

Effects of long pulse width and high pulsing frequency on surface superhydrophobicity of polytetrafluoroethylene in quasi-direct-current plasma immersion ion implantation

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Long pulse, high frequency quasi-direct-current (dc) oxygen plasma immersion ion implantation (PIII) is utilized to create a superhydrophobic polytetrafluoroethylene (PTFE) surface with a water contact angle of over 150°. This technique allows the use of a high duty cycle without deleterious effects such as extensive sample heating encountered in conventional PIII. Scanning electron microscopy images review submicrometer-nanometer structures on the PTFE surface after long pulse, high frequency PIII indicative of ion implantation. On the other hand, plasma modification is the dominant effect in short pulse, low frequency PIII. Quasi-dc PIII is demonstrated to offer adjustable synergistic plasma and ion beam effects. © 2009 American Institute of Physics.

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I. INTRODUCTION

Plasma surface modification and ion implantation have been utilized to modify the wettability, surface energy, mechanical strength, adhesion, wear resistance, electric conductivity, and other properties of polymeric materials.¹⁻⁴ Ion implantation is attractive because of its flexibility, effectiveness, and environmental friendliness.³ Moreover, surface properties can be selectively modified without affecting the bulk characteristics.^{4,5} Plasma modification is another efficient and green technique compared to conventional chemical processes since relatively few toxic wastes are released to the environment. In plasma processes, instrumental parameters such as current, pressure, and voltage can be easily adjusted and controlled to attain reliable and reproducible results. A low sample temperature can also be readily achieved, thereby boding well for polymeric materials typically with poor thermal stability.⁶ In comparison, plasma treatment is more complicated than ion implantation because the plasma consists of different species such as excited neutral atoms and molecules, molecular and monoatomic ions, electrons, and photons. The presence of these species leads to different combinations of interactions between the plasma species and polymer surfaces.⁶ It has also been reported that the surface roughness of polymers can be modified by ion bombardment, physical sputtering, chemical etching, etc.⁶ In ion beam irradiation, the damage caused by energetic ion bombardment is usually irreversible.⁷ The generated damage by nuclear stopping in a polymer is mainly in the form of chain scission. On the other hand, electronic excitation can result in the formation of free radicals that may readily cross link the polymer chains.

A convenient way to couple plasma modification and ion bombardment is plasma immersion ion implantation (PIII).⁸ In this process, the sample is immersed in a plasma and negative high voltage pulses are applied to the sample. When the sample is negatively biased, an ion sheath is established and ions are implanted into the sample. When polymer is subject to PIII, both plasma and ion implantation effects can be attained. In conventional PIII, in order to avoid sample overheating, especially thin polymers, the experiments are typically conducted using a low pulsing frequency such as 50 Hz and a low duty cycle of 0.02. In order to achieve a conformal plasma sheath and maintain good implant fluence uniformity over the entire sample surface, a pulse duration of a few tens of microseconds is usually required.⁹ For a pulse duration of 20 μ s and a total treatment time of 800 s, the polymer surface is exposed to the plasma for 799.2 s. The process is naturally dominated by plasma effects with a small contribution from ion implantation.

The ratio between the plasma treatment time (pulse off period) and ion implantation time (pulse on period) can be readily adjusted in the quasi-direct-current (dc) PIII technique previously proposed by our research group.^{8,10} In this low pressure steady-state dc mode, a grounded conducting grid divides the chamber into two parts. In the lower part, a strong electric field is formed between the negatively biased wafer stage and the boundaries created by the grid and the lower part of the chamber walls. The upper part confines the plasma since the grounded grid stops the expansion of the ion sheath toward the lower part. In this way, a continuous low-pressure discharge can be maintained in the volume above the grid. Positive ions from the plasma diffuse into the lower part through the grid and are implanted into the sample.¹⁰ Since the ion sheath is stopped by the grounded conducting grid, the pulse duration can be increased to over

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100 μs without experiencing the adverse effects encountered in conventional PIII such as extensive sample heating. In addition, by establishing a low density plasma, the pulsing frequency can be increased to 1 kHz without causing deleterious effects to thin polymer films.

