Plasma Processing Update

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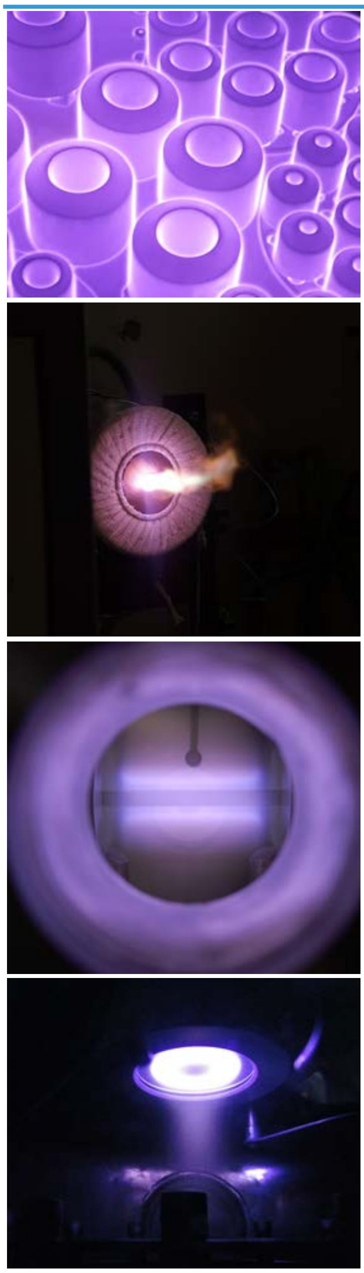

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ARTICLE

Comparative Wettability Study of Bulk and Thin Film of Polytetrafluoroethylene after Low Energy Ion Irradiation

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Polytetrafluoroethylene (PTFE) is a polymer with unique properties such as hydrophobicity, low surface energy, biocompatibility, and chemical inertness. Due to these properties, PTFE is suitable for a variety of industrial applications. PTFE-like thin films and coatings have also been used to provide a hydrophobic layer on various surfaces. Hence, the wetting properties of PTFE, as well as PTFE-like thin films, have been extensively investigated over the last few years. Among different fabrication techniques such as plasma processing, chemical etching, lithography, etc., plasma-based techniques are proven to be more suitable to modify the wetting properties of PTFE over large areas. Ion beam irradiation [1], inert and reactive plasma etching [2], etc. have been used to alter surface morphology and/or surface chemistry for producing superhydrophobic or hydrophilic PTFE. On the other hand, plasma-based deposition techniques such as plasma enhanced chemical vapor deposition (PECVD) and physical vapor deposition (PVD) [3] are commonly used to deposit PTFE-like coatings to achieve functional wetting properties like superhydrophobicity, water-repellency, and self-cleaning properties. While keeping in mind the wide range of applications of bulk PTFE and PTFE thin films, a detailed investigation and a comparative study of surface morphology, wettability, and chemical composition of PTFE and their thin films after ion irradiation are required. In the present work, commercially available bulk PTFE sheets and PVD-grown PTFE-like thin films, having similar initial contact angles have been used to study the wetting dynamics. Both the surfaces were irradiated with low energy ion beam having beam energy of 800 eV, at an angle of incidence from 0° to 70°. The surface morphology of irradiated surfaces was investigated using a scanning electron microscope (SEM). Wettability studies were carried out by measuring the water contact angle from the parallel as well as perpendicular position to the ion beam direction. The changes in the chemical composition of the surfaces before and after the irradiation were investigated using XPS [4].

The ion beam irradiation experiments were performed in an ultra-high vacuum system as shown in Figure 1(a). The cylindrical experimental chamber was pumped using a turbo molecular pump and a rotary pump to achieve the base pressure of 1 × 10^{-5} Pa. The specimens were first placed in the sample mounting chamber and then transferred to the main vacuum chamber using a sample transfer inside a cylindrical magnetron sputtering deposition system. A 3-inch magnetron sputtering gun (Excel Instruments, India) was used to deposit PTFE-like film on the substrates. Argon gas was introduced using a gas dosing valve and the working pressure was maintained at 5 Pa. The substrate-target distance was maintained at 50 mm. A 13.56 MHz radiofrequency (RF) power supply (QEI

