INTERFACIAL INTERACTIONS AFFECTING POLYIMIDE RELIABILITY

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Abstract

The widespread use of polyimides in the microelectronics industry and the corrosion problems associated with them, have stimulated research in studying the interaction of polyimides with metals, semiconductors and a range of gaseous and aqueous environments. The susceptibility of polyimides to moisture is well known, however, their chemical interactions with moisture are still unclear. In this paper, the technique of x-ray photoelectron spectroscopy (XPS) has been used to study interfacial chemistry of the polyimide PMDA-ODA on exposure to air, water and NaCl solution for extended periods of time. It was found that in spite of the near neutrality in pH of the two aqueous solutions, the interactions of the polyimide interfaces were different, indicating the influence of ions on the reaction.

Introduction

On many occasions it has been shown that a packaged device fails prematurely in service, and very often the cause of failure is corrosion damage to the underlying circuitry.[1] This has necessitated a change in the empirical approach to processing and packaging of electronic devices. The increasing device density per chip and the sub-micron feature size of silicon in the device has led to an increase in the interconnect density on the chip.[2] The interconnects between dissimilar metals such as aluminium, copper and gold for example increase the susceptibility of the chip to galvanic attack in the presence of moisture and ions. In addition, the trend to use microprocessor based instrumentation in hostile, chemically aggressive environments, such as chemical plants, automobiles, and manufacturing lines, has placed stringent demands on microelectronics materials to ensure a longer performance life and high reliability. The algorithm for a corrosion process in microelectronics is the same as for a macroscopically corroding system. However, the most important step in microelectronics corrosion is the initiation of corrosion, i.e. the ingress of moisture, ionic species and cathodic reactants through the encapsulant to the underlying circuitry.

Polyimides (PMDA-ODA) are a class of high temperature polymers that are widely used in the fabrication of integrated circuits: as multilevel dielectrics, as die-attach adhesives, as passivants, encapsulants and as a lithographic material. However, their susceptibility to moisture uptake results in degradation of their chemical, mechanical and electrical properties. It is well known that polyimides, on exposure to water, take up between 2 to 5% by weight of moisture.[3-6] It has been reported[7,8] that water occupies microvoids in polyimide and that the diffusion coefficient for moisture is between 3-7 x 10^{-9} cm^2/sec. However, the exact physical or chemical interactions of moisture with bulk polyimide as well as polyimide interfaces are not well characterized.[9] When polyimide is used for encapsulation purposes, the reliability of the encapsulant depends on the interactions occurring at both of its surfaces. Sorption and diffusion of water, gas and ionic species across the polyimide membrane are processes related to the polyimide/environment interface while metal degradation is related to the polyimide/substrate interface.

In this paper the interfacial interactions occurring on and beneath spin coated films of the polyimide pyromellitic dianhydride - oxydianiline (PMDA-ODA) have been studied using x-ray photoelectron spectroscopy (XPS).

Experimental

Three types of samples of PMDA-ODA were prepared: control samples of a single layer (1.2 μm thick) of PMDA-ODA on native oxide covered silicon, samples that were immersed in distilled water and samples of PMDA-ODA immersed in an NaCl solution. All specimens were spin-coated on 5.0 cm diameter silicon wafers.

Samples for studying the polyimide/metal interface were prepared as follows: The substrate for the polyimide films was a 5500 Å thick vacuum evaporated film of aluminium on a silicon wafer. The polyimide precursor, polyamic acid in a solution of n-methyl pyrrolidone (NMP), was applied to the aluminium covered wafers, which were spun at 3000 r.p.m. for 100 seconds. Three separate polyimide layers were coated to minimize pin holes. A ß-stage cure at 140°C for 15 min. in air was carried out after each layer. The final cure was performed at 400°C for 45 min. in a nitrogen environment yielding an after cure thickness of 4.8 μm. The polyimide coated aluminium sample was immersed in a 3 wt.% NaCl solution prepared from analytical grade reagent in distilled water (of 18 MΩ cm resistivity). The solution was air saturated and the sample was immersed for a period of 15 days. The polyimide at the aluminium/polyimide interface was peeled and examined using x-ray photoelectron spectroscopy (XPS).

