

Surface Treatment of Polyethylene Terephthalate Using Plasma Ion Implantation Based on Direct Coupling of RF and High-Voltage Pulse

Chunzhi Gong, Xiubo Tian, *Member, IEEE*, Shiqin Yang, Ricky K. Y. Fu, and Paul K. Chu, *Fellow, IEEE*

Abstract—Plasma immersion ion implantation employing hybrid radio-frequency (RF) and high-voltage (HV) pulses via a single feedthrough is an effective surface modification method. In this technique, the sample holder is connected to both the RF generator and the HV modulator in order to generate a high-density plasma in the vicinity of the sample. HV pulses are applied to the sample in between the RF pulses to conduct ion implantation. Polyethylene terephthalate (PET) samples were modified using an C_2H_2 plasma generated by this technique, and diamond-like-carbon films were successfully deposited. In this process, the pulsed HV changed from 2.5 to 10 kV with an RF power ranging from 0 to 150 W and an RF of 13.56 MHz. The C_2H_2 gas pressure was maintained at 1.0 Pa with a processing time of 15 min. Cleaning effects were observed without arcing damage with increasing sample bias from 2.5 to 10 kV. The negative bias and RF were observed to influence the water contact angles of treated PET samples. The plasma-implanted surface became more hydrophilic with increasing sample bias and RF power, respectively.

Index Terms—Plasma immersion ion implantation (PIII), polyethylene terephthalate (PET), radio frequency (RF), water contact angle.

I. INTRODUCTION

IN CONVENTIONAL plasma immersion ion implantation (PIII), the sample is immersed by a gaseous plasma generated by external plasma sources. When a pulsed negative voltage is applied to the sample, positive ions in the plasma are attracted and implanted into the sample surface [1], [2]. In most PIII systems, the plasma sources are at a distance from the sample holder, and it may be difficult to obtain a high-density and uniform plasma in the vicinity of the sample holder [3]–[7]. High-voltage (HV) glow discharge is an alternative technique to produce the required plasmas without an external plasma source [8] and has been investigated theoretically and experimentally. However, the efficiency of plasma production depends on the

applied voltage and gas pressure, and so, process optimization can be difficult. Nishimura *et al.* have developed a system that incorporates both radio-frequency (RF) and HV inputs via a single cable and feedthrough [9], [10]. The HV modulator is based on a hard-tube switch, and the sample to be treated also serves as the antenna to excite the plasma. When the RF pulses are cut off, negative HV pulses are applied via the same feedthrough to the sample to conduct PIII. In this way, the plasma density and HV pulses can be controlled independently [11], [12]. This innovative technique is thus more suitable for samples with complex 3-D shape, as well as electrically insulating materials such as polymers and ceramics, because the plasma is created by RF discharge.

In this paper, we report the use of a similar technique to treat polyethylene terephthalate (PET) foils. Different from the hardware used by Nishimura *et al.* [9], [10], our modulator is based on serial insulated-gate bipolar transistor (IGBT) modules, thereby offering more flexible control. The effects of sample bias and RF power on the surface structure and hydrophilic properties of PET are investigated.

II. EXPERIMENTAL DETAILS

The PIII equipment consisted of a vacuum chamber, an HV modulator, an RF power supply, and a matching network for both the RF and HV. The cylindrical chamber was 40 cm in diameter and 40 cm in length. The power of the HV pulse generator was 3 kW with a ceiling voltage of 10 kV, a repetition frequency ranging from 500 to 1000 Hz, and pulsewidths between 10 and 50 μs . The modulator was constructed with 12 IGBT modules in series. A 13.56-MHz-RF power generator had a maximum power of 1 kW. A matching network was designed in order to control the timing width of the HV and RF pulses, as shown schematically in Fig. 1. The matching network also served to protect both the RF power supply from overvoltage breakdown and the HV modulator from interference by the RF electromagnetic field.

PET foils with a thickness of 0.1 mm were used in our experiments. The effects of bias voltage and RF power on the structure and hydrophilic properties of PET samples were focused on. The bias voltage changed from 2.5 to 10 kV with RF power varying from 50 to 150 W. Before loading into the plasma chamber, the samples were ultrasonically cleaned in alcohol. Acetylene (C_2H_2) gas was bled into the chamber, and the pressure was controlled jointly by a gas flow controller and a throttle valve. The pulsed voltage was monitored by a digital

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C. Gong, X. Tian, and S. Yang are with the State Key Laboratory of Advanced Welding Production Technology, Harbin Institute of Technology, Harbin 150001, China (e-mail: chunzhigong@163.com; xiubotian@163.com; shiqinyang@163.com).