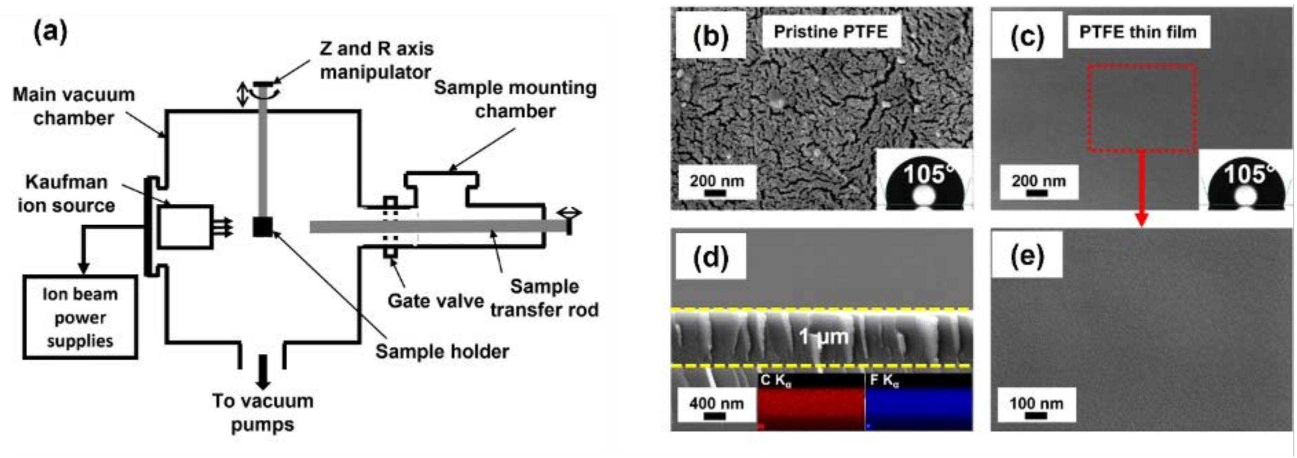

Figure 1: *(a) Schematic representation of ion beam irradiation system, SEM images of (b) pristine PTFE surface and (c) PTFE-like thin film. The cross-sectional view of PTFE-like thin film is shown in (d). Inset images of (c) show the color elemental mapping of carbon and fluorine across the thickness of the film carried out using energy dispersive X-ray spectroscopy. The magnified view of the surface morphology of PTFE-like thin film is shown in (e).*

rod. The sample holder was attached to the Z and R axis manipulator to place the specimens at different angles with respect to the ion beam. The working pressure was maintained at 2 × 10^{-2} Pa by introducing the Ar gas using a mass flow controller. The Kaufman type low energy ion source (Sinaris 40-i, Microsystems GmbH) was used for ion beam irradiation. The specimens were irradiated with beam energy (E_B) of 800 eV for 5 minutes. The angle of incidence of the ion beam (α) was varied from 0° to 70° using the manipulator. On the other hand, PTFE-like thin films were grown on 10 × 10 mm^2 silicon wafer substrates. The same PTFE sheet described above was cut into a 3-inch (75 mm) diameter disc to be used as a sputtering target. The substrates were placed corporation, USA) was used for depositing the film. The deposition was carried out at 100 W RF power for 60 minutes. Figure 1(b)-(e) shows the surface morphology of a pristine PTFE sheet and as-deposited PTFE-like thin film. The pristine PTFE sheet is having some manufacturing cracks on its surface (Figure 2(b)). However, as-deposited PTFE-like thin film grown on Si wafers looks very smooth as shown in Figure 2(c). The magnified view of the surface morphology of the as-deposited film is shown in Figure 2d. The as-deposited film has very fine granular structures on the surface. The thickness of the film obtained from the cross-sectional SEM is found to be 1 ± 0.08 μm (Figure 2(d)). Figure 2(d) (inset images) also shows the distribution of carbon and fluorine throughout the thickness of the film measured using an energy dispersive X-ray spectroscopy (EDX) in color mapping mode. Both carbon and fluorine are uniformly distributed over the whole thickness of the film, confirming the uniform growth of the film.

Figure 2 represents the effect of beam energy (E_B) and angle of incidence (α) on the surface morphology of the ion beam irradiated PTFE sheet and PTFE-like thin films. The direction of the ion beam is from left to right. When the PTFE sheet is irradiated at 20° angle of incidence, tilted flake-like nanostructures are formed on the surface as shown in Figure 2(a). As α increases from 20° to 40°, the elongation of the nanostructures towards the ion beam direction also increased. Upon further increasing the angle of incidence of the ion beam, sharp-edged long flakes appeared on the surface as seen in Figure 2(c)-(d). On the other