Surface analysis of the polyimide was carried out using a Surface Science Instruments SSX-100 ESCA spectrometer with a base pressure of about 10^{-9} torr. Monochromatic Al Kα radiation (1486.6 eV) was used as the x-ray source and the photoelectrons emerging at a take-off angle of 35° to the surface were analyzed. A flood gun was used to prevent charging of the samples and the gun energy was optimized for the given geometry to yield narrow, intense peaks and was about 6.0 eV. All spectra were referenced to the phenyl carbon peak in polyimide at 285.0 eV.[10] An x-ray spot size of 600 μm in the high resolution mode was employed. All spectra are original unsmoothed data that were deconvoluted using 100% gaussian peaks with a chi square fit better than 2.5.

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Results and Discussion

Control Sample

X-ray photoelectron spectroscopy has proven to be a useful tool in the study of polyimides.[11-16] The molecular formula of a repeat unit of PMDA-ODA is shown in Figure 1. The numbering of the carbon atoms in this figure have been used to assign XPS peaks to the type of carbon atoms. Although theoretically a large number of non-equivalent carbons are present in the PMDA-ODA unit[17], the XPS signal for the carbon core level can resolve three types of carbons as shown in Figure 2. The peak positions are referenced to the first major peak at 285.0 eV and this is due to phenyl carbons, labelled 3 in Figure 1. The peak at 286.07 eV has been attributed to carbons bonded to the ether oxygen and the imide nitrogen labelled 4 and to the phenyl carbons of the PMDA ring, labelled 1 in Figure 1. The peak at 288.93 eV corresponds to the carbonyl carbons labelled 4 and the broad peak at 291.38 eV is due to a $\pi \rightarrow \pi^*$ shake-up. The exact origin of the shake-up is not established making carbon shake-up distribution between different carbon atoms difficult.[15]

The oxygen 1s envelope for PMDA-ODA is as shown in Figure 3. The two types of oxygen in the repeat unit give rise to two peaks on deconvolution. The major peak at 532.48 eV is due to carbonyl oxygens while the peak at 533.85 eV is due to the ether oxygen. Only one type of nitrogen is present in polyimide and hence only one peak is expected in photoelectron spectrum. Figure 4 depicts the nitrogen 1s signal with a peak at 401.14 eV and a shoulder on the low binding energy side at about 399.63 eV. The C 1s and O 1s spectra also show a small peak on the low binding energy side that are discernible after deconvolution. These peaks could possibly be due to the incomplete removal of solvent from spin-coated polyamic acid, since there may be a thermodynamic limit to solvent removal (as solvent removal builds-up stresses in the film). In the case of nitrogen some researchers [18] have observed a second nitrogen peak at about 399.3 eV that includes about 8% of the nitrogen intensity. This was attributed to the presence of isoimide in the film. However, no additional peaks for carbon and oxygen were observed making this possibility unlikely in this case. In the spin-coated samples here the low energy peak constitutes about 5, 2.5, and 7% of the respective total intensities of C, O, and N spectra.

The XPS signal can be quantified to asses the stoichiometry of the PMDA-ODA surface after correcting the peak areas for their photoelectric cross-sections.[19] Analysis of the C, O and N stoichiometry revealed an average number of oxygen atoms per repeat unit close to 4, compared to the value of 5 as shown in Figure 1.[20] From the C 1s spectra, the fraction of carbonyl carbon was calculated to be close to 3 of the total of 22, compared to the 4 carbonyl carbons shown in Figure 1. This implies that the polyimide is deficient in one carbonyl group. However, since the total carbon content is 22, one of the carbonyl carbons appears to have transformed to another form of carbon. A deficiency in the carbonyl signal has been observed by several researchers,[9,17,18] but its origin is still an unresolved issue. We have also observed[20] that this apparent deficiency of carbonyls is present up to several monolayers as seen from angle resolved XPS studies of PMDA-ODA.