In this work, polytetrafluoroethylene (PTFE) is used to demonstrate the difference between quasi-dc and conventional PIII techniques because it is a well known semicrystalline polymer with a linear molecular structure comprising $(-\text{CF}_2-\text{CF}_2-)_n$. The materials are used commercially in a myriad of applications, especially biomedical ones, because of favorable characteristics such as relative high-temperature stability, excellent chemical resistance, low dielectric constant, high electrical resistance, as well as very low surface free energy and friction coefficient.^{5,11} Unfortunately, its low surface free energy and poor adhesion to metals and other materials have hampered wider applications.^{4,7} The inherent chemical inertness of PTFE also makes conventional chemical surface modification difficult.¹⁻⁴ For example, bombardment by energetic ions from the plasma can induce desorption of surface species and activate surface states by producing additional surface functional groups such as defluorination and dangling bonds that enable grafting.¹² It has been reported that chain scission is dominated in PTFE followed by release of carbon atoms.⁷ Ion assisted reactions incorporating a low energy ion beam and reactive gas have been proposed.¹³ The PTFE surface irradiated by argon ions induces a chemical reaction between the reactive oxygen gas and the free radicals in the polymeric chains and a permanent hydrophilic surface with a water contact angle below 30° and surface energy of 60–70 mJ/m^2 has been observed.¹³

II. EXPERIMENTAL DETAILS

In our experiments, the PTFE samples were treated using (1) long pulse, high frequency PIII, (2) short pulse, low frequency PIII, and (3) plasma exposure only. The PIII system in City University of Hong Kong¹⁴ consists of a stainless steel plasma discharge chamber ($\phi 600 \times 300 \text{ mm}^2$) and a stainless steel plasma diffusion chamber ($\phi 760 \times 1030 \text{ mm}^2$) with a background pressure of 7×10^{-6} Torr. Four radio frequency (rf) (13.56 MHz) planar inductive coils are located symmetrically above the plasma discharge region and connected to a matching box. rf power between 0 and 2 kW is coupled to the plasma discharge chamber via four pancake inductive antennae through four independent planar quartz windows. Negative high voltage pulses are applied to the metal sample stage by a 100 kV power supply and 300A PowerMod™ solid state modulator made by Diversified Technologies through a ceramic high voltage feed-through underneath the plasma diffusion chamber. The feed-through is connected to a steel cylindrical sample stage 55 mm in height and 160 mm in diameter supported by a 10 mm diameter metal rod. In the previous dc-PIII setup, a grounded conducting grid is used to partition the region of plasma generation from the plasma processing region to block plasma sheath expansion.¹⁵ However, in the present setup, the high voltage sample stage and supporting voltage feed-through rod are shielded from the plasma by a metal cage

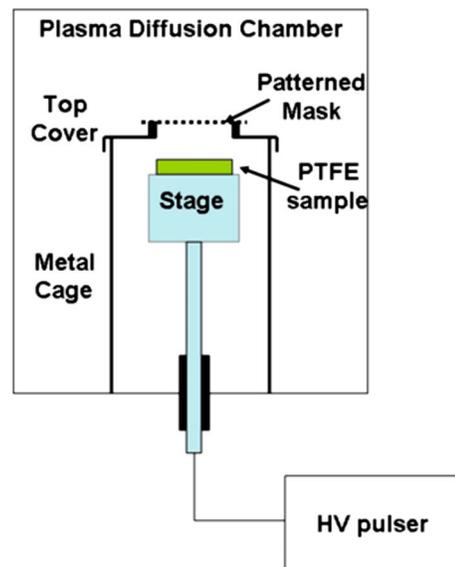


FIG. 1. (Color online) Schematic of the modified long pulse quasi-dc PIII setup.

made of aluminum, as depicted in Fig. 1. The metal cage consists of a cylindrical tube with a thickness of 2 mm and a top cover. A hole with a radius of 100 mm is opened in the center of the top cover. This setup is constructed based on our pattern transfer experiments.¹⁶ Complex patterns can be transferred or implanted into the substrate through this opening of the top cover.