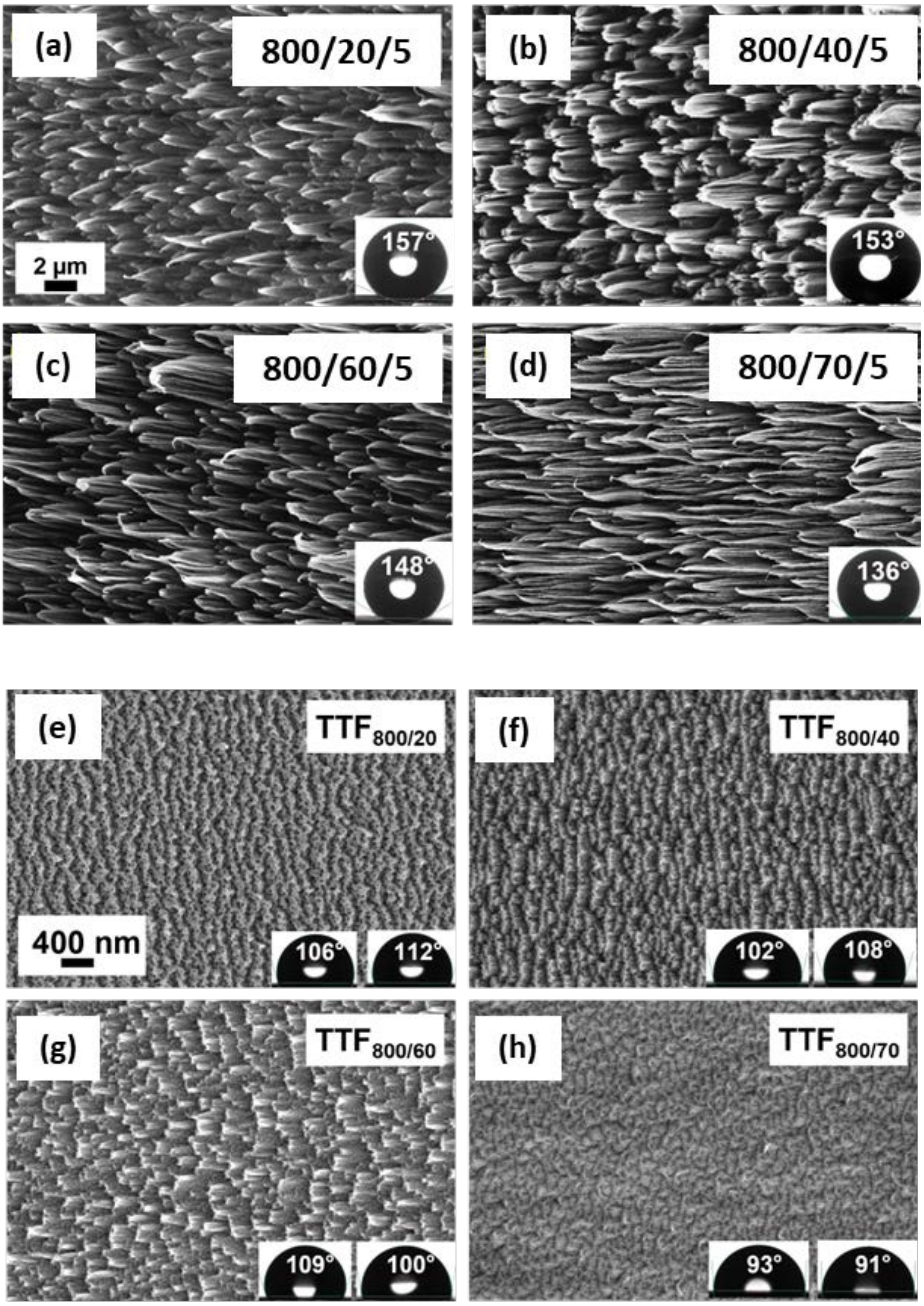

Figure 2: *Surface morphology of PTFE sheets (a-d) and PTFE-like thin films (e-h) after ion beam irradiation at a different angle of incidence. The angle of incidence (α) varied as 20° (a, e), 40° (b, f), 60° (c, g), and 70° (d, h), respectively.*

hand, when PTFE-like thin films are irradiated, initially, at α = 20°, irregular nanopatterns are formed and oriented in the perpendicular direction to the ion beam. As α increases from 20° to 40° regular nanopatterns are formed on the surface. Upon further increasing the angle of incidence to 60°, the periodicity again starts to reduce (Figure 2(g)), and finally the surface becames smooth without any periodic structures after glancing angle (α = 70°) ion beam irradiation (Figure 2(h)). Figure 3 shows the variation in $\theta_{\|}$, and $\theta_{\perp}$ of PTFE and PTFE-like thin films as a function of the angle of incidence of the ion beam. The pristine PTFE surface is hydrophobic in nature having a contact angle of 105°. When PTFE is irradiated with 800 eV beam energy at normal incidence (α = 0°), both $\theta_{\|}$ and $\theta_{\perp}$ also increased from 149° to 153° for normal incidence irradiation (Figure 3(a)). For the initial increment in α up to 20°, a slight increment in $\theta_{\|}$ and $\theta_{\perp}$ (157° and 156°) is observed. After this, both $\theta_{\|}$ and $\theta_{\perp}$ started decreasing with increasing the angle of incidence and reached 136° and 132° respectively for α = 70°. On the other hand, when PTFE-like thin films are irradiated (Figure 3(b)), the water droplet shows anisotropic wetting on the nanoripple like structures. When α is increased from 10° to 20°, $\theta_{\|}$ and $\theta_{\perp}$ increase from an initial values of 107° to 105° and 112°, respectively. After this increment, a systematic decrease in both angles is observed up to α = 40°, where $\theta_{\|}$ and $\theta_{\perp}$ reached 91° and 93° respectively. In contrast to ion beam irradiation of PTFE sheets, where the structures are oriented in parallel to the ion beam directions, for PTFE-like thin films, the nanoripple-like structures are oriented perpendicular to the ion beam direction up to a 50° angle of incidence. Therefore, the water droplet spreads more in the perpendicular direction of the ion beam, and due to this, $\theta_{\perp}$ is