R. K. Y. Fu and P. K. Chu are with the Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong (e-mail: apkyfu@cityu.edu.hk; paul.chu@cityu.edu.hk).

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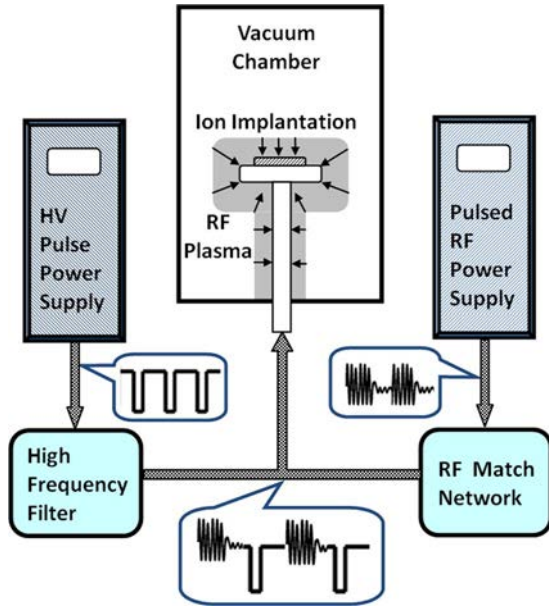


Fig. 1. Schematic of the hybrid hardware that couples RF power and HV pulses to the sample holder via a single HV feedthrough.

TABLE I
INSTRUMENTAL PARAMETERS USED IN PIII OF THE PET SAMPLES

HV Voltage (kV)	RF Width (μ s)	RF Power (W)	RF Width (μ s)	RF/HV interval (ms)	Frequency (Hz)	Time (min)	C ₂ H ₂ Pressure (Pa)
10	20	50	500	1	600	15	1.0
5.0	20	50	500	1	600	15	1.0
2.5	20	50	500	1	600	15	1.0
5	20	0	500	1	600	15	1.0
5	20	50	500	1	600	15	1.0
5	20	100	500	1	600	15	1.0
5	20	150	500	1	600	15	1.0

oscilloscope (Tektronix TDS2012B), and the instrumental parameters are summarized in Table I. The chemical composition was determined by X-ray photoelectron spectroscopy (XPS) on a Physical Electronics PHI-500 using the Cu $K\alpha$ line and a voltage and power of 12.5 kV and 250 W, respectively. The structural changes were studied using Fourier transform infrared (FTIR) spectroscopy. In order to assess the surface energy, the water contact angles were determined using the sessile drop technique.

III. RESULTS AND DISCUSSION

Using this unique technique, instrumental parameters such as frequency, HV pulsewidth, RF pulsewidth, and timing can be adjusted independently. Hence, the HV and RF pulses can be varied without constraints. Fig. 2 shows the typical waveforms of the RF discharge that produces the plasma and the HV pulses that produce the diamond-like-carbon (DLC) layer on the PET foil. The bias pulse is applied to the sample holder 1000 μ s after the RF power was cut off. The width of the HV pulse is 20 μ s, and that of the RF discharge is 500 μ s. The hybrid power supply works well with higher reliability. The protection circuit is very sensitive to overcurrent so that no arcing damage on the samples was observed.

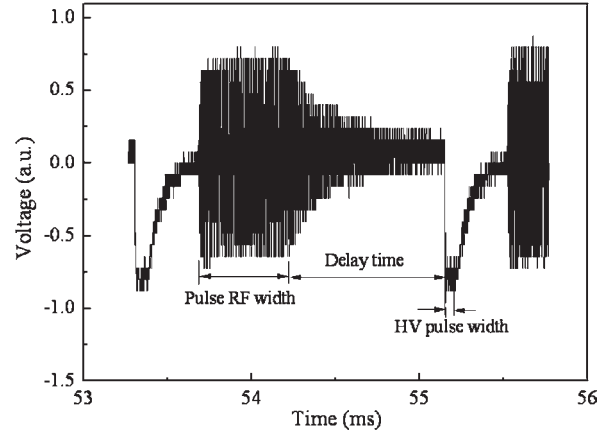


Fig. 2. Typical time interval between the RF and HV pulses.

