Polyimide dielectric breakdown

Polyimide contact angle

Untreated PI

Plasma-treated PI

Enhancement of electrical properties of polyimide films by plasma treatment

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In this study, the effect of oxygen plasma treatment on the electrical and surface properties of polyimide, Kapton HN, film is investigated. The plasma treatment led to an increase in the oxygen presence on the polyimide surface and a marked surface hydrophilicity. The plasma treatment led to an increase in the dielectric breakdown and Weibull modulus as well as a remarkable reduction in the scatter of all electrical measurements. There is a significant reduction in the high field/high temperature leakage current after plasma treatment. These findings have important implications in the development and improvement of dielectric polymer capacitors.

Keywords: Plasma treatment, polymers, electrical properties, dielectric breakdown

1 INTRODUCTION

Many polymers surfaces are chemically inert with low surface energy and low wettability. In addition to presence of contamination, the aforementioned polymer surface properties limit polymers applications as discussed in [1], [2], [3], and [4]. Plasma treatment offers tailorability of the polymer surface by modifying the surface chemical bonds, adding species such as polar and/or functional groups, and forming radicals. Polymer surface properties can be altered by controlling the plasma treatment conditions; namely gas types or mixtures, treatment power, treatment duration and operating pressure. Examples of tailorable surface

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properties are chemical composition [5], [6] and [7], wettability [8], [9] and [10], adhesion [11], [12] and [13], and metal deposition [14] and [15]. Noeske et al. studied the effect of atmospheric-pressure plasma treatment on PET, PA6, PVDF, HDPE and PP and their resulting adhesion properties.[13] The adhesive bondability of the polymers increased after the plasma treatment. The adhesion improvement was associated with the formation of different oxygen-containing functional groups and changes in the topology of the polymers surface. Bhusari et al. studied the effect of plasma treatment on copper buildup process in polyimide films.[14] The polyimide's surface chemical composition was modified by varying the plasma gas, specifically Ar, NH₃ and Ar+NH₃, and varying the plasma power. Overall, the carbon content decreased after different plasma treatment conditions and nitrogen content increased with various levels. The surface chemical composition, such as the nitrogen atomic concentration, was then related to the copper concentration post electroless buildup; the deposited copper thickness increased with the increase of nitrogen concentration. Although research on effect of plasma treatment on polymer surface properties is extensive, there is a much smaller focus on effect of plasma on the electrical properties of polymers such as [16], [17], [18], [19] and [20]. Binder et al. studied the effect of plasma treatment with various gases on dielectric breakdown of a number of polymer films. [16] According to Binder et al., the changes in the dielectric breakdown varied at different levels for the different polymers. Mammone et al. measured an increase in the dielectric breakdown of polypropylene films after plasma-treating the resin prior to melt extruding.[17] Park et al. studied the effect of atmospheric fluorine plasma power and application time on the dielectric permittivity of polyimide films.[19] As the power or application time increased, the dielectric permittivity decreased.

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4 With the limited number of studies on the effects of plasma treatment on polymers
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6 electrical properties and the relationship between the surface and bulk properties, there is a need
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8 to investigate these effects due to the potential impact on dielectric capacitor application. In this
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10 letter, we report the changes in the electrical properties of polyimides after plasma treatment. In
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12 particular, we find that oxygen plasma treatment on Kapton[®] films results in (1) reduction in the
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14 scatter of the measured dielectric properties, (2) increase in the dielectric breakdown, and (3)
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16 reduction in high field/high temperature leakage current. These three findings have important
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18 implications in the development and improvement of dielectric polymer capacitors.
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23 24 **2 MATERIALS AND METHODS**