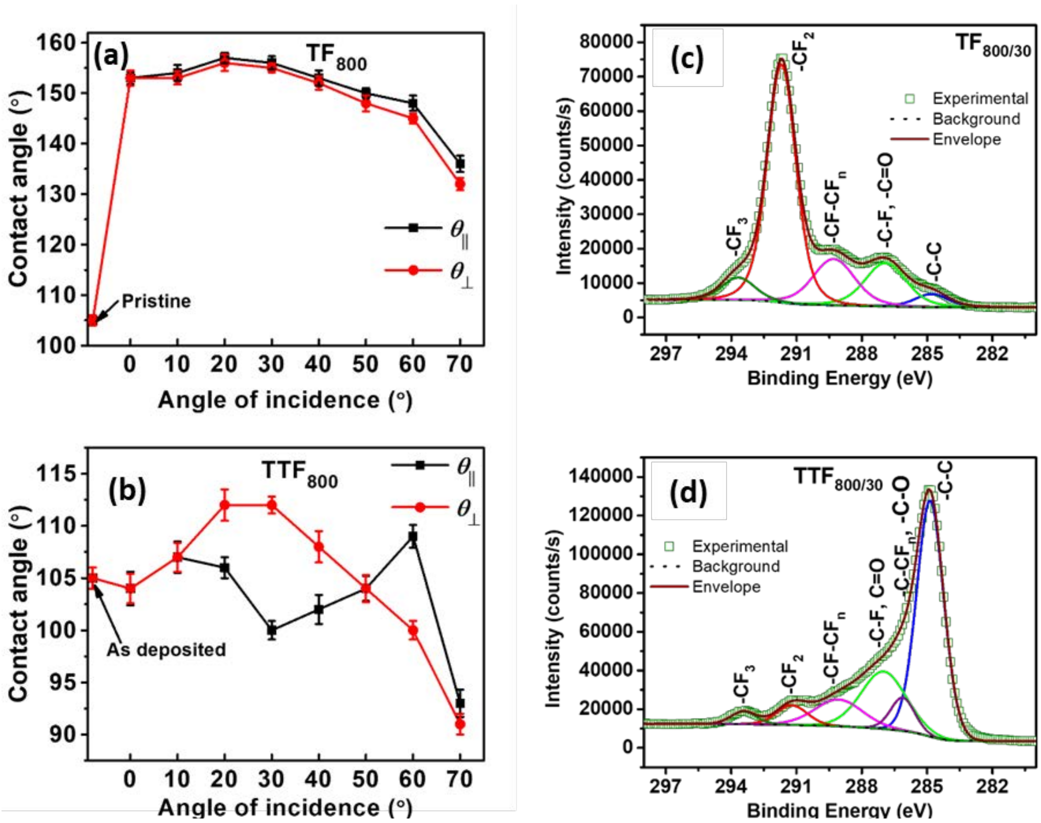

Figure 3: *Variation in the parallel contact angle ($\theta_{\|}$) and perpendicular contact angle ($\theta_{\perp}$) of ion beam irradiated PTFE sheets (a) and PTFE-like thin films (b) as a function of beam energy (E_B) and angle of incidence (α). XPS analysis of ion beam irradiated PTFE sheet and PTFE-like thin film, showing C 1s spectra of (c) 800 eV irradiated PTFE sheet, (d) 800 eV irradiated PTFE-like thin film.*

higher than $\theta_{\parallel}$ for the corresponding irradiated surface up to 50° angle of incidence. The maximum difference between $\theta_{\parallel}$ and $\theta_{\perp}$ for TTF800 is found to be 12°.

Figure 3(c) and (d) represents the C 1s XPS spectra of ion beam irradiated PTFE and PTFE-like thin films. When the PTFE sheets are irradiated with 800 eV at an angle of 30° (Figure 3c), similar to the pristine PTFE, the intensity of the peak corresponding to CF_2 bonding is still higher than the other observed peaks. However, in contrast to the pristine PTFE, three new peaks are observed for TF800/30 at 287.0, 289.5, and 293.7 eV which are corresponding to CF, $CF-CF_n$, and CF_3 bonding, respectively. On the other hand, when PTFE-like thin films are irradiated with 800 eV at an angle of 30° (Figure 3(d)), there is a drastic reduction in the intensity of the main CF_2 peak at 292 eV is observed both for TTF800/30. The F/C ratio is drastically reduced from an initial value of 1.0 to 0.2, indicating the large defluorination of the surface after irradiation. Also, trace amount of nitrogen has been detected in PTFE-like thin film after irradiation due to the bonding of nitrogen from the ambient air with free dangling bonds generated after irradiation. Further, due to irradiation using Ar ion beam, trace amount of argon has also been detected may be due to the incorporation of Ar in the near surface region of the material after irradiation. Hence, XPS analysis confirmed that both bulk PTFE and thin films exhibit different initial chemical compositions. After irradiation, additional $CF-CF_n$ and CF_3 bonding in bulk PTFE are observed, and the intensity of the CF_2 bonding is higher than other peaks. However, in the case of thin films, ion irradiation causes severe chemical changes on the surface. The surface

References:

[1] Y. Lee, Y. Yoo, J. Kim, S. Widhiarini, B. Park, H.C. Park, K.J. Yoon, D. Byun, Mimicking a Superhydrophobic Insect Wing by Argon and Oxygen Ion Beam Treatment on Polytetrafluoroethylene Film, J. Bionic Eng. 6 (2009) 365–370.