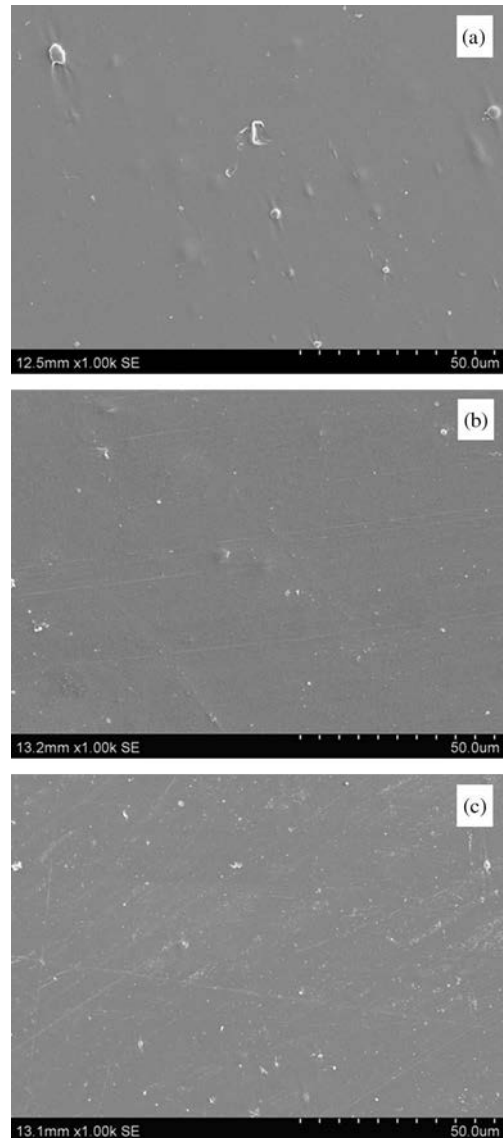


Fig. 3. Surface morphology of the samples: (a) Untreated, (b) 5-kV PIII, and (c) 10-kV PIII.

The scanning electron micrographs acquired from the untreated PET foils and the PET foils treated with an C₂H₂ plasma using different implantation voltages are shown in Fig. 3. The

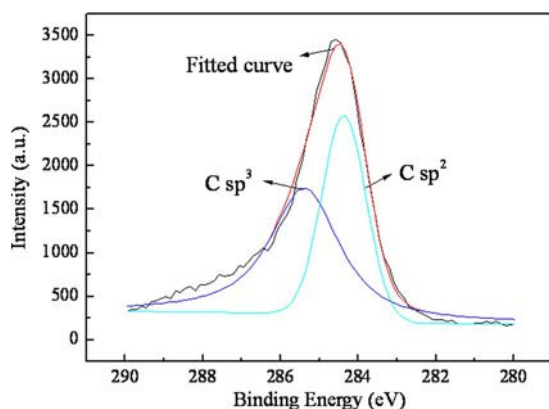


Fig. 4. C1s XPS spectra and fitted spectra of the 10-kV PIII sample.

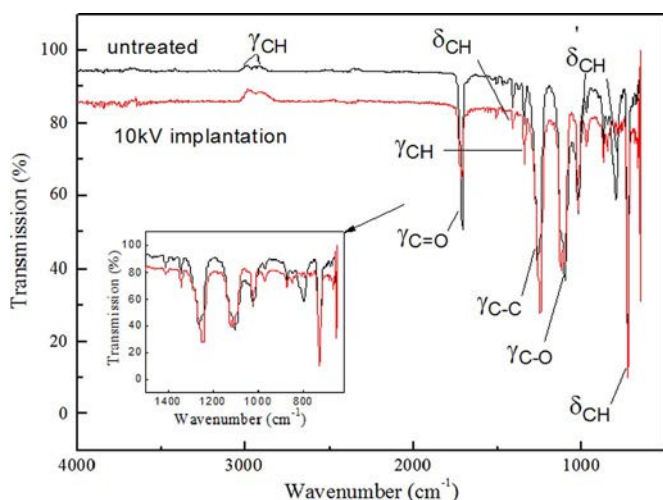


Fig. 5. FTIR spectra obtained from the untreated and 10-kV C₂H₂ PIII PET samples.

surface of the untreated PET substrate exhibits a relatively smooth morphology with several particles of different sizes. No noticeable difference is observed among the surfaces of samples treated with different biases. Comparatively, the surface of the 10-kV implanted sample changes significantly with fewer large protrusions. It can be attributed to the sputtering and cleaning effects induced by energetic ion bombardment. With increasing sample biases, the cleaning effect becomes more evident. No arcing damage is observed on the treated surfaces even at a high sample bias of, for example, 10 kV, implying that charging is insignificant during the experiments.

