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Adhesion of copper to UV photo-oxidized Kapton and Upilex-S polyimide surfaces

Ugur Sener

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ADHESION OF COPPER TO UV PHOTO-OXIDIZED KAPTON AND UPILEX-S POLYIMIDE SURFACES

Ugur Sener
Thesis

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY
ROCHESTER INSTITUTE OF TECHNOLOGY
ROCHESTER, NY

October, 2004
ADHESION OF COPPER TO UV PHOTO-OXIDIZED KAPTON AND UPILEX-S POLYIMIDE SURFACES

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ABSTRACT

Polyimides (PIs), like Kapton® and Upilex-S®, are often used as electrical insulation between levels of circuitry in the manufacture of electronic components. Excellent adhesion between the Cu conductor and the dielectric material is essential in the construction of these microsystem devices.

Polyimide, Kapton® HN500 (PMDA-ODA), and Upilex-S® (BPDA-PDA) were exposed to 185/254 nm radiation in the presence of oxygen at atmospheric pressure. Surface modification of the PI surface was investigated by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Time of Flight Secondary Ion Mass Spectroscopy (TOFSIMS). Copper was sputter-coated onto the modified PI surface. To monitor adhesion, tape tests were applied to the Cu/PI substrate.

SEM micrographs revealed some changes with Upilex-S while did not show any significant differences in surface morphology following photo-oxidation for Kapton HN. With long treatment times, XPS results showed cohesive failure occurring within the modified PI and not at the PI-Cu interface. Coupling the more microscopic view of the surface by TOFSIMS with the results of XPS, that samples a depth of ca. 2-10 nm, suggest adhesion failure occurs at a thickness ≤10 nm. There was good practical adhesion between Cu and the modified PI surface. Adhesion test results showed that cohesive failure occurred quicker within Upilex-S than Kapton HN samples.
1. INTRODUCTION

Polyimides (Pis) have attractive thermal, mechanical and electrical properties and, therefore, are widely used in high-performance military aircraft and spacecraft applications [1] and in microelectronic devices [2]. In the latter application, PIs are commonly employed as a protective overcoat for integrated circuit chips because they possess high thermal stability, have excellent planarizing characteristics, are good barriers to alpha particles, and are low in alpha particle emission. In addition to these attributes, the moderate dielectric constant, low permittivity, and flexibility of PI films makes them attractive as dielectric materials in the fabrication of thin-film electronic packages, for example, those employing flexible circuitry [2] where adhesion of metal circuit traces to the PI is critical [3].

Adhesion between two surfaces results from a combination of mechanical, chemical and electrostatic contributions. In conjunction with these contributions, diffusion characteristics at the mating surfaces of the materials must also be considered. Surface micro-roughness can induce mechanical interlocking as well as produce a greater surface area for chemical interactions between the components of the interface. Chemical interactions include acid-base [4] and dipolar effects. Interfacial characteristics are determined primarily by the strength of chemical bonding between the two surfaces in contact. Numerous investigators have reported that adhesion of Cu coming from the vapor phase to pristine PI is typically quite weak whereas adhesion of Cr is stronger [5, 6]. As such, Cr is often used as a seed layer (or tie layer) for enhancing adhesion of Cu to PI. Ho and co-workers [7-9] found that for polyimide, the chemical bond strength for Cu, Al and Cr increased in the order Cu<Al<Cr. They concluded that Cu atoms diffused into polyimide to form clusters, Al intermixed with polyimide without cluster formation, and Cr formed metal-organo compounds almost immediately upon deposition, leading to a uniform
interface with little intermixing. Murdey and Stuckless [10] made calorimetry measurements of heats of reaction for Cu and Cr on untreated PI. Adhesion of deposited Cu was poor and the heat of reaction could be accounted for by Cu-Cu bonding without significant contribution from Cu-PI bond formation. Cr caused formation of a reaction layer with irreversible cleavage of PI chemical bonds. Wolany et al. [11] conducted in situ time of flight secondary ion mass spectrometry (TOFSIMS) and x-ray photoelectron spectroscopy (XPS) analyses of Cu on untreated PI and observed binding of Cu to carbonyl groups to form Cu-O-C bonds.

Adhesion of metal films to PIs has been addressed extensively by Matienzo and Unertl [3]. A number of techniques can be employed for surface modification of PIs to improve their adhesion to subsequently vapor-deposited, electrochemically deposited, or laminated metal foils. From the earliest studies dealing with plasma treatment of polymers, even brief plasma treatments were observed to alter the nature of polymer surfaces such as PIs. The effect of O2, He, and CF4 plasmas on the wetting of a variety of polymers is given in ref. [12]. By far, the most common gas used in plasmas for treating PIs for improvement of adhesion to metals is O2. Among the means to evaluate the effect of surface modification techniques on polymers are XPS and measurement of the degree of liquid wetting of the polymer surface. The latter is frequently gauged by contact angle measurement, most commonly using water. Katnani et al. [13] showed a correlation among the intensity of the C 1s XPS peak attributed to C=O groups, the water contact angle, and the peel strength of chromium films deposited onto spin-coated and thermally-cured PMDA-ODA (Kapton-HN) polyimide which was treated for various durations using an oxygen plasma. Similar correlation between practical adhesion and wettability has been shown in many other cases [14, 15]. However, the practical adhesion, or bondability, between polymer surfaces and other materials deposited onto them cannot always be correlated with wettability. The presence of a
highly wettable weak boundary layer (WBL) will lead to a low value of practical adhesion. Such weak boundary layers can result from lack of cross-linking at the surface [16]. Reports in the literature related to the effect of UV irradiation on PIs in oxidizing atmospheres are sparse [17]. However, there have been reports indicating that ion bombardment and its absence can produce different response to incoming vapor metal atoms, i.e., polymer cross-linking proportional to ion densities and WBL for treatment in the absence of ions. Egitto et al. [16] measured practical adhesion of sputtered chromium films to Kapton-H (Kapton is a registered trademark of E.I. du Pont de Nemours & Co., Wilmington, DE) PI and Upilex-S (Upilex is a registered trademark of UBE Industries, LTD., Tokyo, Japan) PI treated downstream from an oxygen microwave (MW) plasma (devoid of ion bombardment) and in a oxygen DC-glow discharge (in the presence of ion bombardment) using 90° peel tests. Kapton film is a polyimide formulation produced by curing a poly(amic acid) whose precursors are pyromellitic dianhydride (PMDA) and oxydianiline (ODA) (Fig. 1a). Precursors for Upilex-S PI are biphenyl tetracarboxylic dianhydride (BPDA) and phenylene diamine (PDA) (Fig.1b). Downstream-plasma treatment reduced practical adhesion levels for Kapton-H and Upilex-S while treatment in the DC glow produced adhesion about triple the value measured for untreated films. These adhesion results were attributed to the difference in degree of ion bombardment in the various plasma conditions and the concomitant difference in the relative amount of chain scission and cross-linking reactions.