[2] V. Pachchigar, M. Ranjan, S. Mukherjee, Role of Hierarchical Protrusions in Water Repellent Superhydrophobic PTFE Surface Produced by Low Energy Ion Beam Irradiation, Sci. Rep. 9 (2019) 1–10.

[3] R. Jafari, R. Menini, M. Farzaneh, Superhydrophobic and icephobic surfaces prepared by RF-sputtered polytetrafluoroethylene coatings, Appl. Surf. Sci. 257 (2010) 1540–1543.

[4] V. Pachchigar, B. K. Parida, S. Augustine, S. Hans, M. Saini, K. P. Sooraj, M. Ranjan Comparative wettability study of bulk and thin film of polytetrafluoroethylene after low energy ion irradiation, , Thin Solid Films, 777 (2023) 139888.

ARTICLE

Plasma Treatment: A Single Step Eco-friendly Solution for Prevention of Bacterial Colonization on Abiotic Solid Surfaces

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Bacterial cells are small single cell organisms and found almost everywhere around us as well as within our human body. Adhesion and colonization of bacterial cells on to any solid surfaces is a burning issue worldwide considering their public health and economic consequences in various sectors such as food and medical device packaging, indwelling medical devices, food processing, textile and many more.

Free floating bacterial cells (planktonic cells) are always in search of a solid surface where they can settle and grow as shown in Figure -1. Once bacterial cells are successful in their primary attachment to solid surface, they quickly start adhering among themselves as well as to the surface irreversibly. This process results in the formation of three-dimensional microbial cities called 'Biofilm'. Bacterial cells which grow beneath biofilm, exhibit very high resistance against anti-biotics requiring 100 – 1000 times more antibiotics to kill them compared to planktonic bacterial cells. Biofilm bacteria are highly pathogenic and responsible for most Hospital Acquired Infections including Catheter Associated Urinary Tract Infection (CAUTI). Bacterial adhesion on to solid surfaces can be avoided majorly by two ways,1) by killing them and 2) by repelling them. As shown in Figure -2.

In bacteria killing approach, either the biomaterial surface is coated with antibiotic molecules, or the bulk biomaterial is impregnated with antibiotic molecules which is allowed to release in a controlled manner. When

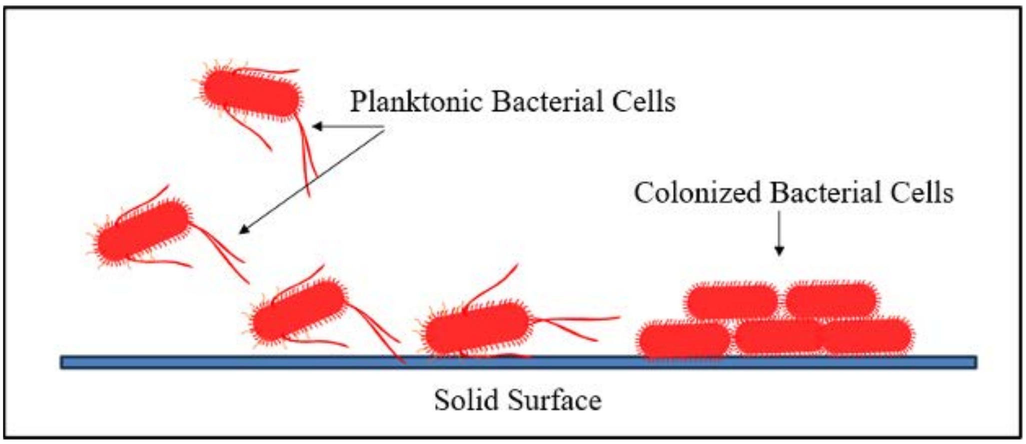


Figure 1:*Schematic Diagram of Bacterial Adhesion on Solid Surface*

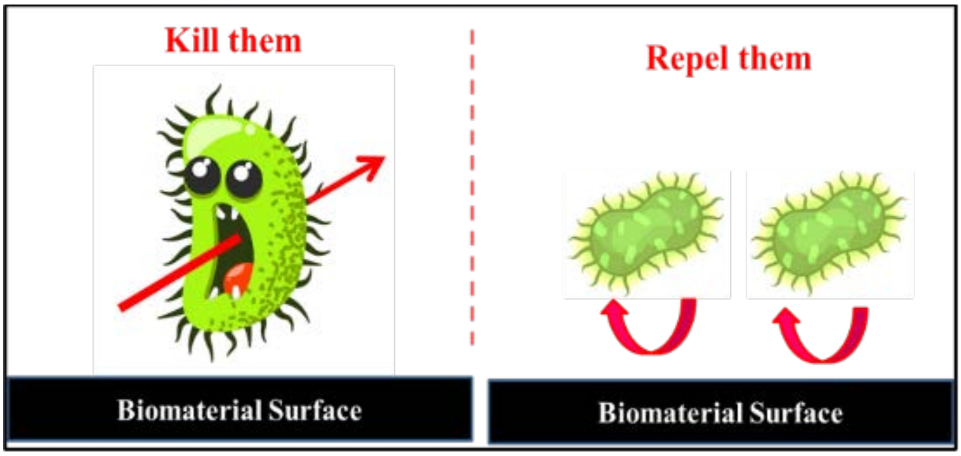


Figure 2: *Schematic diagram of bacteria killing and* repelling approach.