Water Immersed Sample

The susceptibility of polyimide to moisture is well documented.[3-6] The PMDA-ODA samples were analyzed with XPS, after immersion in distilled water for a period of 22 days. Figures 6, 7 and 8 show the corresponding C 1s, O 1s and N 1s spectra. Water immersed samples show considerable peak broadening with little or no change in the peak positions. From the C 1s spectrum depicted in Figure 6 it can be seen that the peak at 286.12 eV broadened considerably, while the phenyl carbon peak was altered only slightly. This could be explained due to the interaction of water with polyimide that involves carbons other than the phenyl carbons of the ODA part of the polyimide. The carbonyl peak at 288.85 eV is still intensity deficient indicating the irreversible nature of carbonyl carbons. The O 1s envelope in Figure 7 was deconvoluted to give a carbonyl oxygen peak at 532.27 eV and a peak due to ether type linkages at 533.49 eV. Both the O 1s peaks appeared to have broadened as those of C 1s spectrum. The N 1s signal gave a peak at 400.61 eV and was apparently unaffected in intensity or peak shape on water immersion. It may be noted however that all the three spectra of water immersed PMDA-ODA do not show the additional peak on the low binding energy side of the main peak. This could possibly be due to displacement of solvent by water, since NMP and water are miscible.

PMDA-ODA 3wt.% NaCl

Water uptake by polyimide is perhaps the first step in degradation of the film. In the presence of ions in solution, permeation of ions through the film initiates the corrosion process beneath the film. Permeation studies of NaCl were carried out[21] in a two compartment cell on a free standing film of spin coated polyimide. An ion selective electrode was used to detect the sodium ions that permeated through the sample. Figure 8 shows a representative permeation plot of Na^+ concentration through a 1.2 μm thick polyimide. A range of concentrations of Na^+ were seen on various samples; the lower limit denoted by squares in Figure 8 corresponds to the permeation through an apparently defect free film while the upper limit indicated by crosses corresponds to a film with a highest apparent defect density.

For a 4.8 μm thick defect free film spun on an aluminium covered substrate, sodium was not detected by XPS on the backside of the peeled film, due to the detection limit of XPS of about 1000 ppm. However the influence of the ions on the nature of the polyimide layer was apparent; both of sodium and chlorine were seen on the solution side of the film and are not shown here. Figure 9 shows the C 1s photoelectron spectrum of a PMDA-ODA film after immersion in a 3 wt% NaCl solution for 15 days at room temperature. The main carbon peak was completely unresolved and the carbonyl peak had almost doubled in its full width at half of the maximum intensity (FWHM). Figure 9a depicts the top surface of the polyimide while Figure 9b shows the spectrum for the backside of the film after peeling. The carbon envelope was deconvoluted with a minimum number of peaks and an unusually high intensity in the carbonyl carbon region was evident. Multiple states of carbon may be present in this peak, however, the deconvolution shown here resulted in peak positions that were unchanged from those for the spin coated control sample. The top film of polyimide showed the presence of sodium and chloride ions but on the backside of the

peeled film no Na^+ or Cl^- could be detected. However the carbonyl peak shape changes in NaCl solution as compared to water only, suggest a different reaction at the polyimide surfaces due to the ions in solution. The oxygen spectrum on the front and backside of the film are shown in Figure 10a and 10b respectively. The decrease in the ether oxygen intensity was similar on both sides of the film, with peaks at 534.1 eV and 533.65 eV, while the carbonyl oxygen peak was observed at 532.7 eV on the top surface of the polyimide and at 532.15 eV on the back surface of the polyimide. The oxygen spectra were broad on both surfaces of PMDA-ODA but the back surface showed broader peaks due to a greater spread in binding energies as may be expected.

The nitrogen peaks on the top and back surfaces of the polyimide were dissimilar. The imide nitrogen peak was positioned at 401.34 eV on the top and at 401.56 eV on the back of the film. The latter is on the higher side of binding energy when compared to the control sample. In addition, the peak at 399.9 eV on both surfaces indicates that the interaction of polyimide with a neutral solution depends on the composition of the aqueous medium. Such a peak was absent on the water immersed sample and hence the presence of Na^+ and Cl^- in water must have altered the reaction with polyimide. On the back surface of the polyimide the nitrogen peak at 399.99 eV constituted about 60% of the nitrogen total intensity.