A 0.25 mm thick PTFE sheet purchased from Good Fellow was cut into smaller pieces of $70 \times 80 \text{ mm}^2$ and placed on top of the sample stage. A mask with a square opening of $60 \times 70 \text{ mm}^2$ was covered by a stainless steel mesh [120 mesh per 2.5 cm (1 in.) and $65.0 \mu\text{m}$ (0.0026 in.) wire diameter].¹⁶ The sample stage was 1.6 cm away from the metal mask. Oxygen gas was bled into the chamber at a flow rate of 6.0 SCCM (SCCM denotes cubic centimeter per minute at STP). 1000 W rf power was introduced to the plasma discharge chamber to generate the oxygen plasma. The oxygen plasma was ignited at a higher pressure of a few millitorrs by raising the flow rate of oxygen to 40 SCCM. After the oxygen plasma had been ignited, the flow rate was reduced to 6.0 SCCM within a minute. The working pressure was 3.0×10^{-4} Torr and the reflected power was less than 100 W. The plasma density is estimated to be $3 \times 10^9 \text{ cm}^{-3}$ based on the previous probe measurement.¹⁷

III. RESULTS AND DISCUSSION

In order to investigate independently the effects of ion implantation and plasma modification in the quasi-dc PIII treatment, different sets of instrumental parameters were used. The important instrumental parameters are summarized in Table I. The sample voltage was -5 kV and the total treatment time was 30 min. The ion implantation effect was enhanced by elongating the pulse duration to a long duration of 200 μs at a frequency of 500 Hz. In this case, the ratio of ion implantation to plasma activation was 1:10. Owing to the low plasma density, the Teflon samples were not heated significantly during the process. In the second experiment, a

TABLE I. Main instrumental conditions.

Sample group	Sample voltage (kV)	Pulse duration (μs)	Pulsing frequency (Hz)	Treatment time (min)
A (long pulse, high frequency)	-5	200	500	30
B (short pulse, low frequency)	-5	30	50	30
C (plasma)	nil	nil	nil	30

typical short pulse of 30 μs and frequency of 50 Hz were applied to another set of samples. The control experiment was performed by exposing the Teflon samples to the oxygen plasma without a sample bias for 30 min.

The surface wetting properties of the specimens were investigated using contact angle measurements. The static contact angles were measured by the sessile drop method using a JY-82 contact angle goniometer at ambient humidity and room temperature. 2 μl de-ionized water droplets were deposited on the surfaces and the angles on both sides of the droplet were measured. The results presented here are statistical averages of multiple measurements. However, due to the superhydrophobic properties of the sample treated by long pulse, high frequency PIII (group A in Table I), larger water droplets of 6 μl were applied. The control experiments involved a virgin untreated PTFE. The results are summarized in Table II. The untreated PTFE has a normal average contact angle of 107.5° with a standard deviation of 5.6°. After half an hour of oxygen plasma exposure, the contact angle increases to 122.1° with a standard deviation of 4.9°. After a short pulse, low frequency oxygen PIII treatment for half an hour, the contact angle increases to 127.5° with a standard deviation of 4.1°. In contrast, a superhydrophobic surface is created after long pulse, high frequency oxygen PIII. The average water contact angle is 153.9° with a standard deviation of 4.5°. Selective water droplet images on the PTFE surfaces are depicted in Fig. 2. Superhydrophobic PTFE surfaces have been reported after ion implantation.^{7,18} However, the beam energies were very high, for instance, 40 keV C⁺ ions⁷ and 200 keV Xe⁺ ions.¹⁸ A large water contact angle has not been reported below 5 keV energy.³ In our experiments, the net impact energy of each oxygen atom is 2.5 keV because the main species in the plasma is O₂⁺. On the other hand, a high power oxygen plasma has been reported to create a superhydrophobic PTFE surface but not at relatively low plasma density.¹⁹ The long pulse, high frequency PIII treatment (group A in Table I) reported here is thus unique and offers a good balance be-

TABLE II. Water droplet contact angles.