Figure 3: *Silicone catheter segments under plasma treatment*

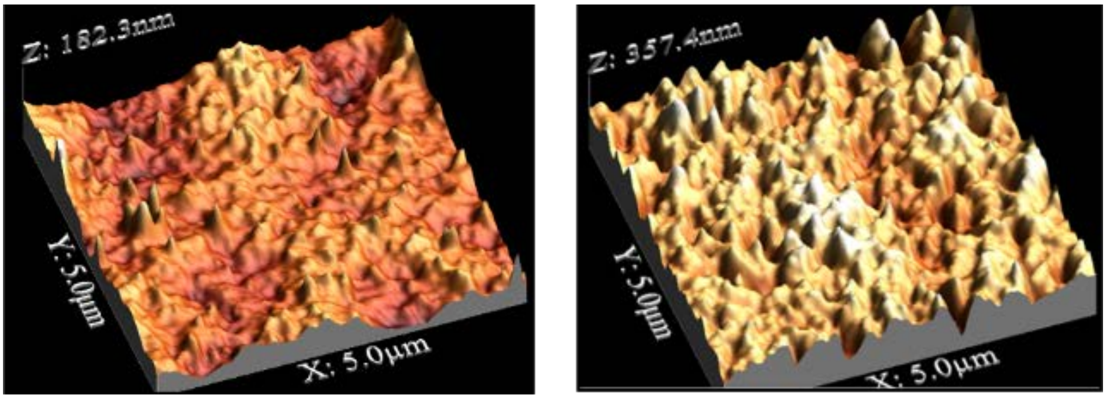


Figure 4: *Surface morphology of untreated (L) and plasma treated (R) Catheter surface*

bacterial cells encounter these antibiotic molecules, they are killed. A major drawback of this approach is development of antibacterial resistance in bacterial cells hence the effectiveness of this method remains up to limited time period.

At APD, IPR we have developed a single step eco-friendly process for prevention of adhesion and colonization of bacterial cells on silicone catheter surfaces. This process does not use any antibiotic molecules or complex coating on catheter surface. Figure-3 shows catheter tube segments under plasma treatment. Plasma treated catheter surfaces exhibit nanoscale physico-chemical surface modification.

Plasma treatment turns hydrophobic catheter surface into hydrophilic surface and imparts morphological changes as shown in figure -4. Altered hydrophobicity and surface morphological changes enable catheter surfaces to deter bacterial adhesion followed by biofilm formation. Plasma treated catheter surfaces show > 99 % reduction in Uropathogenic E-coli bacterial adhesion compared to bare catheter surfaces. Effectiveness of plasma treatment against bacterial colonization is checked up till 30 days after plasma treatment and found only ~ 10 % rise in bacterial adhesion.

Figure -5 shows SEM image of three-dimensional biofilm formation on to bare catheter surface and biofilm free plasma treated catheter surfaces.

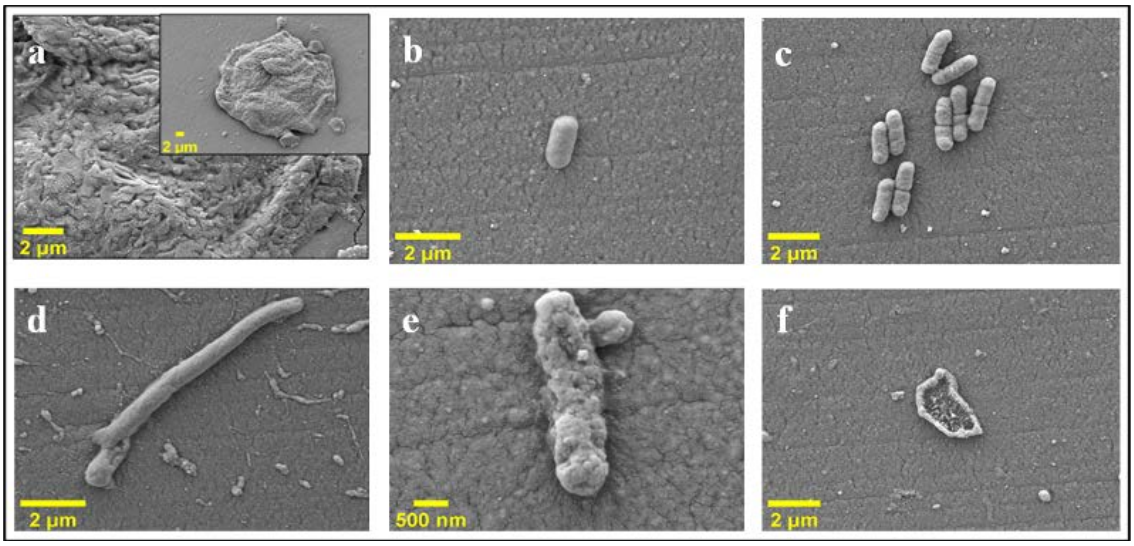


Figure 5: *SEM images of untreated (a) and plasma treated (b-f), (10 minutes plasma exposure time) silicone catheter surfaces with bacterial load: (a) three-dimensional biofilm with EPS layer, (b) individual e-coli cell (c) small cluster of cells (d) elongated stressed cell, (e) and (f) dead cell with ruptured cell wall*