A similar nitrogen peak was observed by Leary and Campbell[9] on PI 5878 polyimide after exposing it at 280°C to 80% relative humidity, and was attributed to de-imidization of the surface. A more complex reaction is thought to be occurring in this situation.

Summary

A spin-coated polyimide layer is oxygen deficient and possibly contains peaks due to the solvent. In the present work one carbonyl moiety per repeat unit was found to be deficient and could not be regenerated by water immersion. On immersing spin-coated PMDA-ODA in water, the solvent peaks were eliminated. For PMDA-ODA in NaCl, although no ions were detected on the backside of the polyimide, substantial reaction of the polyimide was observed that was different from the interaction of polyimide with water.

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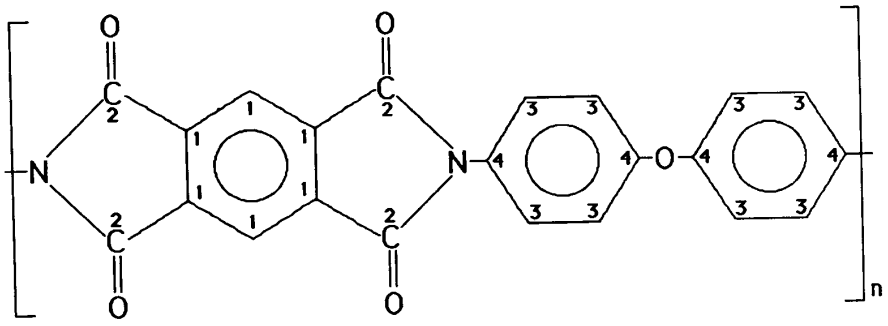

Figure 1: PMDA-ODA repeat unit. Numbers represent carbon positions referred to in the text.

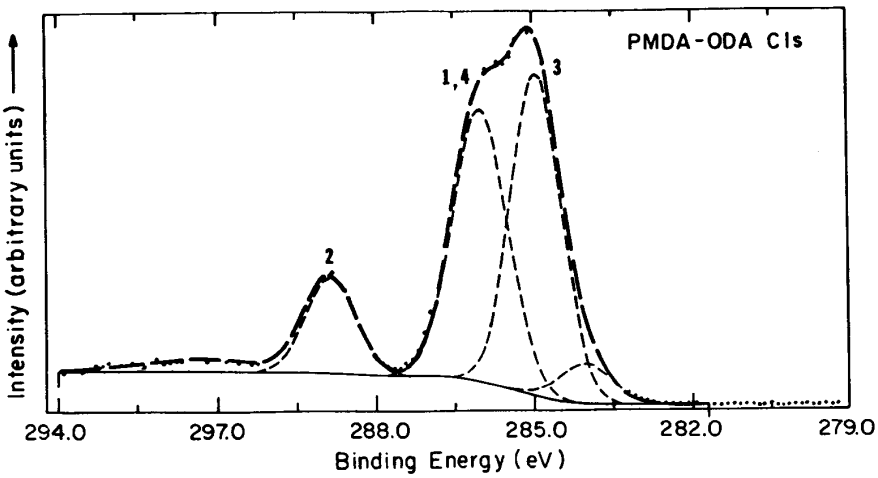

Figure 2: C 1s spectrum for as-cured PMDA-ODA.

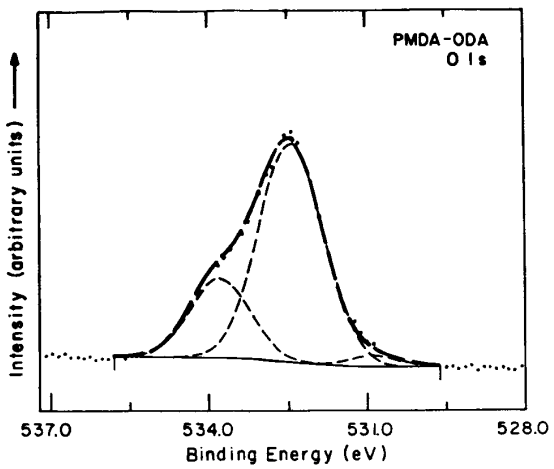

Figure 3: O 1s spectrum for as-cured PMDA-ODA.