Hence, the characteristics of PI surfaces well prepared for adhesion to other materials include an abundance of favorable (in terms of acid-base type interactions with the other material) functional groups on the surface, with no treatment-induced degradation of the structural/mechanical integrity (e.g., cohesive strength) of the polyimide surface. Rozovskis et al. [18] conducted
oxygen reactive ion etching of PI and observed a correlation between enhancement of Cu peel strength and content of oxygen-containing groups at PI surface. Their conclusions confirmed the idea of competing rates for strengthening (crosslinking) and weakening (bond scission) effects associated with formation of a WBL.

Although PIs have a propensity toward cross-linking upon UV irradiation [19], it is also known that such polymers will undergo scission, and potentially degradation, when irradiated in an oxygen-containing environment [20, 21]. Photolysis of PIs in the presence of oxygen with the broad-band radiation from medium pressure Hg lamps is dominated by the charge transfer interactions between PMDA and ODA [22]. However, little has been reported with respect to the effect of shorter wavelength UV and VUV irradiation on adhesion of metals to PIs. George et al. [23] studied 184.9 nm photolysis of Kapton-H in the presence and absence of air and reported enhanced adhesion of Au to the treated-PI surface.

This thesis describes a method of exposing the surface of the polymer to UV photons of 253.7 and 184.9 nm wavelengths from low pressure Hg lamps to photo-oxidize the PIs Kapton HN 500 (PMDA-ODA, pyromellitic dianhydride-oxydianiline) (Fig. 1a) and Upilex-S (BPDA-PDA, polybiphenyl dianhydride-p-phenylenediamine) (Fig. 1b) in order to control adhesion with Cu. The effect of treatment on adhesion to deposited copper was measured and the locus of failure was investigated using XPS and TOFSIMS.
a) Kapton-HN Polyimide

b) Upilex-S

Fig. 1 Polyimide Structures a) Kapton-HN and b) Upilex-S
2. EXPERIMENTAL

2.1 Materials

Commercially available 125µ thick PI films (Kapton-HN 500 and Upilex-S) were obtained from American Durafilm, Holliston, MA and ICI, respectively. The samples were cut to dimensions of 1.0 inch x 2.5 inch. The PI sample (Kapton HN 500 and Upilex-S) substrates were cleaned with MEK (Methyl Ethyl Ketone) [24] to remove any grease oil contamination from the surface for 5 minutes in ultrasonic bath and then air-dried at room temperature. This procedure has been demonstrated to effectively clean PI surfaces. The oxygen and nitrogen gases were purchased from Airgas East and were at least 99.99% purity. The copper targets for sputtering were purchased from Ontario Metals, Rochester, NY.

2.2 Light Source, Photochemical cell and reaction mixture

The 25.4 cm i.d. Rayonet photochemical chamber (manufactured by Southern New England Ultraviolet Co., Inc., Branford, CT) was equipped with 16 low-pressure Hg lamps, as shown in Fig. 2, that emit 184.9 and 253.7 nm photons with about a 1:6 intensity ratio. The UV treatment chamber and cell was purged with nitrogen and oxygen gas, respectively, for 10 min before starting the low-pressure mercury lamps.

A cylindrical photochemical cell (2.54 cm diameter, 17.8 cm long) was constructed of Suprasil quartz and a Cajon removable high vacuum stainless steel fitting to allow placement and removal of the sample from the cell (Fig. 3). Most of the PI films were placed in the quartz cell parallel to the lamps so that both sides of the films were treated.
Oxygen Out

UV (Low pressure Mercury Lamp)

Nitrogen In

Fig. 2 Experimental apparatus for UV surface modification of polymers

Oxygen In

Oxygen Out

Oxygen In

Oxygen Out

Sample In/out

Quartz Suprasil Cell

Polyimide Sample

Fig. 3 Quartz Suprasil Cell with Cajon Fittings for Oxygen In/Out and Sample In/Out
High purity nitrogen and oxygen were flowed through the chamber and cell to displace air prior to ignition of the radiation source. Flowmeters (manufactured by TA Instruments Co., Inc., New Castle, DE) were calibrated for nitrogen and oxygen and the data are shown in Table 1, Fig.4 and Table2, respectively. A one liter volumetric flask was filled with water, and placed upside down in a container of water. Nitrogen gas flowed into the volumetric flask and the time to displace the water measured. The nitrogen and oxygen flow rates were kept at ca. 5 l/min and 43 cm³/min, respectively. A flow meter reading of 80 on silver ball corresponded to the flow rates.

Table1: Calibration Data for Flow meter used for Nitrogen Gas

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Black Ball</th>
<th>Silver Ball</th>
<th>Volume (L)</th>
<th>Flow Rate (L/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.575</td>
<td>35</td>
<td>20</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td>0.261</td>
<td>73</td>
<td>40</td>
<td>1</td>
<td>3.8</td>
</tr>
<tr>
<td>0.189</td>
<td>112</td>
<td>60</td>
<td>1</td>
<td>5.3</td>
</tr>
<tr>
<td>0.205</td>
<td>132</td>
<td>70</td>
<td>1</td>
<td>4.8</td>
</tr>
<tr>
<td>0.209</td>
<td>152</td>
<td>80</td>
<td>1</td>
<td>4.8</td>
</tr>
<tr>
<td>0.208</td>
<td>160</td>
<td>100</td>
<td>1</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Fig.4. Calibration graph for flow meter used for nitrogen gas
Table 2: Calibration data (table) for flow meter used for Oxygen gas

<table>
<thead>
<tr>
<th>Actual Flow in (cm$^3$/min)</th>
<th>Scale Reading (mm)</th>
<th>$O_2$</th>
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<tr>
<td></td>
<td>150</td>
<td>131</td>
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<td></td>
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<td>114</td>
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Molecular nitrogen is transparent to the UV radiation while ground state oxygen molecules in the photochemical cell absorb 185 nm photons [25] which have sufficient energy to break the molecular bond to form two ground state $O(^3P)$ atoms as shown in reaction (1) [26].

