I. INTRODUCTION

Amorphous hydrogenated carbon (a-C:H) films have been widely investigated in the past two decades due to their excellent properties including high hardness, good wear resistance, low friction, high infrared penetrability, good chemical inertness, and high thermal and low electrical conductivity. These favorable properties bode well for a myriad of mechanical, optical, biomedical, and electrical applications. In particular, the use of a-C:H as a gas barrier coating on a plastic film can mitigate penetration of oxygen and water vapor. For instance, the walls of polyethylene terephthalate (PET) bottles coated with a-C:H films exhibit the ability to inhibit oxygen permeation and a-C:H can potentially be applied to food packaging and preservation of beverages such as wine and beer.

Amorphous hydrogenated carbon films can be deposited by a variety of techniques such as filtered cathodic vacuum arc, ion beam assisted deposition, plasma-enhanced chemical vapor deposition, sputtering, and pulsed laser deposition. Among these techniques, plasma immersion ion implantation and deposition (PIII&D) is more suitable for amorphous film deposition on polymers due to its capability to treat irregularly shaped components and a relatively low processing temperature avoiding thermal degradation of the polymeric materials.

This article discusses the effects of the gas pressure, precursors, and bias voltage on the mechanical properties of the a-C:H films synthesized on PET by PIII&D. The mechanical properties are extremely important in food packaging applications. Moreover, the capability to resist mechanical folding is also investigated in this work.

II. EXPERIMENTAL DETAILS

The deposition process can be divided into three steps: (1) cleaning in an organic solution, (2) plasma cleaning, and (3) film deposition by PIII&D. The size of the PET substrate is 20×100×0.6 mm³. The samples were first ultrasonically cleaned in ethanol before loading into the vacuum chamber. They were placed on a stainless steel plate. A circular rf antenna was utilized to generate the overlying plasma. Prior to film deposition, the samples were bombarded by argon ions for about 5 min to remove surface contamination and

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generate radicals on the substrate surface using a radio frequency (rf) power of 200 W and sample bias voltage of −300 V. During ion bombardment, collisions between the energetic particles and PET molecules induce C–C or C–H bond breakage to create radicals that promote adhesion with the subsequently deposited amorphous carbon films. The a-C:H films were deposited for 30 min using a mixture of C2H2/Ar or C2H2/N2 gases. In our experiments, the gas pressure was varied from 0.5 to 2.0 Pa and pulse bias voltage from −50 to −250 V to examine the effects of these parameters. Nitrogen was also introduced during deposition to study its influence. The nitrogen content was varied by adjusting the N2/C2H2 ratio using a mass flow controller. The important instrumental parameters are shown in Table I.

The surface chemical composition of the treated samples was determined using a PHI-500 x-ray photoelectron spectrometer (XPS). XPS was performed using the Cu Kα line and power of 250 W. Energy calibration was based on the C 1s peak at 286.4 eV. The hardness of the a-C:H films was evaluated using the Nano indenterXP indentation system (MTS Systems Corporation). Indentations were made using a Berkovich diamond tip. The hardness was measured continuously during indentation according to the continuous stiffness measurement technique. The friction measurement was performed using a ball-on-disk tribometer. The carbon films were subjected to loads of 0.1 and 0.3 N and the diameter of the steel ball was 6.35 mm. The friction tests were carried out at a sliding speed of 40 rpm at room temperature and relative humidity of 30%. Mechanical folding tests were performed on the homemade mechanical folding tester, which can curve polymer membranes or sheets coated with thin film at a certain frequency and angle. The PET samples with the same size of 40×5×0.6 mm3 were fixed on the tester with their ends clamped by two holders made of aluminum alloy, respectively. The one holder reciprocates linearly relative to the other which was fixed. The samples were folded with angle from 0° to 180°. After folding the surface morphology of the selected zone 1 mm away from the folding centerline was observed by optical microscopy.

### III. RESULTS

Figure 1 shows the C 1s XPS spectra of sample 8. The atomic ratio of O 1s to C 1s is about 13:84. The positions of C 1s peak of a-C:H films are in the range of 284.5–286.4 eV, while the full width of half maximum (FWHM) of the C 1s peak of a-C:H is about 1.6–1.7 eV, relatively large than the corresponding FWHM for diamond and for graphite. The C 1s peak of an a-C:H film is observed to consist of two subpeaks, one from carbon atoms in the sp3 configuration and the other from sp2, in addition to C bonded to O. Therefore, three peaks at 284.5, 285.2, and 286.4 eV are used here to employ the Lorentzian-Gaussian functions. The peaks include the contributions from sp2 carbon (C=C), sp3 carbon (C–C), and C–O. The fitting procedure may be described as in the subtraction of a Shirley background to each C 1s core level spectrum and in the fit to the spectrum with three components. The three peaks were fitted allowing the FWHM to vary while the binding energies were fixed. Figure 2 displays the XPS spectrum of the C 1s