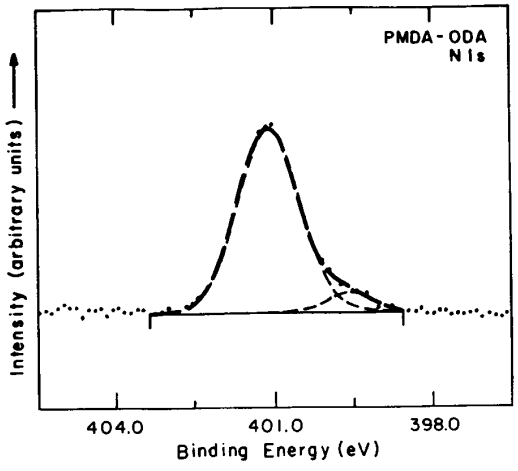

Figure 4: N 1s spectrum for as-cured PMDA-ODA.

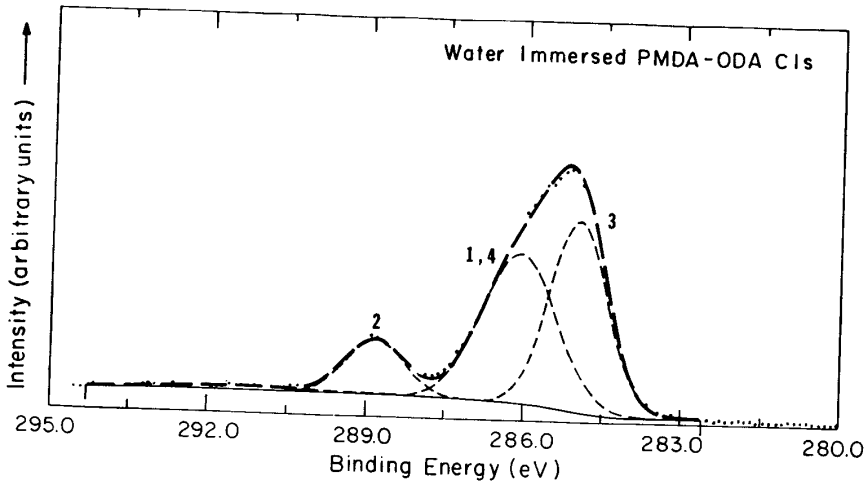

Figure 5: C 1s spectrum for PMDA-ODA after immersion in distilled water for 22 days at room temperature.

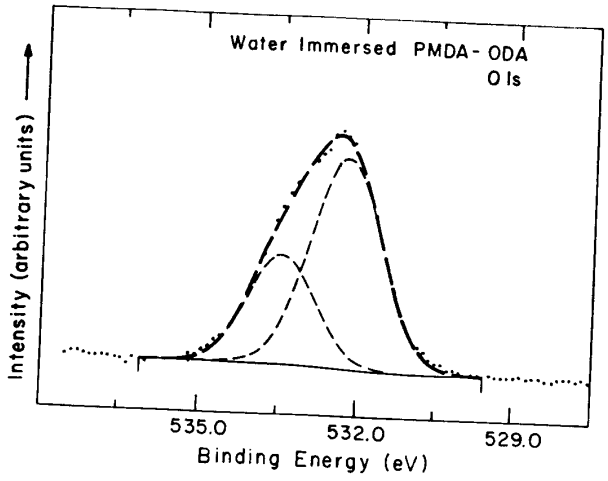

Figure 6: O 1s spectrum for PMDA-ODA after immersion in distilled water.

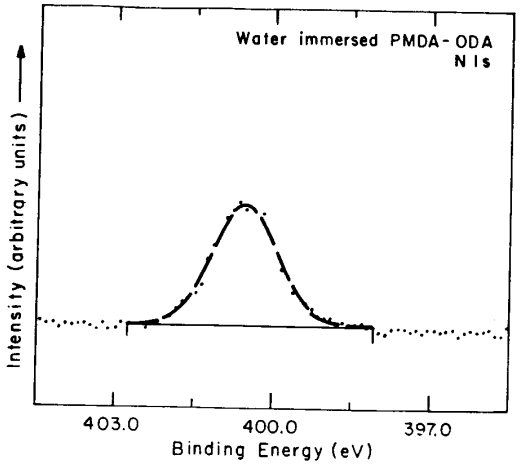

Figure 7: N 1s spectrum for PMDA-ODA after immersion in distilled water.

