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Surface Modification of Polycarbonate by Low Pressure RF Discharge

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Department of Physics, University of Malaya, Kuala Lumpur, Malaysia

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Applications of PC

components

Housing and Industrial components

Physical Properties of PC

Density	**1200 - 1220 Kg/m^3**
Refractive index	**1.584 - 1.586**
Coefficient of friction	**0.31**
Melting Point	**267^{0}C**
Linear Thermal expansion coefficient	**65-70 x 10^{-6}/K**
Specific heat capacity	**1.2-1.3kJ/Kg.K**
Dielectric Constant	**2.9**
Light transmission index	**89% to 91%**
UV light transmission	**No**
Water Contact Angle	**> 80°**

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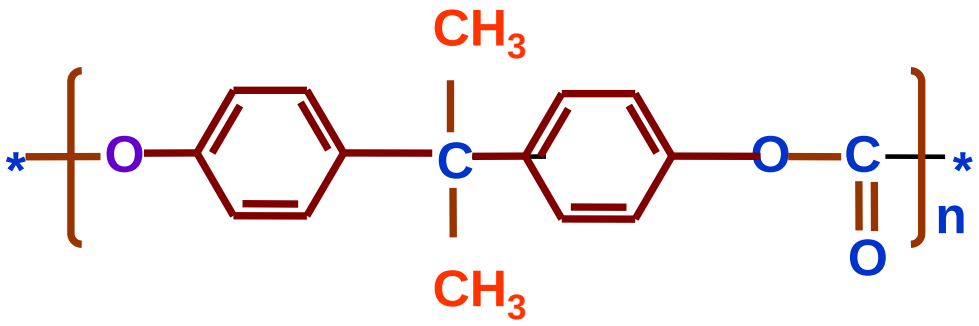
Molecular Structure of PC



Characteristics of PC

- Excellent optical and mechanical properties
- High strength to weight ratio
- Easily recyclable and moldable
- Cheaper
- Non-corrosive

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Limitations

- Thermally sensitive having low melting point
- Low surface energy and hence have poor adhesion and wettability
- Low hardness and poor scratch resistance unlike metal and glass

Remedy

- **Use of hard transparent coatings : for scratch resistance**
- **Grafting hydrophilic functional groups : for good wettabilty**
- **Formation of cross-linked layers : for better adhesion**

All these processes require an increased surface free energy for which the surface has to be modified.

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Methods of Surface modification

1. **Chemical treatment**
2. **Mechanical roughening**
3. **Treatment with flames, photons and ion beams**

But these methods have inherent problems of uniformity, reproducibility , controllability and environmental Sanitation

Plasma Surface modification

Modification of polymer surface by plasma treatment, both corona and low-pressure glow discharge, presents many important advantages and overcomes the drawbacks of the other methods mentioned above.

Therefore, plasma processes have been gaining wide acceptance over the years in diverse industrial applications.

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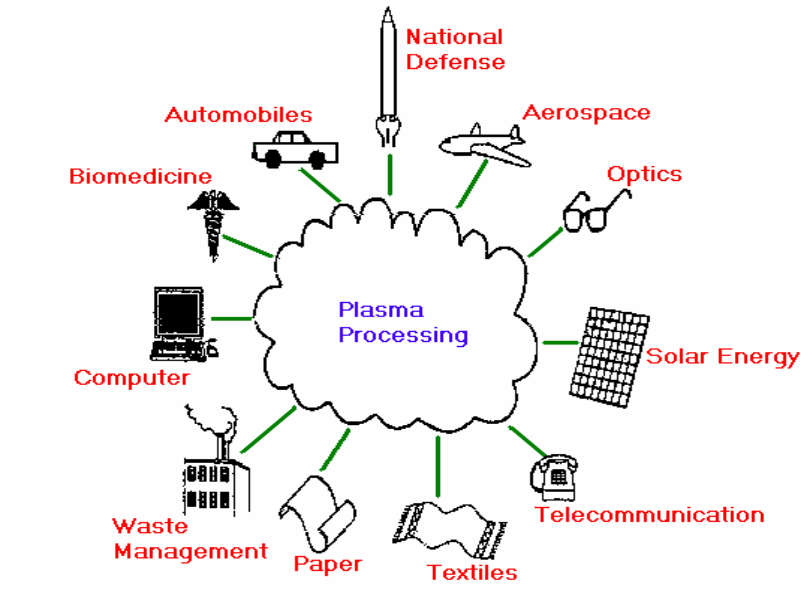
Plasma Processing