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**Table I. Instrumental parameters in plasma immersion ion implantation and deposition.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas pressure (Pa)</th>
<th>Gas composition</th>
<th>rf power (W)</th>
<th>Bias voltage (V)</th>
<th>Pulse width (μs)</th>
<th>Pulse repetition rate</th>
<th>Treated time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>C2H2:Ar=8:2</td>
<td>100</td>
<td>0</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>C2H2:Ar=8:2</td>
<td>200</td>
<td>0</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>C2H2:Ar=8:2</td>
<td>300</td>
<td>0</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>C2H2:Ar=8:2</td>
<td>200</td>
<td>−50</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>C2H2:Ar=8:2</td>
<td>200</td>
<td>−150</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>C2H2:Ar=8:2</td>
<td>200</td>
<td>−250</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>C2H2:Ar=8:2</td>
<td>200</td>
<td>−50</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>C2H2:Ar=8:2</td>
<td>200</td>
<td>−50</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>0.5</td>
<td>C2H2:N2=95:5</td>
<td>200</td>
<td>−50</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>C2H2:N2=90:10</td>
<td>200</td>
<td>−50</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>0.5</td>
<td>C2H2:N2=85:15</td>
<td>200</td>
<td>−50</td>
<td>20</td>
<td>0.2</td>
<td>30</td>
</tr>
</tbody>
</table>
resolved into the three components representing C–C (sp³), C=C (sp²), and C–O. A calculation of the sp²/sp³ hybridization ratio is then derived from the relative intensities of the fitted components. The hybridization ratio of sp³ to sp² is 0.24, indicating that the deposited layer is amorphous and mainly composed of graphitelike carbon.

Representative plots of load versus depth and load versus square of depth obtained from the indentation tests with a 0.06 mN peak load on the a-C:H coatings deposited by PIII&D are shown in Figs. 3(a) and 3(b), respectively. The indentation depth at the peak load is about 50 nm which is deeper than the film thickness. The beginning and end of the plots shown in Fig. 3(b) can be fitted by two linear lines with different slopes. Figure 4 shows that deposition of a-C:H films leads to a higher surface hardness which is over 6 GPa compared to 0.5 GPa of the control sample, which is typical for a-C:H films of this type. The hardness of the films decreases sharply and then gradually to a minimum value corresponding to the substrate materials. The elastic modulus initially increases rapidly with increasing indentation depths and then diminishes throughout the entire indentation-depth range eventually converging to the elastic modulus of the PET substrate (7 GPa).

The influence of the substrate bias voltage on the tribological properties of the a-C:H films is shown in Figs. 5(a). The a-C:H films are observed to effectively improve the tribological properties. The a-C:H film deposited at the low negative bias voltage tends to fail earlier. The friction coefficients of the control and samples treated at different gas pressures are shown in Fig. 5(b). The friction coefficient of the control sample is as high as 0.4, whereas those of a-C:H films are much lower. In particular, the film deposited at 2.0 Pa exhibits a longer punch-through time indicating excellent tribological properties. The friction coefficient of the N incorporated a-C:H films is shown in Fig. 5(c) and nitrogen incorporation is shown to significantly improve the tribological properties of the a-C:H films. Figure 6 shows the optical micrograph of the wear track made on the a-C:H film with the steel ball. The film appears to be brittle as delamination is observed at the edge of the groove.
Mechanical folding test was applied to evaluate the cracking behavior of the a-C:H films deposited on PET. Specimens of the same size were used to examine the influence of fabrication conditions on the film cracking behavior. Because there is directionality associated with the crack pattern due to either some preferred cleavage direction or certain degree of uniaxiality in the stress, the cracks made under these conditions always manifest as a series of parallel lines. The spacing between two cracks is not uniform, but there is a mean value that depends on the stress in the film. Parallel surface cracks are observed in the film perpendicular to a tensile stress axis, as shown in Fig. 7. The crack spacing provides information about the fragmentation of adherent films on a ductile substrate. The number of cracks across three transverse lines observed in the optical micrograph is counted and the relationship between the mean crack number and processing parameters are shown in Fig. 8. It can be inferred that the crack spacing of the films prepared at a higher bias voltage and/or higher content of nitrogen incorporation is larger.

Fig. 5. Variation of friction coefficients of a-C:H films deposited using different (a) bias voltages (with C<sub>2</sub>H<sub>2</sub> pressure of 0.5 Pa and without nitrogen incorporation), (b) pressures (with bias voltage of −50 V and without nitrogen incorporation), and (c) nitrogen incorporation contents (with bias voltage of −50 V and pressure of 0.5 Pa).

Fig. 6. Optical micrographs of the wear track of sample 7.

Fig. 7. Optical micrograph showing film cracks in the a-C:H/PET after mechanical folding test.
IV. DISCUSSION

The films deposited in our experiments are mainly composed of carbon with a small amount of oxygen. The existence of oxygen may stem from absorbed oxygen on the film surface due to air exposure\textsuperscript{17} and residual oxygen in the PIII&D vacuum chamber which is not under ultrahigh vacuum.\textsuperscript{18} In spite of the presence of a small amount of oxygen contamination, the carbon films improve the surface hardness substantially. The maximum of the hardness and modulus occur at a depth of about 6 nm, as shown in Figs. 3 and 4. The plastic and elastic behaviors of the materials can be dissociated and the relationship between the load \( P \) and depth \( h \) can be written as \( P = K_p h^2 \) according to the plastic response, where \( K_p \) is a function of the yield strength \( Y \) or hardness \( H \).\textsuperscript{19} The curve in Fig. 3(b) is observed to deviate from linearity at a load of 0.006 mN and a penetration depth of approximately 9 nm. Different effects of the substrate and deposited film can be observed indicating transition from the film to the substrate.