$$O_2 + hv = O(^3P) + O(^3P) \quad \lambda \leq 242.4\text{nm} \quad (1)$$

Ozone, which is formed in the photochemical cell by reaction (2) involving a stabilizing molecule (M), absorbs photons from the low pressure Hg lamps that are energetic enough to photodissociate ozone to produce reactive electronically-excited oxygen atoms, O($^1D$) and O($^1S$), and oxygen molecules ($O_2(^3\Sigma_u^-), O_2(^1\Delta_g), O_2(^3\Sigma_u^+)$) [27].

$$O(^3P) + O_2 + M = O_3 + M \quad (2)$$

Using this cell design (i.e., optical path length), known photo-absorption spectra for oxygen and ozone, calculations show that a significant fraction of the UV radiation is transmitted through the reaction mixture to interact with the PI surface. The percent of radiation passing through $O_2$ that
reaches the PI surface was calculated using the Beer-Lambert Law, \( \log \frac{I_0}{I} = a \times b \times c \), where \( a \) is photo-absorption coefficient \( (10^{-1} \text{ cm}^{-1} \text{ atm}^{-1} \text{ at } 184.9 \text{ nm} \text{ [30]}) \), \( b \) is path length in cm, \( c \) is the concentration in atmosphere. For a pressure of 1 atm and pathlength of 4 cm \( (\frac{I}{I_0} = 10^{-0.4} = 0.398) \), ca. 40% of the 184.9 nm radiation reaches the PI surface.

2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy is a widely used method of determining the chemical composition of a surface. X-rays impinge upon a sample and ionize atoms, releasing core-level photoelectrons. The escaping photoelectron's kinetic energy limits the depth from which it can emerge, giving XPS its high surface sensitivity and sampling depth of a few nanometers. Photoelectrons are collected and analyzed by the instrument to produce a spectrum of emission intensity versus electron binding energy. Peak areas at nominal binding energies can be used to quantify elemental composition, and small shifts in these binding energies (chemical shifts) provide powerful information about sample chemical states and short-range chemistry. XPS is suitable for the analysis of conductors and insulators such as polymers.

The samples were analyzed with X-ray Photoelectron Spectroscopy (XPS), surface analysis technique that provides elemental, chemical state and quantitative analyses for the top 2-5 nm of the sample’s surface. A Physical Electronics Model 5800 XPS system was employed for the characterization. A region about 800 microns in diameter was analyzed. The Kapton-HN and Upilex-S samples were prepared by cutting sections from the sample provided and mounting them beneath a molybdenum sample mask for exposing to x-ray beam. The samples were irradiated with monochromatic Al K\( \alpha \) radiation (1486 eV) and charge neutralized with a flood of low energy electrons from a BaO field emission charge neutralizer. The basic analysis was performed with angles of 10\(^\circ\), 45\(^\circ\) and 80\(^\circ\) between the sample and analyzer. The angle between the sample and
analyzer was varied to determine if composition of the surface varied over the approximately topmost 10 nm of the surface. The depth of analysis increases by about a factor of three when the angle is increased from 10° to 80°. The XPS system contained ion milling capability with 3 keV argon ions which could be rastered over an area of 4 X 4 millimeters in order to estimate the depth of polymer adhering to copper after adhesion failure.

2.4 Copper Deposition

A DC planar magnetron (manufactured by US Inc., Campbell, CA) was used to sputter deposit about 300 Å of copper onto the treated PI films. The thicknesses of film and deposition rate were read on a quartz crystal rate deposition monitor. The deposition rate was around 2.5-3.0 Å/s. A 99.99 % pure copper target (50 mm diameter and 5 mm thick) was used. Argon gas (99.997 % pure) was introduced to sputtering chamber through flow meters. The discharge voltage, current and power for the sputtering system with argon was kept in the range of 540-570V, 0.3-0.4A, and 190-220 W, respectively. The operating pressure in the chamber was around 3.3x10⁻³ Pa. When the pressure reached the desired pressure, the shutter was moved to the side and the PI samples were sputtered with copper. The sputtering chamber is shown in Fig. 5.

2.5 Scotch tape test (Measurement of Adhesion)

3M Scotch Brand Tape (3650) was used to estimate the amount of copper remaining on modified PI films. “% Adhesion” was determined visually after the tape test. The copper-on-polyimide substrate was taped onto the ceramic plate by Duct tape to keep the flexible substrate as flat as possible and Scotch tape was used to mask over PI film. The tape was slowly peeled from the copper deposited PI film at the angle of about 160-170° as shown in Fig 6.
**Fig. 5 Sputtering Chamber**

- Argon Gas
- DC Planar magnetron
- Copper target
- PI film
- Substrate Holder
- Shutter

**Fig. 6 Peel Test for adhesion measurement**

- PI
- Scotch tape (3650)
- Ceramic Plate
2.6 Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS)

TOF-SIMS is a useful technique for the characterization of organic materials, which is based on the ion bombardment induced by secondary ions from the investigated surfaces and subsequent mass spectroscopy. In general, TOF-SIMS spectra give directly chemical information including molecular structure of the materials [29].

A pulse of ions bombards the specimen and sputters it. This produces a cloud of atoms and molecules some of which are ionized. The ionized particles of one polarity, atomic and molecular secondary ions, are accelerated into a reflectron type spectrometer. They travel two meters through a tube to arrive at ion detection and counting system. However, because they all depart from the sample at the same time and were subject to the same accelerating voltage, the lighter ones arrive at the detection system before the heavier ones. The "Time-of-Flight" of an ion is proportional to the square root of its mass, so that all the different masses are separated during the flight and can be detected individually.

The next pulse of primary ions cannot start until the secondary ions of the first pulse have cleared the analyzer. Otherwise the slower heavy ions of the first pulse are overtaken by the faster light ions of the second pulse. However, the time interval between consecutive pulses can be used for other activities, such as sputtering and charge neutralization.

Xerox’s Physical Electronics Model CE Trift TOFSIMS is equipped with a gallium liquid metal gun capable of operating with a spatial resolution of less than 0.2 μm at 25 kV potential. For the short duration ion pulse that was used, the mass resolution of the spectrometer exceeds 9000 mass/delta mass as described in ref. [30]. The spectrometer has charge neutralization capability for
the analysis of polymers and may be operated in a high mass resolution mode for chemical analysis and lower resolution high transmission mode for chemical mapping of the surface. The TOFSIMS analysis receives secondary ions from an area of 20 μm x 20 μm and was performed to help determine the locus of adhesion failure and spatial distribution of copper.