MOU SIGNED

Recently IPR has signed a MoU agreement with M/s. Lab-India, Mumbai for the template of Surface Enhanced Raman Scattering (SERS) based sensing. SERS template technology is developed by Team of Mr. Sooraj KP, Mr. Sebin Augustine, Dr. Mahesh Saini and Dr. Mukesh Ranjan from SSMAS/Plasma Surface Engineering Division (PSED)/IPR. Developed SERS templates has the capability to detect various molecules under very low concentrations and has been tested for various food adulterants. Under the MoU SERS template will be tested for various industry relevant molecules.

MoU signed between IPR and M/s Lab India, Mumbai

OTHER EVENTS

Fire Safety training at FCIPT campus:

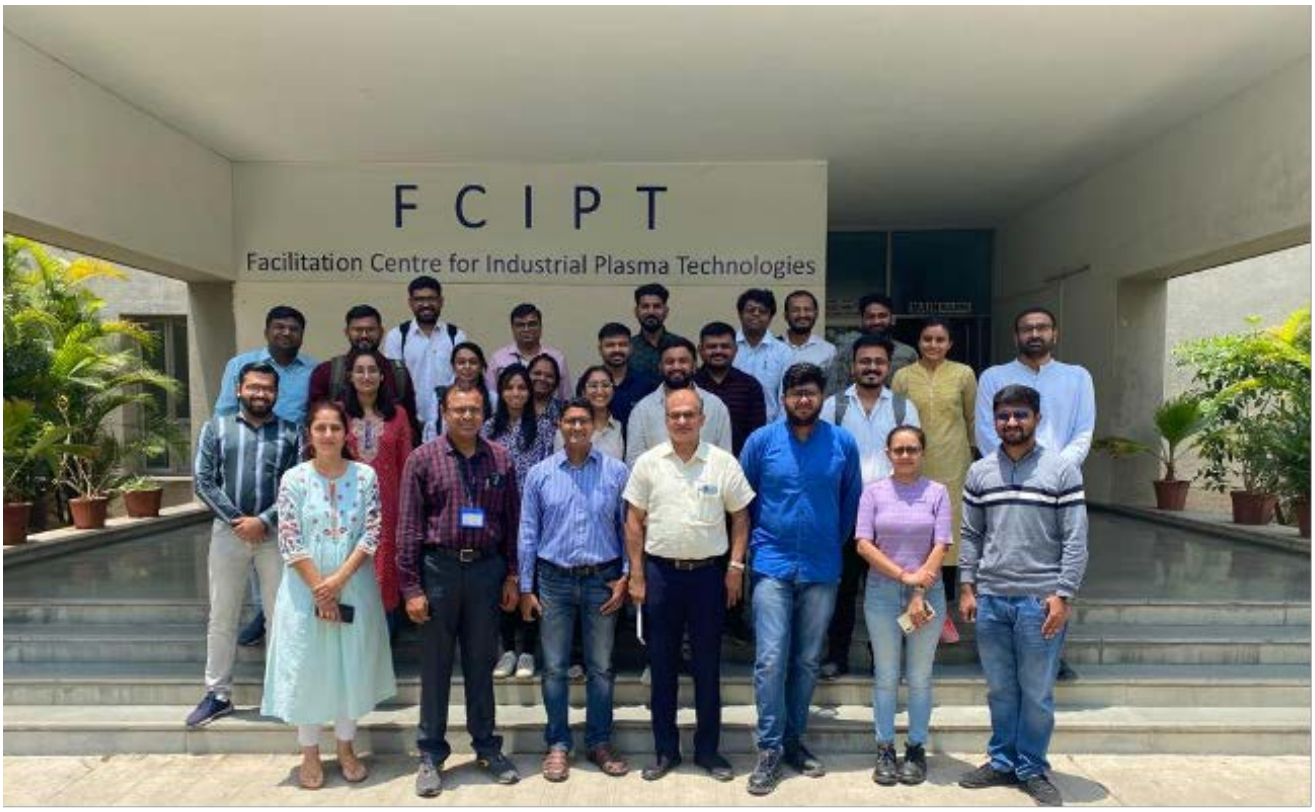
‘Fire safety demonstration & basic training’ was conducted by IPR, Safety section; at FCIPT campus on 20.04.2023. A total of 41 members – including permanent employees, temporary staff, Research Scholars, security personal – have taken part in the demonstration. Participants were demonstrated about how to operate various fire extinguishers available and were also provided with the basic hands-on training. A few photographs of the occasion are presented below.