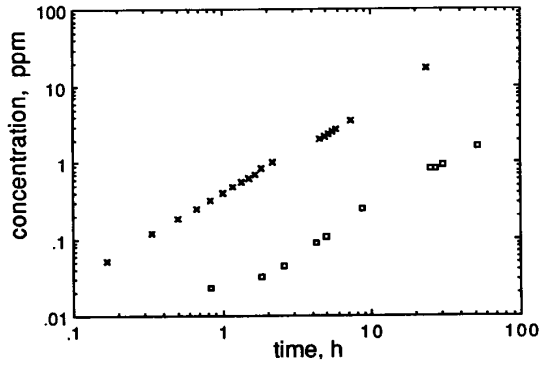

Figure 8: Plot of log[Na^+] vs log(t) for permeation of Na^+ through a 1.2 μm PMDA-ODA membrane.

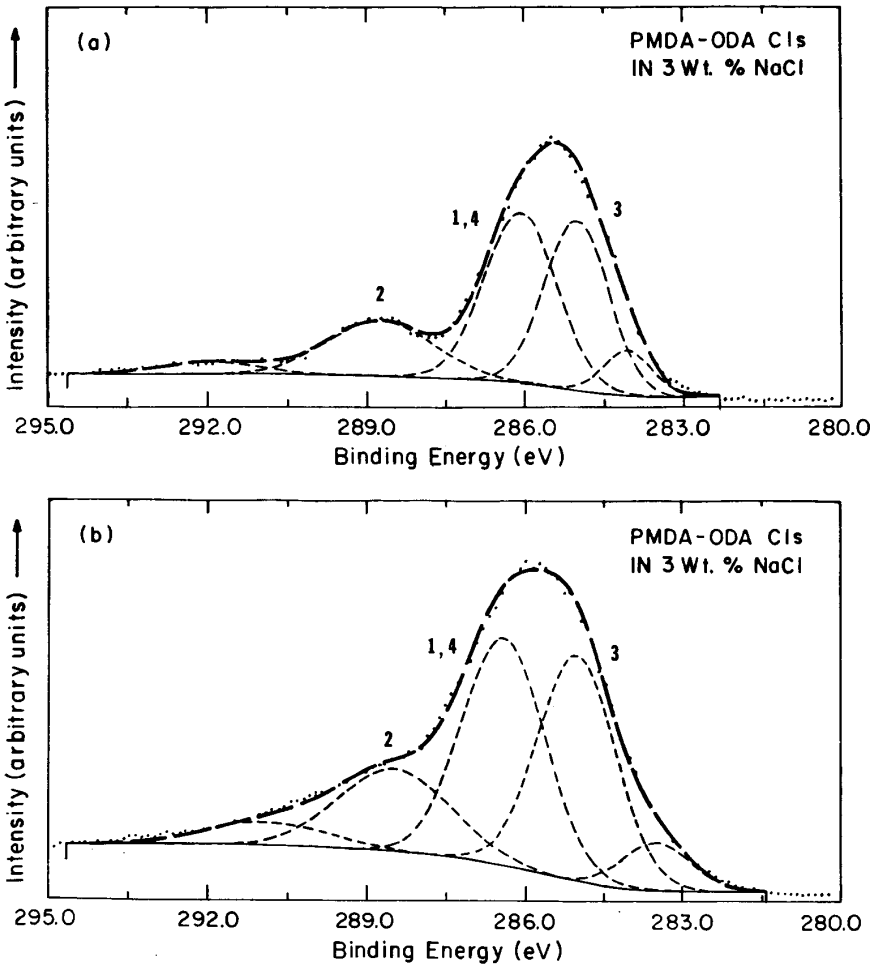

Figure 9: C 1s spectra for PMDA-ODA after immersion in NaCl for 15 days: (a) top surface of polyimide, (b) back surface of polyimide after removal from aluminium substrate.