2.7 SEM

Hitachi S-4500 field emission SEM at an accelerating voltage of 5 kV was used to study the surface morphology of modified samples. A 1 cm² section was cut from the substrate and mounted on a sample stub with a adhesive tab, and coated with a thin film of gold to eliminate electrostatic charging. SEM was used to study the surface morphology of the control and treated samples. Electron micrographs were acquired at magnification of 100kX and sizing bar 300 nm.

3. RESULTS

3.1 Adhesion Results

The percentage of Cu remaining on the substrate surface after the peel test which is a measure of the % Adhesion was measured. For Kapton-HN sputtered copper came off by tape test after 40 min treatment time or longer Fig 7. For Upilex-S (BPDA-PDA), with treatment time of 20 min and longer, all the copper was removed by the tape test Fig 8. Since different configurations of the sample in the cell were used for the data in Fig. 8 compared to Fig. 7, Fig. 8 also shows a comparison curve for Kapton-HN. The results showed that UV treatment reduced adhesion strength to the substrate with increasing treatment time for Upilex-S as well as Kapton-HN.
Fig. 7 Percent Adhesion on Modified PI (Kapton-HN) Following Tape Test

Fig. 8 Percentage of Copper Remaining on Modified PI (Kapton-HN) and PI (Upilex S) Surface Following Tape Test Using a Different Sample Configuration than in Fig. 7
3.2 XPS Results for Adhesion Test Specimens

3.2.1 XPS Results for Adhesion Failure for Treated Kapton-HN Samples

XPS analysis was done on the tape side after tape test and small amount (0.2%) copper was found on Kapton HN. This indicates that cohesive occurred in the bulk of the sample. Cu was not observed on the substrate side after the tape test (Table 3) where At% means atomic percent.

Table 3 Quantitative Surface Analyses Results for Kapton for Adhesion Failure

<table>
<thead>
<tr>
<th>Sample</th>
<th>At% C</th>
<th>At% O</th>
<th>At% N</th>
<th>At% Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min O₂ Cu tape side</td>
<td>74.4</td>
<td>20</td>
<td>5.8</td>
<td>0.8</td>
</tr>
<tr>
<td>10 min O₂ Kapton side</td>
<td>75.5</td>
<td>18.3</td>
<td>6.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>20 min O₂ Cu tape side</td>
<td>73.7</td>
<td>18.7</td>
<td>7.3</td>
<td>0.2</td>
</tr>
<tr>
<td>20 min O₂ Kapton side</td>
<td>76.4</td>
<td>16.8</td>
<td>6.9</td>
<td>0</td>
</tr>
<tr>
<td>40 min O₂ Cu tape side</td>
<td>74</td>
<td>19</td>
<td>6.8</td>
<td>0.2</td>
</tr>
<tr>
<td>40 min O₂ Kapton side</td>
<td>74.4</td>
<td>18.8</td>
<td>6.8</td>
<td>0</td>
</tr>
<tr>
<td>Calculated composition</td>
<td>76.7</td>
<td>16.3</td>
<td>7.1</td>
<td>0</td>
</tr>
</tbody>
</table>

To determine if treatment resulted in a well-adhered modified surface, the modified surface was wiped with a cotton swab wetted with hexane and reanalyzed by XPS. Hexane is typically used in surface analysis to remove any silicone oil or grease due to contamination from processing samples in a low vacuum system. Table 4 shows that after the hexane wash the oxygen and nitrogen concentrations decrease and the carbon concentration increases such that the surface begins to resemble the unmodified Kapton surface suggesting that some of the modified material did not adhere or was weakly bonded.
Table 4 Results of Quantitative XPS Analyses for Hexane Washed Treated Kapton Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C, At%</th>
<th>O, At%</th>
<th>N, At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEK washed Kapton</td>
<td>79.2</td>
<td>16</td>
<td>4.8</td>
</tr>
<tr>
<td>40 min oxygen, UV</td>
<td>65.6</td>
<td>26</td>
<td>8.4</td>
</tr>
<tr>
<td>40 min oxygen, UV, Hexane Washed</td>
<td>71.5</td>
<td>21.5</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Angle resolved XPS measurements showed the surface composition of the treated surfaces was invariant over the sampling depth of the technique (5-10nm).

Figure 9 and Figure 10 show the C1s spectra acquired for the Kapton-HN adhesion test species.
Figure 9 C 1s Spectrum for Kapton Surface Post Adhesion Test. Sample from 40 Minute Exposure Test
Figure 10 C1s Spectrum for Copper Side of Kapton-HN Adhesion Test Specimen. 40 Minute Oxygen Exposure Test Specimen
From the spectroscopic data it can be concluded that rupture occurs within the Kapton. There is good practical adhesion between the copper and the treated Kapton surface however damage to the near surface bonding in the Kapton is so extensive that the integrity of the Kapton has been compromised.

3.2.2 XPS Results for Adhesion Failure for Treated Upilex-S Samples

After adhesion testing the treated Upilex-S surfaces contained carbon, oxygen and nitrogen. Copper was not detected on the surface at the limits of detection of the technique, approximately 0.1 atomic percent. The copper sides of the adhesion test pull couples contained carbon, oxygen, nitrogen and copper.

Figures 11 and 12 illustrate the overlapped C 1s spectra for the Upilex-S and tape side of the adhesion test pair for the 15 minute and 20 minute exposure, respectively. Figures 13 and 14 show the C 1s spectra for bulk Upilex-S and the surface of the adhesive test respectively. The C 1s spectra for the tape and Upilex-S are very similar as expected since both materials contain carbonyl groups (288eV). The broad band at about 291 eV in the spectrum is the characteristic of the $\Pi \rightarrow \Pi^*$ transitions in the aromatic ring. The strength of the $\Pi \rightarrow \Pi^*$ transition does not change significantly. This implies most of the aromatic character of the Upilex is maintained post treatment.
Figure 11 Overlapped C 1s Spectra for the Upilex-S side and Tape side for 15 Minutes Treatment
Figure 12 Overlapped C 1s Spectra for the Upilex-S side and Tape side 20 Minutes Treatment
Figure 13 C 1s Spectrum Obtained from Bulk Upilex-S
Figure 14 C 1s Spectrum Obtained from the Adhesive Side of the Tape from the Adhesion Test
Figure 15 shows the overlapped O 1s spectra for the four Upilex-S samples reported in Table 5. Figure 16 contains the overlapped O 1s spectra for the tape and bulk untreated Upilex-S. The oxygen spectra are clearly different. The tape has an oxygen spectrum characteristic of an acrylate. The O 1s spectra obtained from the treated samples show no significant evidence for the presence of exposed tape.