The DLC films formed on the PET samples are shown in Fig. 4. The C1s peak of an amorphous hydrogenated carbon (a-C:H) film observed by XPS is composed of two subpeaks, one from carbon atoms in the sp³ configuration and the other one arising from sp² [13], [14]. Here, the sp³ carbon content is calculated to be roughly 58% that is higher than typical values previously reported [15]. The result demonstrates that the surface of PET foils can be successfully coated with a carbon layer by this hybrid PIII technique.

HV ion bombardment influences the surface bonding configuration [16]. Fig. 5 shows the FTIR spectra to indicate the position and intensity of the transmission bands of the treated and untreated PET samples. The position of the bands as indicated by the FTIR spectra is similar for all the PET samples,

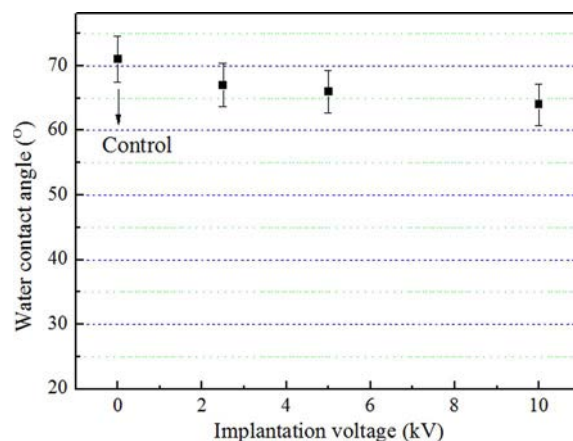


Fig. 6. Water contact angles determined from the PET samples implanted at different implantation voltages.

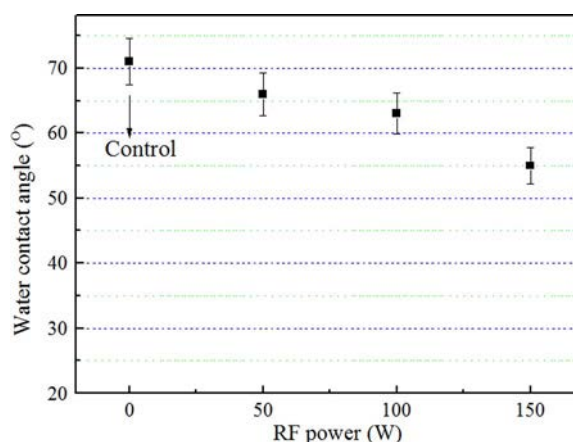


Fig. 7. Water contact angles of the PET samples implanted using different RF powers.

but the intensities are slightly different. The region from 795 to 1020 cm⁻¹ reveals C–H bending in the benzene ring. The peaks at 1710 and 1110 cm⁻¹ stem from C=O and C–O stretching vibrations, and the peaks at 2960, 2910, and 1340 cm⁻¹ are C–H stretching vibrations of paraffin hydrocarbon. The band at 1410 cm⁻¹ is due to C–H bending vibrations of paraffin hydrocarbon [17]. The difference between the FTIR spectra obtained from the untreated and treated samples is mainly at the smaller wavenumbers. This variation is more evident for the 10-kV PIII sample. The intensity of the peak at 795 cm⁻¹ becomes weaker due to HV ion implantation which gives rise to weakened C–H vibration due to damage to the benzene ring. PIII can, in fact, lead to sufficient bond breaking that can affect the surface properties.

The contact angle of a liquid on a solid surface, which is closely related to the surface free energy, can be evaluated by means of the sessile drop technique using deionized water at room temperature [18]. Fig. 6 shows that C₂H₂ PIII effectively improves the surface hydrophilic properties. With increasing sample bias, the water contact angle decreases from 71° on the untreated sample to 65° on the sample treated at –10 kV. Our results are consistent with previous studies, showing that ion bombardment is an effective technique to change the surface contact angle [19], [20]. Fig. 7 shows the effects of RF power on the water contact angle. With higher RF power, the hydrophilic

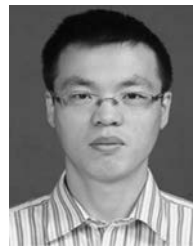
properties are obviously enhanced. The contact angle observed is found to change from 71° on the untreated sample to 53° on the sample treated with an RF power of 150 W.