Sample group	Angle (deg)	Standard deviation (deg)	Number of measurements
A (long pulse, high frequency)	153.9	4.5	24
B (short pulse, low frequency)	127.5	4.1	16
C (plasma)	122.1	4.9	14
Virgin Teflon (control)	107.5	5.6	28

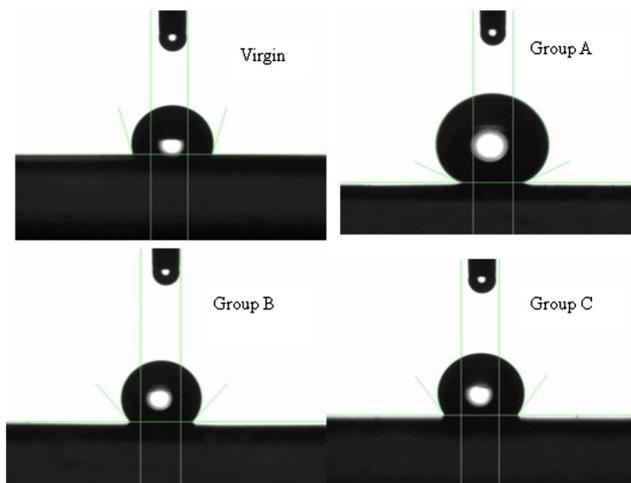


FIG. 2. (Color online) Representative water droplet images (side view) on top of a virgin PTFE, group A (long pulse, high frequency PIII), group B (short pulse, low frequency PIII), and group C (oxygen plasma exposure).

tween ion implantation and plasma modification. It is believed to be the main reason for the creation of the superhydrophobic PTFE surface.

The surface morphology of the pristine and modified PTFE samples was investigated by scanning electron microscopy (SEM) (JEOL JSM 6335F field emission system) after a thin layer of gold was deposited onto the samples to prevent sample charging. The images of the PTFE samples at a magnification of 20 000 are displayed in Fig. 3. A typical rough surface is observed on the untreated PTFE. After half an hour of oxygen plasma modification (group C), submicrometer holes are observed on the PTFE samples. It is believed to stem from etching effects rendered by the reactive oxygen plasma. The morphological difference is quite small between the short pulse, low frequency oxygen PIII samples (group B) and plasma exposed ones (group C). Submicrometer holes are also observed from the group B samples. It can thus be inferred that plasma modification is dominant in short pulse, low frequency PIII. In contrast, tiny 100 nm rods are observed on the samples after undergoing long pulse,

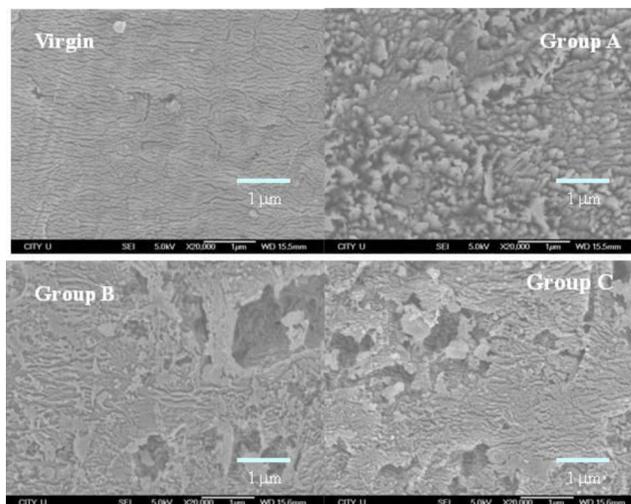


FIG. 3. (Color online) SEM images of the treated and untreated PTFE surfaces.

high frequency PIII (group A). Similar tiny nanometer rods have been reported after high energy ion implantation.³ The results suggest that the effect caused by ion implantation dominates the effect generated by plasma in the long pulse, high frequency PIII (group A in Table I) process. When a long pulse is used in the bias voltage, a dc plasma can be created between the stage and patterned mask as a counter electrode. To verify the creation of dc plasma, an experiment was conducted by using the same PIII parameters as in group A of Table I and the same working pressure, but the rf power was turned off such that no plasma was supplied externally. The Teflon surface was not modified at all and it can be inferred that the dc plasma created between the stage and patterned mask is weak. As shown in Fig. 3, the distribution and sizes of the tiny nanometer rods are not uniform. In some locations, the rods are larger and deeper, but at other areas, the rods are smaller and shallower. We believe that the submicrometer holes etched by the oxygen plasma generate the large and deep nanometer rods and the other area is covered by the smaller nanometer rods. This submicron-nanometer scale feature also affects the adhesion properties of the PTFE surfaces.²⁰