Figure 16 Overlapped O 1s Spectra Obtained from the 15 Minute and 20 Minute Treated Upilex and Copper Films Post Adhesion Test
Figure 16 Overlapped O 1s Spectra for the Adhesive Tape and Bulk Upilex-S
Quantitative surface analyses were performed and the results are summarized in Table 5. The tape surface exhibited several atomic percent of copper. The calculated composition for Upilex-S is included in the table for comparison. The results for bulk Upilex-S and the adhesive side of the tape used for the adhesion tests are included in the table. The results show the treated surface contains more oxygen and less carbon than the bulk Upilex-S. The 20 minute treatment yielded a slightly higher oxygen concentration than the 15 minute treatment. The nitrogen concentration did not change significantly with treatment.

Table 5 Results of the Quantitative XPS Analyses for the Upilex-S Adhesion Test Specimens

<table>
<thead>
<tr>
<th>Sample</th>
<th>At% C</th>
<th>At% O</th>
<th>At% N</th>
<th>At% Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min O₂ Cu tape side</td>
<td>71.6</td>
<td>20.9</td>
<td>4.9</td>
<td>2.7</td>
</tr>
<tr>
<td>15 min O₂ Cu tape side post ion etch</td>
<td>75.4</td>
<td>8.9</td>
<td>5.9</td>
<td>9.9</td>
</tr>
<tr>
<td>15 min O₂ Upilex-S side</td>
<td>76.2</td>
<td>17.4</td>
<td>6.4</td>
<td>0.0</td>
</tr>
<tr>
<td>20 min O₂ Cu tape side</td>
<td>69.4</td>
<td>21.3</td>
<td>4.6</td>
<td>4.7</td>
</tr>
<tr>
<td>20 min O₂ Cu tape side post ion etch</td>
<td>72.3</td>
<td>9.6</td>
<td>6.1</td>
<td>12.1</td>
</tr>
<tr>
<td>20 min O₂ Upilex-S side</td>
<td>74.4</td>
<td>18.9</td>
<td>6.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Tape surface</td>
<td>84.1</td>
<td>15.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Clean bulk Upilex-S</td>
<td>78.0</td>
<td>15.3</td>
<td>6.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Calculated composition Upilex S</td>
<td>78.6</td>
<td>14.2</td>
<td>7.1</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The data from the XPS characterization indicates cohesive failure within the Upilex-S takes place during the adhesion test.
Post argon ion etch experiment (Table 5) show that the amount of copper detected increased significantly due to the removal of Upilex-S from the surface of the copper. The oxygen concentration decreased significantly with ion etching due to the removal of copper oxide and hydroxide and ion induced damage to the polyimide. Figure 17 shows the C 1s spectrum for the tape side of the Upilex-S peel test that was treated for 15 minutes and argon ion etched. The spectrum appears to be due to Upilex residue that is highly oxygen deficient and rich in carbon-carbon bonding. Analysis of the O 1s spectrum obtained post ion etch indicates about half of the oxygen detected post ion etch is due to copper oxide and hydroxide. Only about 4-5 atomic percent of the oxygen is due to residual Upilex-S. That is only about 25% of the oxygen concentration expected for bulk Upilex-S. Ion etching obviously carbonized the Upilex-S on the copper surface.
Figure 17 C 1s Spectrum for Upilex-S 15 Minute Exposure Post Argon Ion Etch
3.3 XPS Results

3.3.1 XPS Results for Surface Modification of Kapton

The C1s, O1s, N1s and valence bands of the Kapton were characterized at maximum energy resolution to determine if changes in the surface chemistry could be detected after UV-oxygen treatment. Figure 18 shows the C 1s spectra acquired for the untreated and treated Kapton films. Three observations can be made regarding the spectra. First, there is little change in the shape of the bands between 282 and 286 eV except for a decrease in the contribution due to the ring C-C binding. Second, treatment causes a significant increase in the strength of the band at ca. 288 eV and third the band at about 291 eV in the untreated Kapton is weaker after treatment.

The broad band at about 291 eV in the spectrum for untreated PI is characteristic of $\Pi \rightarrow \Pi^*$ transition originating in the aromatic ring. The decrease in the strength of this peak relative to untreated Kapton PI indicates the decrease in the aromatic character of the surface as a result of the exposure to the ultra-violet photo-oxidation. The increase in the strength of the peak at ca 288 eV is caused by an increase in the number of C=O moieties on the surface. The subtle changes in the structure of the peak at lowest binding energy indicate little change in the carbon-carbon, carbon-nitrogen and C-O-C moieties although, there is a noticeable change in the baseline at ca. 287 eV.

The O1s Figure 19 and N1s Figure 20 spectra for Kapton samples show a subtle increase in the intensity of the high binding energy shoulder of the O1s peak. The low binding energy oxygen peak at about 532 eV is due to the C=O moiety and the size of the shoulder at 533 eV is due to a C-O-C moiety. The N1s peaks are identical for treated and untreated Kapton.
Figure 18 Overlapped C 1s spectra for Untreated Kapton (Red) and Kapton Treated for 5 (Magenta), 10 (Green), 20 (Dark Blue) and 40 Minutes (Light Blue)
Figure 19: Overlapped O 1s Spectra for Untreated Kapton (light blue), Kapton Exposed to Excited Oxygen for 20 min (red) and Kapton Exposed to Excited Oxygen for 40 min. (Dark blue)
Figure 20 Overlapped N1s Spectra for Untreated Kapton (red), 20 min UV-Oxygen Treatment (light blue) and 40 min UV-Oxygen Treatment (dark blue)
Angle resolved XPS measurements showed the surface composition of the treated surfaces were invariant over the sampling depth of the technique (5-10nm). Quantitative analyses were obtained for the three samples at three angles, 10, 45, and 80 degrees (Table 6). The angle between the sample and analyzer was varied to determine if the composition of the surface varied over the approximately topmost 10 nm of the surface. The purpose of the quantitative analyses was to determine if the UV excited oxygen treatment resulted in an increase in the amount of oxygen at the surface of the Kapton.