IV. CONCLUSION

PET foils are treated using hybrid RF and pulsed HV PIII via a single HV feedthrough. This technique provides a higher plasma density in the vicinity of the samples. No damage from surface charging can be observed. With increasing sample bias and RF power, the implanted surface becomes more hydrophilic based on water surface contact angle measurements. The sp^3 carbon content in the DLC film fabricated by this hybrid technique is higher than that produced by conventional PIII.

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Chunzhi Gong was born in Heilongjiang, China, in 1979. He received the B.S., M.S., and Ph.D. degrees in materials science and engineering from Harbin Institute of Technology, Harbin, China, in 2002, 2004, and 2008, respectively.

He is currently an Assistant Researcher with the State Key Laboratory of Advanced Welding Production Technology, Harbin Institute of Technology. His research interests include modulators for ion implantation and deposition, numerical simulation of plasma processing, and plasma sources and

applications.



Xiubo Tian (M'01) was born in 1969. He received the B.S. and M.S. degrees in materials science and engineering from Harbin Institute of Technology, Harbin, China, in 1990 and 1993, respectively, and the Ph.D. degree in physics and materials science from City University of Hong Kong, Kowloon, Hong Kong, in 2002.

From 1993 to 1998, he was with the State Key Laboratory of Advanced Welding Production Technology, Harbin Institute of Technology. From 1998 to 2002, he was with the Plasma Laboratory, City University of Hong Kong. He is currently a Professor with the School of Material Science and Engineering, Harbin Institute of Technology, where he is also the Vice Director of the State Key Laboratory of Advanced Welding Production Technology. He has authored/coauthored over 100 articles. His research interests include plasma ion implantation, nitriding, hybrid processes, numerical simulation of plasma processing, and plasma sources and applications.



Shiqlin Yang received the B.S. degree in materials science and engineering from Harbin Institute of Technology, Harbin, China, in 1961.

From 1980 to 1982, he was a Visiting Scholar with the University of Wisconsin, Madison. From 1985 to 2002, he was the President of Harbin Institute of Technology, where he has been since 1961. He has authored/coauthored over 100 publications. His research interests include ultrasonic equipment and processes for welding applications, plasma welding, plasma ion implantation/nitriding, and surface

engineering.



Ricky K. Y. Fu received the B.S. degree in materials science and technology and the M.S. and Ph.D. degrees in plasma physics from City University of Hong Kong, Kowloon, Hong Kong, in 2000, 2002, and 2005, respectively.

He joined the director board in Plasma Technology Ltd., Kowloon, in 2006. He is currently a Researcher with the Department of Physics and Materials Science, City University of Hong Kong. He is the author/coauthor of over 130 publications and several book chapters. His current research interests

include plasma processing and ion implantation, material surface modification, PVD, and plasma-related techniques, including filtered cathodic arc discharge, microarc oxidation, and magnetron sputtering, as well as high-voltage and high-power pulse supply study and applications.

Dr. Fu was the recipient of the Excellent Young Scientist Award from the Chinese Materials Research Society, Beijing, China, in 2004.



Paul K. Chu (F'03) received the B.S. degree in mathematics from The Ohio State University, Columbus, in 1977 and the M.S. and Ph.D. degrees in chemistry from Cornell University, Ithaca, NY, in 1979 and 1982, respectively.

He is a Chair Professor of materials engineering with the Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong. He has coauthored more than 20 book chapters, 800 journal papers, and 750 conference papers. He is the holder of 15 U.S., European, and

Chinese patents. He is a Coeditor of six books on plasma science, biomedical engineering, and nanotechnology. He is an Associate Editor of *Materials Science & Engineering Reports* and the *International Journal of Plasma Science and Engineering*. His research activities are quite diverse, encompassing plasma surface engineering and various types of materials and nanotechnology.

Dr. Chu is a fellow of APS, AVS, and the Hong Kong Institution of Engineers. He is a member of the Plasma-Based Ion Implantation and Deposition International Committee, the Ion Implantation Technology International Committee, and the IEEE NPSS Fellow Evaluation Committee. He is a Senior Editor of the IEEE TRANSACTIONS ON PLASMA SCIENCE. He was the recipient of a number of awards, including the 2007 IEEE NPSS Merit Award.