IV. CONCLUSION

In summary, a superhydrophobic PTFE surface is produced by quasi-dc oxygen PIII using a high frequency of 500 Hz and long pulse duration of 200 μ s in half an hour. Samples undergoing typical PIII treatment (50 Hz and 30 μ s) and plasma exposure are only compared. The surface morphology, the latter two samples, is almost the same and the water contact of the short pulse, low frequency sample is only 5° larger than that of the control suggesting that plasma modification is the dominant effect. However, a superhydrophobic surface with an average water contact angle of 153.9° is achieved after long pulse, high frequency quasi-dc PIII demonstrating that ion implantation is the dominant process here. Quasi-dc PIII is thus a flexible technique offering ad-

justable synergistic plasma and ion beam effects while sample damage due to overheating can be effectively minimized.

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- ¹R. K. Y. Fu, Y. F. Mei, G. J. Wan, G. G. Siu, P. K. Chu, Y. X. Huang, X. B. Tian, S. Q. Yang, and J. Y. Chen, *Surf. Sci.* **573**, 426 (2004).
- ²T. L. Schiller, D. Sheeja, D. R. McKenzie, D. G. McCulloch, D. S. P. Lau, S. Burn, and B. K. Tay, *Surf. Coat. Technol.* **177–178**, 483 (2004).
- ³J. Zhang, X. Yu, H. Li, and X. Liu, *Appl. Surf. Sci.* **185**, 255 (2002).
- ⁴L. Guzman, B. Y. Man, A. Miotello, M. Adami, and P. M. Ossi, *Thin Solid Films* **420–421**, 565 (2002).
- ⁵J. M. Colwell, E. Wentrup-Byrne, J. M. Bell, and L. S. Wielunski, *Surf. Coat. Technol.* **168**, 216 (2003).
- ⁶N. Vandecasteele and F. Reniers, *Surf. Interface Anal.* **36**, 1027 (2004).
- ⁷J. Zhang, L. Xu, X. Yu, and X. Liu, *Mater. Lett.* **56**, 410 (2002).
- ⁸D. T. K. Kwok, X. C. Zeng, C. Chung, and P. K. Chu, *J. Appl. Phys.* **87**, 4094 (2000).
- ⁹A. Kondyurin, N. J. Nosworthy, and M. M. M. Bilek, *Acta Biomater.* **4**, 1218 (2008).
- ¹⁰X. C. Zeng, P. K. Chu, Q. C. Chen, and H. H. Tong, *Thin Solid Films* **390**, 145 (2001).
- ¹¹M. Sadiq, S. Ahmad, M. Shafiq, and M. Zakaullah, *Plasma Processes Polym.* **4**, 186 (2007).
- ¹²A. Kinbara, A. Kikuchi, S. Baba, and T. Abe, *J. Adhes. Sci. Technol.* **7**, 457 (1993).
- ¹³S. K. Koh, J. S. Cho, K. H. Kim, S. Han, and Y. W. Beag, *J. Adhes. Sci. Technol.* **16**, 129 (2002).
- ¹⁴D. Tang and P. K. Chu, *J. Appl. Phys.* **94**, 1390 (2003).
- ¹⁵D. Tang and P. K. Chu, *Appl. Phys. Lett.* **82**, 2014 (2003).
- ¹⁶D. T. K. Kwok, *J. Phys. D* **41**, 225501 (2008).
- ¹⁷D. L. Tang, R. K. Y. Fu, X. B. Tian, and P. K. Chu, *Rev. Sci. Instrum.* **74**, 2704 (2003).
- ¹⁸Y. Chen, Z. Zhao, J. Dai, and Y. Liu, *Appl. Surf. Sci.* **254**, 464 (2007).
- ¹⁹N. Vandecasteele, B. Nisol, P. Viville, R. Lazzaroni, D. G. Castner, and F. Reniers, *Plasma Processes Polym.* **5**, 661 (2008).
- ²⁰L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia, and L. Jiang, *Langmuir* **24**, 4114 (2008).