OTHER EVENTS

Out-reach activities :

A total of 27 MBBS doctors, undertaking a course at Indian Institute of Public Health (IIPH), Gandhinagar, visited FCIPT campus of IPR on 01/05/23; as a part of Industrial visit with an emphasis towards safety practices. After an introductory presentation about 'plasma applications in health sector', the visitors have visited various labs in FCIPT.



PATENTS / PUBLICATIONS / TALKS DELIVERED

Patents applied / granted:

1. An Apparatus to generate large plasma arc plume for waste disposal and thermal applications
   Vishal Jain, S K Nema, Adam Sanghariyat, Chiraya Patil, Bhupendra K Patel, Atik Mistri
   Patent granted; Patent number 432380

2. An apparatus for treating matter using Inductively coupled plasma
   Vishal Jain, Anand Visani, B K Patel, Chirayu Patil, S K Nema, P B Jhala
   Patent granted; Patent number 426773

3. A system to generate high power density dielectric barrier discharge plasma in ambient air medium
   Vishal Jain, Anand Visani, Adam Sanghariyat, S K Nema, S Mukherjee
   Patent granted; Patent number 408755

Publications in peer reviewed journals:

1. Label-free detection of Oral cavity cancer by multivariate analysis of SERS spectra of Saliva
   Sebin Augustine, Arti Hole, Sooraj K P, Mahesh Saini, Pankaj Chaturvedi, Mukesh Ranjan, C. Murali Krishna
   Frontier in Physics: Condensed Matter Physics 11 (2023), doi: 10.3389/fphy.2023.1212865

2. Role of micro- and nano-CeO2 reinforcements on characteristics and tribological performance of HVOF sprayed Cr3C2-NiCr coatings
   HetalR. Chauhan, Sekar Saladi, Sahil Variya, Ajaykumar Solanki, Satish Tailor, K.P. Sooraj, Mukesh Ranjan, Shrikant Joshi
   Surface & Coatings Technology (2023) 129684

3. SERS sensing of Metanil yellow in turmeric solution using self-organized nanoparticle arrays grown on Ion beam patterns
   Sebin Augustine, Sooraj K P, Mahesh Saini, Sukriti Hans, Basanta Kumar Parida, Vivek Pachchigar, Mukesh Ranjan
   Photonics and Nanostructures-Fundamentals and Applications (2023)

4. Comparative Wettability Study of Bulk and Thin Film of Polytetrafluoroethylene after Low

Energy Ion Irradiation
Vivek Pachchigar , BasantaKumar Parida, Sebin Augustine , Sukriti Hans , Mahesh Saini , K.P. Sooraj , Mukesh Ranjan
Thin Solid Films (2023) 139888

5. Selective generation of reactive oxygen species using carbon dioxide plasma in plasma activated water
Vikas Rathore, Sudhir Kumar Nema
Journal of Vacuum Science & Technology A; 41 (4), p 042702, May 2023

Research / Technical Reports :

1. Numerical study of DBD plasma based Inline textile treatment system
Jyoti Agarwal, Shahrukh Barejia , R. Srinivasan, Nisha Chandwani, Vishal Jain, S.C. Jakhar, Manika Sharma, S.K. Nema
IPR/RR/1442

Talks delivered :

1. A keynote lecture was delivered by **Dr. Mukesh Ranjan** on “Nanostructuring using Ion Beams for Surface wettability and sensing applications” in ‘International Conference for Emerging Technologies (ICAMET-2023)’ organized by Netaji Subash Chandra Bosh University of Technology (NSUT), New Delhi during May 04-05, 2023.

2. An invited talk was delivered by **Dr. Vishal Jain** on “Plasma Pyrolysis Technology in IPR” in a seminar on “Swatchhata & Health” at BARC, Mumbai; on 28 Feb 2023.

3. A talk was delivered by **Dr. Vishal Jain** on “आईपीआर में 24 x 7 संचालन के लिए ग्रेफाइट इलेक्ट्रोड आधारित उच्च शक्ति प्लाज्मा आर्क प्रणाली का डिजाइन और विकास” during Hindi web sangoshthi 2022.

4. An invited talk was delivered by **Mr. Vikas Rathore** on “Different Techniques and Equipment for Plasma Generation” in ‘(KARYASHALA) High-End International Workshop on *Recent Innovations in Sustainable Postharvest Handling and Value Addition of Agriculture Produces*’, at Department of Food Process Engineering, National Institute of Technology, Rourkela on 14-06-2023.

M.Tech. Project work :

Ms. Shruti Jha from Central Institute of Petrochemical Engineering and Technology (CIPET), Ahmedabad, has completed her M.Tech. project on ‘Development of Superhydrophobic PTFE Polymer Surface using Oxygen Plasma Processing’ under the guidance of Dr. Mukesh Ranjan.

Ph.D. Thesis defence :

Mr. Vivek Pachchigar has successfully defended his Ph.D. thesis titled “Superhydrophobic surfaces developed through argon plasma processing for self-cleaning and water harvesting technologies” on 5th June 2023 under the guidance of Dr. Mukesh Ranjan. A photograph of Mr. Vivek, along with his doctoral committee, after finishing his defence talk, is shown below.

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