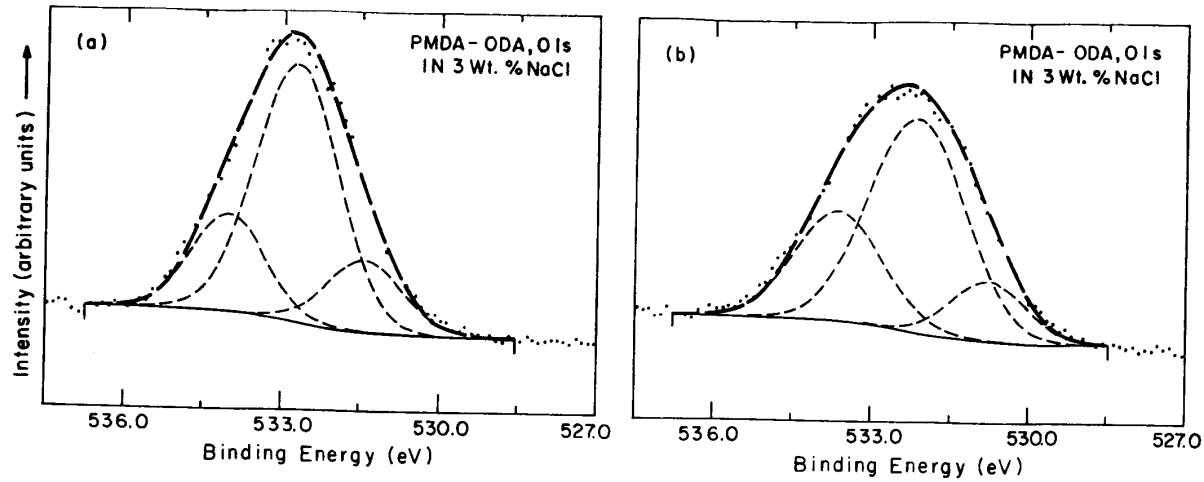

Figure 10: O 1s spectra for PMDA-ODA after immersion in NaCl for 15 days: (a) top surface of polyimide, (b) back surface of polyimide after removal from aluminium substrate.

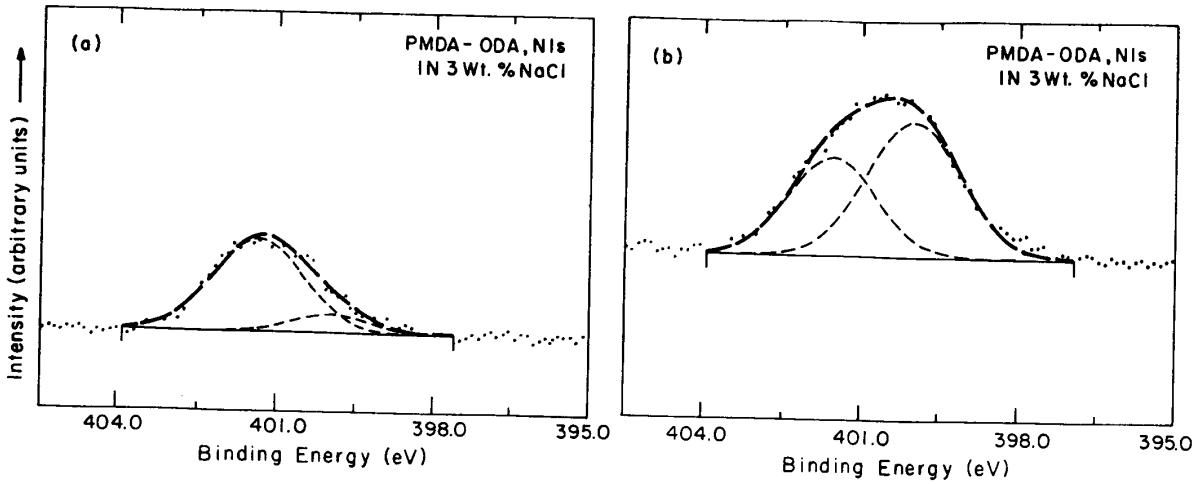

Figure 11: N 1s spectra for PMDA-ODA after immersion in NaCl for 15 days: (a) top surface of polyimide, (b) back surface of polyimide after removal from aluminium substrate.