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26 Polyimide Kapton[®] films, 13-micron thick, were provided by Dupont. The polyimide's
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28 (PI) surface was treated using a M4L RF plasma system (PVA TePla America, Inc.) under
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30 oxygen flow. The power was set to 200W, oxygen flow set to 200 sccm, and the plasma was
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32 applied for 5 minutes under a pressure of 250 mTorr. Two treated samples were tested: single-
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34 sided (SS), where one side of the film was treated, and double-sided (DS), where both sides of
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36 the film were treated.
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42 The untreated and treated surfaces were characterized using contact angle and XPS. The
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44 effects of the plasma treatment on the electrical properties were assessed by dielectric
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46 spectroscopy, I-V and dielectric breakdown measurements.
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51 Contact angle was measured using ramé-hart Model 295 Automated Goniometer using a
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53 water drop. Contact angle was measured on the untreated PI, PI surface right after the plasma
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55 treatment and on a treated sample 30 days after the plasma treatment.
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4 A Kratos Analytical Axis Ultra spectrometer (Chestnut, NY) fitted with a monochromatic
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6 AlK α (1486.6 eV) X-ray source was used to characterize the samples. X-ray Photoelectron
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8 Spectroscopy (XPS) tests were run on untreated PI, plasma treated PI immediately and 30 days
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10 after treatment. Survey scans and high-resolution narrow binding energy range scans of the C 1s,
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12 O 1s, N 1s peaks were conducted at 80 and 20 eV pass energies, respectively. The binding
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14 energies of all elements are corrected with the adventitious alkyl peak assigned binding energy of
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16 285eV.
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22 Prior to dielectric spectroscopy and I-V measurements, 100nm-thick 1cm-diameter silver
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24 electrodes were deposited on the PI samples using a Kurt Lesker Lab18 evaporator. Dielectric
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26 properties were measured on four samples for each film using an Agilent 4284A Precision LCR
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28 meter from 100Hz to 1MHz. I-V measurements were carried out using an HP4140B pA
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30 meter/DC voltage source and a Trek model 677B high voltage amplifier; for each film, three
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32 samples were tested. The leakage current was measured as a function of voltage at 25 and 150°C.
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34 The voltage was swept from 100V to 1.5kV with a step of 100V. The voltage was applied for 20
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36 seconds, after which the steady state current was measured.
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42 For DC dielectric breakdown measurements, unmetallized films were tested with a total
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44 of 24 breakdown events to be used for Weibull statistical analysis for each sample. A Labview
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46 program controlling a DAQ card voltage source connected to a Trek Model 30/20 high-voltage
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48 amplifier system was used. The current limit was set at 3mA. A ball-on-plate setup immersed in
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50 Galden oil was used on the treated and untreated films. The probe is a ¼" diameter 304SS ball
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52 bearing. The voltage was ramped continuously at 500V/s. For breakdown at higher temperatures,
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54 the Galden oil was heated to 150°C and its temperature stabilized for 15 minutes before starting
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56 the measurements. For all tested treated samples, the treated surface was in contact with the
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higher potential when measuring dielectric breakdown. Prior to measuring the dielectric breakdown, the samples were conditioned in a vacuum oven at 125 °C for 10 hours.

3 RESULTS AND DISCUSSIONS

While measurements on the untreated PI resulted in a contact angle of 85°, the contact angle decreased after plasma treatment. Specifically, the contact angle was 25° and 30° for the freshly treated and the 30-day old treated sample, respectively. Figure 1 shows a water droplet taken 10 seconds after it was placed on the PI surfaces, showing that the plasma treatment resulted in an increase in the film's hydrophilicity. Similar hydrophilization effects were reported after plasma treatment of PI under a variety of gases in references [6], [10] and [12]. Similar results were reported on PC, PP and PET film when treated under argon gas.[9]

Figure 1. Droplet images on (a) PI (b) freshly plasma-treated and (c) 30-day old plasma-treated PI

The effect of plasma treatment on the surface chemical composition was studied by XPS measurements. Table 1 summarized averages of atomic concentration of oxygen, nitrogen and carbon from the three measurements, as well as the N/C and O/C ratios for untreated and plasma treated PI surfaces. The XPS data shows that the plasma treatment increased oxygen and nitrogen atomic concentration while decreasing carbon concentration. The O/C and N/C ratios increased by around 60% and 110%, respectively. The O/C and N/C ratio values for untreated and treated PI are comparable to the values reported in reference [6] post O₂-plasma treatment. Figure 2 shows XPS spectra of C1s from untreated (PI) and plasma treated (PPI) films

measurements. The ratio between 286eV (C-OH) and 285eV (C-C or C-H bonds) peaks increased following plasma treatment indicating the creation of hydroxyl groups. The increase in the hydroxyl groups can be related to the increase in the polyimide's hydrophilicity.[7] In addition, in the PPI spectrum, according to the changes that can be seen between 287 and 288eV, there is a possible increase in the carbonyl and carboxylic groups presence as compared to the untreated PI. Inagaki et al. reported the presence of carboxyl groups on Kapton® surface after O₂ plasma treatment. [6]

Table 1. XPS results quantifying the percent atomic concentrations and O/C and N/C ratio percentages