Curve fitting can be employed to estimate the increase in the C=O functionality on the treated surfaces. Although exact curve fitting of the numerous spectrally unresolved peaks responsible for the binding energy portion of the C1s spectra cannot be performed with a significant degree of confidence, it is possible to determine the increase in the C=O peak area since it is a spectrally well resolved feature. In the untreated Kapton PI, the peak due to C=O accounts for 14% of the area of the fitted carbon peaks. In the treated Kapton films, the C=O peak contributes about 29% of the area of the fitted carbon peaks. The number of C=O groups has almost doubled. This is consistent with the decrease in carbon and increase in oxygen determined by the quantitative analysis (Table 6).
Table 6 Results of the Quantitative XPS Analyses for the Kapton Films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Angle</th>
<th>At% C</th>
<th>At% O</th>
<th>At% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>10</td>
<td>76.5</td>
<td>16.9</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>76</td>
<td>17.4</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>74.8</td>
<td>18.3</td>
<td>6.9</td>
</tr>
<tr>
<td>40 min oxygen no UV</td>
<td>45</td>
<td>74.8</td>
<td>18.9</td>
<td>6.3</td>
</tr>
<tr>
<td>0.5 min oxygen, UV</td>
<td>45</td>
<td>74.7</td>
<td>19.1</td>
<td>6.2</td>
</tr>
<tr>
<td>1 min oxygen, UV</td>
<td>45</td>
<td>72.2</td>
<td>21.6</td>
<td>6.3</td>
</tr>
<tr>
<td>5 min oxygen, UV</td>
<td>45</td>
<td>66.6</td>
<td>26.2</td>
<td>7.2</td>
</tr>
<tr>
<td>10 min oxygen, UV</td>
<td>45</td>
<td>65.6</td>
<td>26.6</td>
<td>7.7</td>
</tr>
<tr>
<td>20 min oxygen plasma</td>
<td>10</td>
<td>67</td>
<td>25.6</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>67</td>
<td>25.2</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>66.6</td>
<td>25.5</td>
<td>7.9</td>
</tr>
<tr>
<td>40 min oxygen plasma</td>
<td>10</td>
<td>65.6</td>
<td>26.1</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>65.6</td>
<td>26</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>65.56</td>
<td>26.1</td>
<td>8.3</td>
</tr>
<tr>
<td>Calculated composition</td>
<td></td>
<td>76.7</td>
<td>16.3</td>
<td>7.1</td>
</tr>
</tbody>
</table>

UV-oxygen treatment increased the amount of oxygen at the surface. The composition of the treated Kapton did not vary with angle of the analysis indicating the treatment modified the surface to a depth up to or exceeding the sampling depth of X-ray Photoelectron Spectroscopy (5-10nm).

3.3.2 XPS Results for Surface Modification of Upilex-S

X-ray Photoelectron Spectroscopy was employed to determine if exposure to UV radiation in the presence of oxygen has any effect upon the surface composition of Upilex-S.

Figure 21 shows the C 1s spectra for the samples. The C 1s spectrum for the washed, but untreated film shows a stronger peak at about 285 eV and a weaker peak at about 288 eV relative to the treated samples. The peak at 285 eV is due to carbon-carbon bonding and the peak at 288 eV is due to the carbon in the ring bonded to nitrogen and oxygen, that is the N-C=O moiety. The treated films yielded identical C 1s spectra.
Figure 21 Overlapped and Normalized C 1s Spectra for the Control and Treated Upilex S Films

The O 1s spectra are shown in Figure 22. The peak at about 532 eV is due to the C=O moiety in Upilex S. The peak at about 533 eV is due to a C-O-C moiety. The size of the shoulder at 533 eV does not correlate with the length of treatment, that is, it does not increase in size with increasing length of treatment.
Figure 22: Overlapped and Normalized O 1s Spectra for the Control and Treated Upilex Films

The N 1s spectra are shown in Figure 23. The peak is due to the (C=O)$_2$-N-R in Upilex S. The nitrogen spectra do not change with the length of the time of treatment.
Figure 23: Overlapped and Normalized N 1s Spectra for the Control and Treated Upilex Films
Quantitative analyses were obtained for the samples listed in Table 7. The purpose of the quantitative analyses was to determine if the ultra-violet excited oxygen treatment resulted in an increase in the amount of oxygen at the surface of the Upilex-S. XPS established that exposing Upilex-S to oxygen excited by ultra-violet radiation has ~ 50% change effect upon the surface composition of the material. The data shows that the significant changes occurred within 5 min of photooxidation. There was a slight increase in the nitrogen concentration on the surface of treated Upilex-S as carbon concentration decreases.

Table 7 Results of the Quantitative XPS Analyses for the Upilex-S Films Treated for Various Times of Photo-oxidation

<table>
<thead>
<tr>
<th>Sample</th>
<th>At% C</th>
<th>At% O</th>
<th>At% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>79.2</td>
<td>14.5</td>
<td>6.4</td>
</tr>
<tr>
<td>5 min</td>
<td>72.9</td>
<td>20.2</td>
<td>6.9</td>
</tr>
<tr>
<td>10 min</td>
<td>73.7</td>
<td>19.6</td>
<td>6.7</td>
</tr>
<tr>
<td>15 min</td>
<td>73.3</td>
<td>19.5</td>
<td>7.2</td>
</tr>
<tr>
<td>20 min</td>
<td>73.3</td>
<td>19.3</td>
<td>7.4</td>
</tr>
<tr>
<td>30 min</td>
<td>73.0</td>
<td>19.4</td>
<td>7.6</td>
</tr>
<tr>
<td>40 min</td>
<td>73.0</td>
<td>19.3</td>
<td>7.8</td>
</tr>
<tr>
<td>Avg without untreated</td>
<td>73.16</td>
<td>19.5</td>
<td>7.27</td>
</tr>
<tr>
<td>Std dev without untreated</td>
<td>0.47</td>
<td>0.44</td>
<td>0.51</td>
</tr>
</tbody>
</table>

3.4 Time of Flight Secondary Ion Mass Spectroscopy (TOFSIMS)

Since the depth of analysis for TOFSIMS is confined to only the top one or two atomic layers of a surface, the depth profile of the material on the Cu side of the tape after adhesion failure was investigated. TOFSIMS and XPS, that samples a depth of ca. 2-10nm, suggest adhesion failure due
to a WBL (weak boundary layer) occurs at depth in the Kapton and Upilex-S PI of ≤10nm. The initial top surface mass spectra obtained from sample treated for 30 and 45 min showed a very high signal from copper, indicating a very thin and/or discontinuous coating. Depth profiling would then be useless and was not pursued. (Figure 24)

Figure 24 The TOFSIMS Surface Mass Spectra Copper Ion Images (180u x 180u) for Kapton HN treated for 30 and 45 minutes of photo-oxidation

