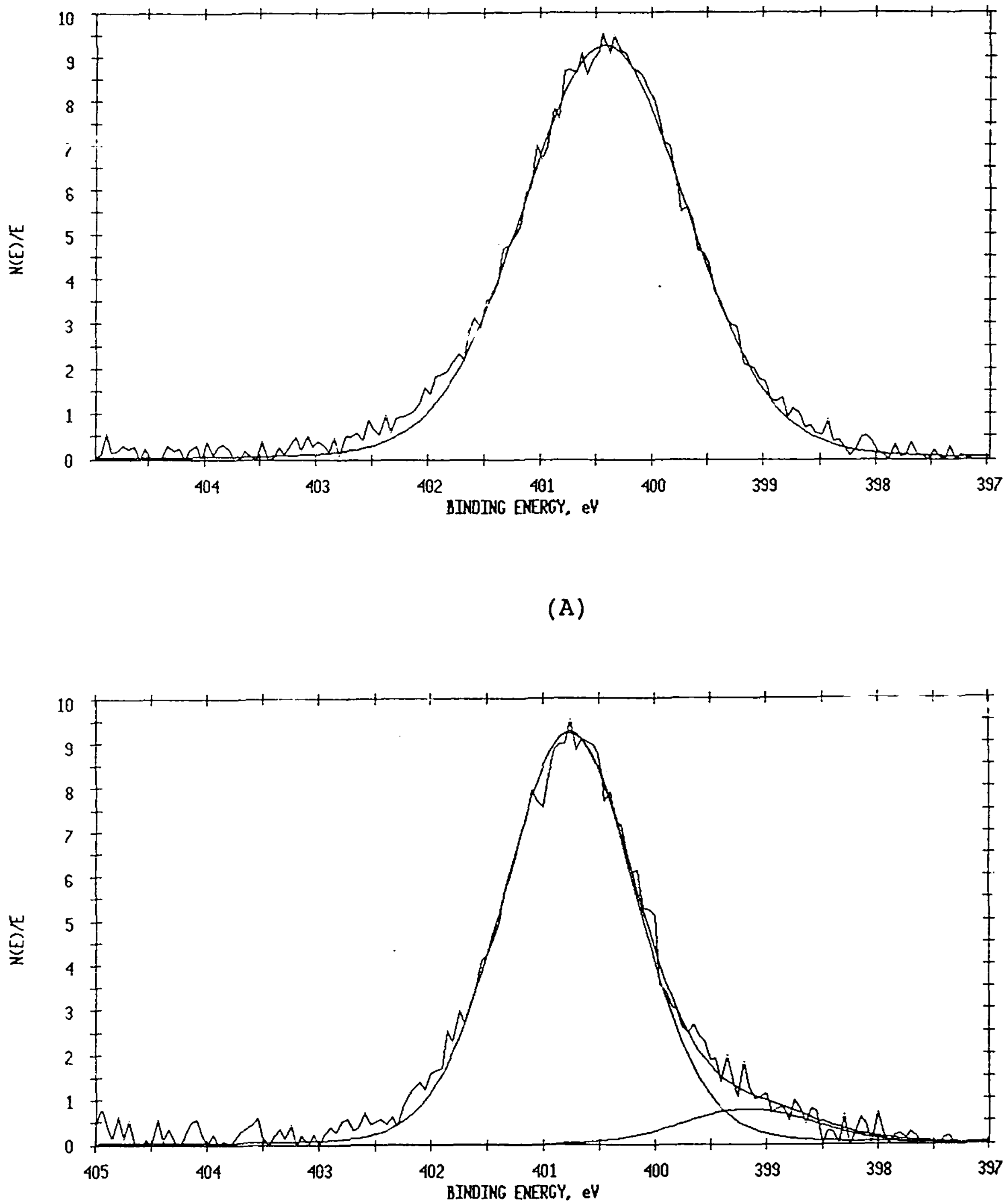


Figure 11. C(1s) multiplex spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF deposited onto HOPG substrates from a 0.05% solution in N-methylpyrrolidone (A) - before and (B) - after curing. The take-off angle was 45°.



(A)

(B)

Figure 12. N(1s) multiplex spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF deposited onto HOPG substrates from a 0.05% solution in N-methylpyrrolidone (A) - before and (B) - after curing. The take-off angle was 45°.

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