	O	N	C	O/C	N/C
PI	17	5	78	21	7
PPI_F	28	7	65	44	11
PPI_30day	25	7	68	37	10

Figure 2. C1s XPS spectra of untreated polyimide (PI) and plasma treated polyimide (PPI)

The dielectric measurements show no significant changes in the dielectric permittivity after the plasma treatment, Figure 3(a). Untreated PI and single-sided (PPI-SS) samples dielectric loss increases as the frequency increases. The dielectric loss of the double-sided (PPI-DS) treated samples exhibits a maximum between 100kHz and 1MHz, i.e., a relaxation-like behavior that is not present in the untreated PI. However since there is no corresponding drop in the real part of

the dielectric permittivity in the higher frequencies for the post-plasma treated films, the change in the dielectric loss is not considered to be substantial. The significant effect of the plasma treatment is the reduced scatter seen in the films post-treatment. While the standard deviation in the dielectric permittivity measurements was 10% for the untreated PI; post-treatment, the standard deviation was reduced to only 1 to 2% for the PPI-SS and PPI-DS. This consistency in the measurements originates from decontamination of the film surface and enhancement in the adhesion between film and electrodes following plasma treatment.

Figure 3. Dielectric properties of untreated and plasma-treated PI (a) dielectric permittivity (b) Loss tangent

Table 2 summarizes the dielectric breakdown results based on Weibull statistics for untreated and treated PI films. The 90% confidence limits are presented in the number range between parentheses in the dielectric breakdown column. At room temperature, the dielectric breakdown increased by 12% after the plasma treatment. The range of the 90% confidence shifted to higher electric fields as a result of the plasma treatment. The enhancement in the dielectric breakdown can be associated with a change in the chemical structure on the surface and introduction of radicals during plasma treatment, therefore creating a trapping region, which increases the barrier height against charge injection, as observed by other researchers as well

[21], [22]. In reference [22], Mizutani et al. attributed the increase of the dielectric breakdown and reduction in high-field current after plasma treatment of poly-p-xylylene thin films by the enhancement in carrier scattering and suppression of hole injection at the treated surface. The suppression of hole injection is associated with the formation of radicals during plasma treatment.

There is a significant increase in the Weibull modulus, β , after the treatment. The increase in β can be associated with decontamination done by plasma and the changes in the surface chemistry. At 150°C, The dielectric breakdown remained at the same range after the plasma treatment and the Weibull modulus increased from 39 to 54.

Table 2. Dielectric breakdown results for treated and untreated PI films at room temperature and 150°C.
90% confidence limits are included between parentheses

	At room temperature		At 150°C	
	E_b [MV/m]	β	E_b [MV/m]	β
Untreated PI	547 (544-549)	45	468 (462-468)	39
Single-side treated PI	615 (614-615)	71	467 (466-468)	47
Double-side treated PI	609 (606-610)	70	467 (466-468)	54

Leakage current was measured as a function of voltage using the I-V measurement technique as described in the experimental section. Figure 4 shows leakage current as a function of electric field at room temperature and 150°C. At room temperature, Figure 4(a), the average current is in the same range for all samples from low to higher electric fields. However the plasma treatment resulted in lower standard deviations (i.e., less scatter in the data). At 150°C, Figure 4(b), the average leakage current for the untreated PI is an order of magnitude higher than that of DS treated PI at high electric fields.

Furthermore, the standard deviations decreased dramatically post-plasma treatment at high temperature and high electric fields.

Thermal and electrical breakdown mechanisms are generally related to electrical conduction.[23] As the applied electric field approaches the dielectric breakdown value, both local Joule heating and local field enhancement combine to increase the high-field conduction. Comparing leakage current of treated and untreated PI at high temperatures and high electric field, Figure 4(b), there is a reduction in conduction by surface treatment which correlates to the increase in dielectric breakdown post-plasma treatment at room temperature.

Figure 4. Leakage current as a function of electric field for untreated and plasma treated PI at (a) room temperature and (b) 150°C

4 CONCLUSIONS

After a brief oxygen-gas plasma treatment, the properties of polyimide Kapton® films were altered to show: (1) an increase in the hydrophilicity and the oxygen presence on the PI surface that appear to be stable after a month of the treatment; (2) an increase in dielectric breakdown at room temperature and a significant increase in Weibull modulus at room temperature as well as at 150°C; and finally (3) a reduction in the high field/high temperature leakage current after plasma treatment. The changes in the electrical properties can be associated

with the chemical structure changes on the surface, that can either lead to trapping regions or scattering effects. These three findings have important implications in the development of better dielectric polymer capacitors.

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