Figure 25 shows elemental copper depth profiles (counts of copper vs. gallium ion treatment time) obtained from the 15 minute (upper curve) and the 20 minute (lower curve) treatments of Upilex-S. Copper signal dominates the TOFSIMS spectra of each sample as -received, which means that very little material covers the deposited copper.
3.5 SEM

Figure 26 and 27 are the SEM micrographs (magnification 100K) for untreated and treated Kapton PI. The length of the sizing bar on the image is 300 nm. SEM didn’t reveal any significant differences in surface morphology following photo-oxidation.
The control, 10 min. and 20 min. treated Upilex-S samples (Fig. 28, 29, 30) were similarly featureless, except at very high magnification (50kX and 100kX), where they both displayed a fine granular texture. The control exhibited some fine, small cracking at 100kX that was not observed in the 10 minute treated sample. In contrast, 20 min treated sample had a more highly structured and cracked surface.
Fig. 28 SEM micrograph for untreated Upilex S PI sample

Fig. 29 SEM micrograph for 10 min Upilex S PI sample
Fig. 30 SEM micrograph for 20 min Upilex S PI sample
4. DISCUSSION

PMDA-ODA and BPDA-PDA have intense photo-absorption (Figs. 33, 34) which initiates surface modification via the chain scission reaction (3).

\[
\text{Polymer} + h\nu = R\cdot + R'\cdot \quad (3)
\]

Photo-absorption above ca. 300 nm eventually results in cleavage of the weak N-C bond either at the N-CO bond within the imide ring or at the N-Ar bond to give a triplet biradical or a triplet radical pair, respectively [22]. Interaction between the triplet biradical and oxygen is a key step in the photodegradation at these wavelengths. The more energetic photons at 253.7 and 184.9 nm correspond to 112 and 155 kcal/mol, respectively, which are sufficient to break most chemical bonds and open sites for reaction with oxygen. Reaction (3) is used to represent all of these possible bond breaking steps.

The photo-absorption coefficients at 253.7 and 184.9 nm for Kapton-HN are about $2 \times 10^5$ and $4 \times 10^5$ cm$^{-1}$, respectively [31], that correspond to penetration depths (the depth at which the incident intensity has decreased to $1/e$ of the initial value) of ca. 50 and 25 nm, respectively.

A number of investigators have previously studied the photo-oxidation of PMDA-ODA using low pressure Hg lamps [23, 32-36] and explained their results on the basis of photochemical bond scission, reaction (3), followed by a free-radical chain mechanism for $R\cdot$, reactions (4)–(6) [23, 36]. Similar reactions can be written for $R'\cdot$ and $R''\cdot$ which can be formed on the aromatic rings or on single bonds along the polymer chain.

\[
R\cdot + O_2 = ROO\cdot \quad (4)
\]

\[
ROO\cdot + \text{Polymer} = ROOH + R''\cdot \quad (5)
\]

\[
ROOH + h\nu = RO\cdot + \cdot OH \quad (6)
\]
Oxygen reacting with the treated PI surface produces oxygenated free radicals with long lifetimes as observed by ESR [23, 34, 35] which enhance photo-etching [32, 36] compared to photolysis of PI in the absence of oxygen where there is significant cross-linking at the surface due to combination reactions involving the free radicals \( R \cdot \) and \( R' \cdot \) [32, 33, 36, 38]. In the presence of air, photo-oxidative etching of PI with 253.7 and 184.9 nm photons has been reported to have an ablation rate of 0.7 nm/min [32].

Additional steps in the mechanism most likely include reactions of oxygen atoms and ozone formed from photo-dissociation of oxygen. Ground state oxygen molecules, \( O_2(\Sigma_g^+) \), absorb 185 nm photons [25] (Fig. 31) which have sufficient energy to break the molecular bond to form two ground state \( O(^3P) \) atoms as shown in reaction (1) [26].

\[ O(3\Sigma_g) = O(\Sigma_g^+) + O(\Sigma_g) \]

\( O(^3P) \) causes little etching of PI [39, 40] but does react with free radicals on the PI surface and at depths more than 5 nm to promote ablative degradation with the formation of carbonyl-containing compounds, CO and CO\(_2\) [41, 42].

Ozone, formed by reaction (2), directly reacts with PI [43] and a number of polymer surfaces including polysiloxanes [44], poly(methyl methacrylate), polycarbonate, poly(tetrafluoroethylene) [45], polypropylene [46, 47] and poly(ethylene terephthalate) [46, 47], or with free radicals as illustrated in reaction steps (7) and (8) to produce alkoxyl radicals (RO•).

\[ R \cdot + O_3 = RO \cdot + O_2 \]  
\[ ROO \cdot + O_3 = RO \cdot + 2 O_2 \]

Both oxygen atoms [47] and ozone [28] are known to oxidize by adding across unsaturated carbon bonds. Jeong et al. [49] proposed, using an atmospheric-pressure plasma jet of helium and oxygen, that oxygen atoms, not ozone, were the principal reactive species involved in etching PI. However,
ozone has been shown to be effective in enhancing the hydrophilic nature of poly(ethylene teraphthalate) and polypropylene surfaces [50].

In addition, the photo-dissociation products of ozone (Fig. 32) which may include electronically-excited oxygen atoms, O(1D) and O(1S), and molecules (O2(3Σ_u^−), O2(1Δ_g), O2(1Σ_g^+)) [27] may also react with the polymer and free radicals to oxidize the surface.

The XPS results of this study for Kapton-HN are in agreement with the earlier reports using 253.7 nm photons in air [34], 253.7/184.9 nm in air [36] and 184.9 nm in oxygen [37] that found an increase in O 1s concentration on the PI surface via the above mechanism. Momose et al. [34] observed an increase of the O 1s signal to a near doubling of its value at the maximum and then after hours of treatment time found the concentration to decrease. As expected, the time required to achieve the maximum O 1s concentration is different in this study and refs. 34 and 36 since it is dependent on the intensity of the lamps employed in the studies.