The deposited DLC films possess improved tribological properties but the degree of enhancement depends on processing parameters such as the bias voltage, pressure, and content of incorporated nitrogen. The films prepared with a low bias are easily damaged during the friction test. The early failure may be attributed to high internal stress and poor adhesion typical of low substrate bias voltages.\textsuperscript{20,21} The higher bias has a beneficial effect on the tribological properties. On the one hand, a higher bias may increase the quantities of \( sp^3 \)-bonded carbon and consequently the areas of high strain. On the other hand, the number of small islands on the \( a\)-C:H films decreases leading to reduced surface roughness with increasing bias voltage. The synergistic effects of more \( sp^3 \)-bonded carbon and smaller roughness achieved at higher bias are believed to lead to the higher wear resistance of the films.\textsuperscript{22,23}

When the gas pressure increases, the deposited films have better tribological properties, as indicated by the longer punch-through time, as shown in Fig. 5(b). The better tribological behavior of the films is related to the ability of the \( a\)-C:H to form graphitic surface layers under most tribological conditions.\textsuperscript{24} During the frictional test, the transition from a soft polymeric material to the graphitic film may occur as the deposition pressure increases,\textsuperscript{25} whereas the graphitization transition process may prevent the formation of the less concave area induced by pressing the steel ball onto film surface.\textsuperscript{26} More importantly, a higher gas pressure may produce more radicals leading to thicker layers\textsuperscript{27} and this is one of the reasons why the tribological properties are substantially improved.

Nitrogen incorporation in carbon layers tends to decrease the friction coefficient and prolong the punch-through time, as shown in Fig. 5(b). Most of the nitrogen is bonded to \( sp^2 \) carbon in the materials.\textsuperscript{28} Consequently, the fraction of \( sp^2 \) C–C in the N incorporated \( a\)-C:H film is reduced consequently increasing the \( sp^3:sp^2 \) ratio. The wear resistance of the \( a\)-C:H film also increases as the \( sp^3:sp^2 \) ratio increases. As a result, higher wear resistance can be obtained by intro-

![Fig. 8. Number of cracks in the \( a\)-C:H films deposited using different pressures, (b) bias voltages, and (c) nitrogen contents. Each group of specimens has the same size and is mechanically folded 500 times.](image-url)
Reducing N into the a-C:H films. In addition, incorporation of nitrogen into amorphous carbon films may reduce the internal stress\textsuperscript{29} thereby resisting damage and further improving the wear resistance.

Mechanical folding is an effective method to evaluate the crack resistance of deposited films on soft substrates. Our results show that the crack spacing on the films deposited at gas pressures of 1.0 and 2.0 Pa is larger than that of film deposited at 1.5 Pa, as shown in Fig. 8(a). The crack spacing increases with the thickness of the brittle film on the ductile substrate.\textsuperscript{10,30} The amorphous carbon layer prepared at a high gas pressure (e.g., 2 Pa) may be thicker and more effectively mitigate crack initiation during mechanical folding. In comparison, the thinner films show a higher density of narrow cracks compared to thicker films with the same strain, but thinner films need a larger strain before the onset of cracking,\textsuperscript{31} consequently leading to a lower crack density at a lower pressure such as 0.5 Pa. The crack density in the film which was deposited at bias voltage of \(-250\) V is much smaller than that of the films deposited at bias voltage of \(-50\) and \(-150\) V, as shown in Fig. 8(b). The carbon atom deposition rate and resulting growth rate of the film are promoted by increasing the bias voltage applied to the substrate.\textsuperscript{32} This may be beneficial to the reduction of the number of cracks. In fact, a higher bias voltage may not only increase the film thickness but also enhance the interfacial strength between film and substrate, thereby effectively hampering film cracking. Nitrogen incorporation may decrease the number of cracks, as shown in Fig. 8(c). It has been reported that the mechanics of a cracked film is influenced by the elastic mismatch between the film and substrate.\textsuperscript{33,34} Elastic mismatch between the film and soft substrate may be reduced by relaxing the internal stress in the film. Proper nitrogen content may release the stress in the film\textsuperscript{29} and so the resistance to deformation failure can be enhanced.

V. CONCLUSION

Hydrogenated amorphous carbon films are fabricated on PET foils by acetylene plasma immersion ion implantation and deposition under different deposition conditions. The carbon layers are dominantly graphitic or amorphous and have enhanced surface properties. The hardness and elastic modulus of the a-C:H coated PET are substantially improved. A higher gas pressure or higher bias voltage is observed to yield better tribological properties. Introduction of nitrogen into the films further improves the wear resistance. Our mechanical folding tests suggest that a higher bias voltage and nitrogen incorporation can reduce deformation failure.

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