The observed formation of carbonyl functional groups with treatment time as detected by XPS may be due to: (1) reaction of oxygen atoms [48] and ozone [28] with unsaturated groups, like aromatic bonds, that lead to chain scission, (2) reaction of oxygen molecules with a hydrogen atom on a carbon atom to which the alkoxy oxygen is attached, reaction (9) [28], (3) reaction of oxygen atoms with free radicals on PI [44, 42] and (4) free radical reactions (10) and (11).

\[
\text{RHO} + \text{O}_2 = \text{RO} + \text{HO}_2
\]  
\[
\text{ROO} + \text{R'}\text{OO} = \text{RO} + \text{R'}\text{O} + \text{O}_2
\]  
\[
\text{ROO} + \text{R'} = \text{RO} + \text{R'}\text{O}
\]

Vacuum UV radiation has been reported to cause similar photo-etching and oxidation of Kapton and Upilex PI surfaces [51, 52].
The intense absorption of UV radiation by PI [31], that occurs within low penetration depths, causes chain scission reactions at the surface and near-surface to produce free radicals which react with oxygenated species to contribute to photo-etching and degradation of the mechanical properties of the substrate [32, 36, 38]. Therefore, a WBL was formed which was washed away with hexane. Other workers have reported that Kapton and Upilex films act as positive photo-resists when exposed to UV radiation in air and the treated surfaces may be effectively washed away with water [23, 36] and methanol [36] solutions. After washing, the concentration of O 1s, as detected by XPS, approaches the value for the unirradiated Kapton [23, 36, 37]. The independence of O 1s XPS signal on the angle between the sample and the analyzer (Table 6, 7) indicates a uniformity of oxidation throughout the 2-10 nm WBL, consistent with an earlier observation when Kapton PI was treated with UV radiation and atomic oxygen that penetrated to a depth of more than 5 nm [41]. A recent report has found that 248 nm UV excimer laser penetrates an ultra-thin (ca. 50 nm) Cu/Cr coating on Upilex PI to cause adhesion failure at the metal-polymer interface and produce laser direct patterning of structures less than 15 μm [53].

Ion etching of the Upilex-S present on the surface of the copper on the tape side of the peel test resulted in removal of some of the Upilex-S and carbonization of the remaining Upilex-S. Post etch the Upilex-S on the copper is oxygen deficient and the C 1s peak exhibits mainly carbon-carbon bonding. Ion etching the Upilex from the back of the copper on the tape appears to remove the carbonyl oxygen atoms, but leaves the nitrogen attached. This causes a low oxygen concentration for the etched Upilex, more C-C or very little C-O bonding and nitrogen that is affected little.

Consistent with the SEM results of this study for Kapton HN (Fig. 24,25), little changes in the physical appearance were observed for PI surfaces after exposure to 184.9 and 253.7 nm radiation.
in air [33] and for chitosan, a biopolymer containing C, O, N, and H, at the AFM scale after treatment with UV/ozone [54]. SEM results for Upilex S, the control exhibited some fine, small cracking at 100kX that was not observed in the 10 minute treated sample. In contrast, 20 min treated sample had a more highly structured and cracked surface (Figs. 26, 27, 28).

Good practical adhesion of Cu to the treated surface occurs at short treatment times, where the mechanical integrity of the PI substrate is maintained (Fig. 7), due to the chemical modification of the surface and the resultant increase in O 1s concentration (Table 7) and not to surface roughening. The change around 287 eV in Fig.16 may add some insight to the observed adhesion. The C 1s binding energies of the carboxylate, C(O)OC(O)C₆H₂C(O)OC(O)/Ag, and carboxylic acid, HSCH₂CH(NH₂)C(O)OH, occur at 287.1 eV [54] and 287.4 eV [55], respectively, and carboxylate groups may be formed from the photo-dissociation of C-N imide bonds in the presence of oxygen to lead to the anhydride [17]. PI films contain water or absorb water very easily, and, hence, may convert carboxylate anhydrides into carboxylic acids. The carboxylate groups have an enhanced adhesion with Cu relative to carbonyl groups [57] and have been proposed to contribute to the increased adhesion strength of Cr to PI modified with ion bombardment [16]. The peaks around 287.0 eV may also have contributions from energy loss peaks due to eight peaks consisting of five carbon peaks between 284.6 and 286.3 eV and C-OH, C-O-C, and C-O-C=O (286.5- 287.0) [11]. For PI substrates treated in a low-pressure MW oxygen plasma, that typically contains O(³P), O₂(¹Δg) and O₂, the peel strengths have been found to be higher than untreated samples because of copper binding to plasma-induced carbon-oxygen and carbon-nitrogen moieties [11]. Consistent with the results of this study, maximum peel strengths of the adhesion of Cu were achieved at short treatment times with the MW oxygen plasma [11].
The adhesion strength between the Cu thin film prepared by sputtering with untreated Kapton HN (PMDA-ODA) and Upilex-S (BPDA-PDA) has been previously measured [58]. Iwamorp et al [58] observed higher adhesion strength of Cu with untreated PMDA-ODA than BPDA-PDA and attributed the result due to the enhanced chain flexibility of the ether moiety in ODA compared to rigidity of the conjugated in PDA [58, 59]. The polymers treated with 400W radiofrequency O2 plasma showed Cu adhesion strength for modified PMDA-ODA five times larger than for BPDA-PDA [58].

Previously, good practical adhesion of Cu to PI was achieved by reduction of palladium acetate layers using dielectric barrier discharge and UV excimer lamps to form palladium which allowed initiation of the electroless deposition of copper [60–62].
Figure 31 Plot of $\log_{10}$ absorption coefficient for $O_2$ as a function of wavelength [25]

Figure 32 Photo-absorption spectra of $O_3$ [27]
Figure 33 Photo-absorption spectra of polyimide (PMDA-ODA) [31]

Figure 34 Photo-absorption spectra of polyimide Upilex S (BPDA-PDA) [63]
5. CONCLUSIONS

Photo-oxidation of Kapton HN PI (PMDA-ODA) and Upilex-S with 253.7/184.9 nm low pressure lamps resulted in an approximate doubling of the atomic oxygen concentration on the modified surface which appeared mostly as the carbonyl functional group. No significant changes in surface morphology were observed for Kapton-HN. For Upilex-S, photo-oxidation resulted in a more highly structured and cracked surface. At show treatment times, good practical adhesion of sputter coated copper was achieved to the chemically modified PI surfaces. Extensive treatment resulted in cohesive failure within the modified substrates (Kapton-HN 500 and Upilex-S). XPS and TOFSIMS analyses of failure surfaces after tape test showed a thin (<10nm) weak boundary layer of PI adhering to Cu side. The weak boundary layer (WBL) could be removed with a hexane wash.

6. FUTURE WORK

Investigate photo-oxidation of Kapton-HN and Upilex-S with low pressure mercury lamps that only emit 253.7 nm radiation. At 253.7 nm, no oxygen atoms or ozone should be participating in the mechanism since oxygen molecules do not photo-absorb at this wavelength.
REFERENCES