Plasma-Solid Interaction & Plasma Chemical Reactions

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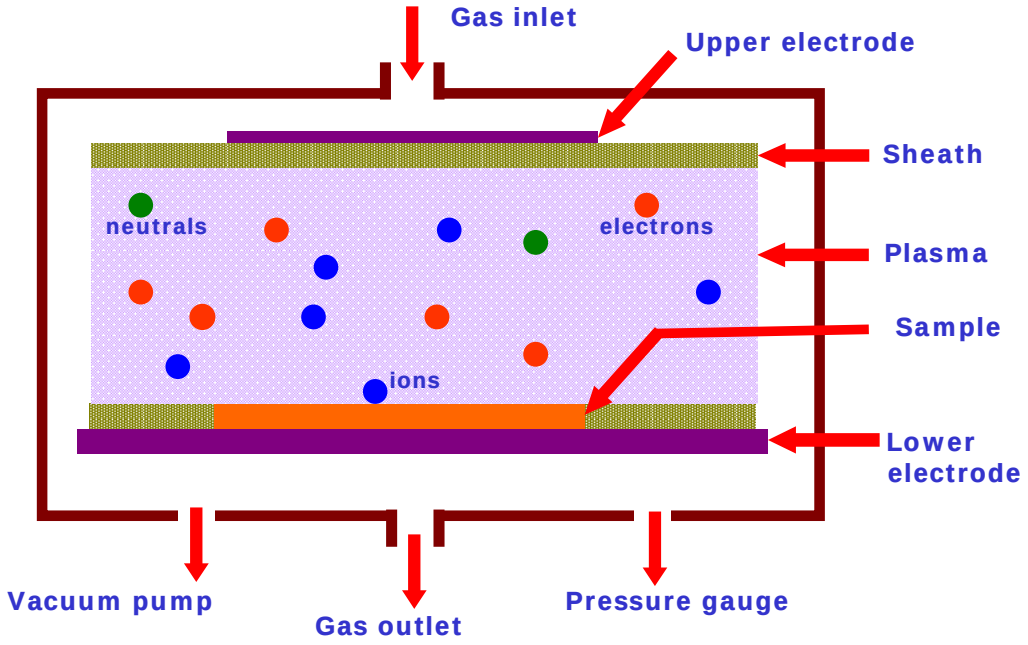
A Typical low pressure Plasma



Some Important Plasma Chemical Reactions

Excitation	$e + A_2 \rightarrow e + A_2^*$
Ionization	$e + A_2 \rightarrow 2e + A_2^+$
Dissociation	$e + A_2 \rightarrow e + 2A$
Dissociative Ionization	$e + A_2 \rightarrow 2e + A + A^+$
Electron attachment	$e + A_2 \rightarrow A_2^-$
Dissociative attachment	$e + A_2 \rightarrow A^- + A^+$
Electron detachment	$A^- + A^+ \rightarrow e + A_2$
Atom recombination	$2A + A_2 \rightarrow 2A_2$
Photoemission	$A_2 \rightarrow h\nu + 2A_2$

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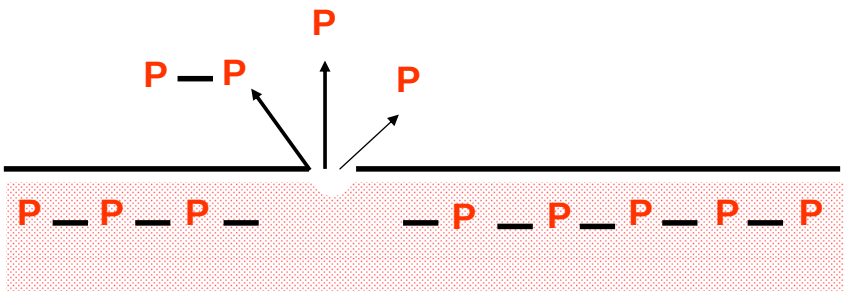
Effects of Plasma Treatment on a solid

1. **Plasma Etching: dry removal of material from the surface of an object**
2. **Surface Modification: altering the surface specific properties e.g. wettability, adhesion**
3. **Deposition of thin films: Plasma chemical reaction gives rise the formation of thin solid film**

Plasma Etching of a Polymer



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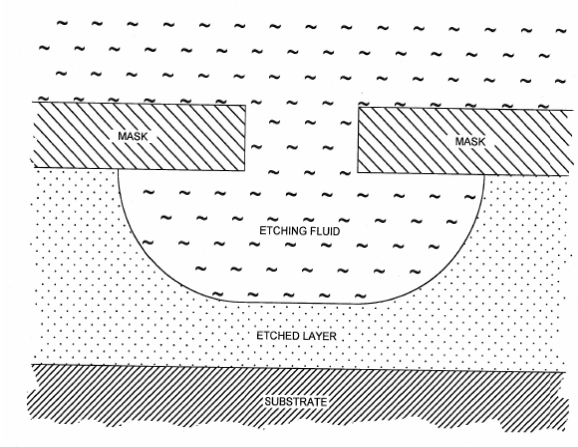
Surface Modification	Change in Surface	Surface Characteristics	Improvement of functionality
Chemical	Functional group	Wetting	Printing
Physical	Cross-linking	Adhesion	Adhesion
Additive	Crystallization	Reflectance	Coating
Clearance	Free radical implantation	Refractance	Transmittance
	Etching	Surface Tension	Medical Suitability
	Grafting	Surface Roughness	Anticlouding
		Porosity	Soaking Properties
		Hardness	

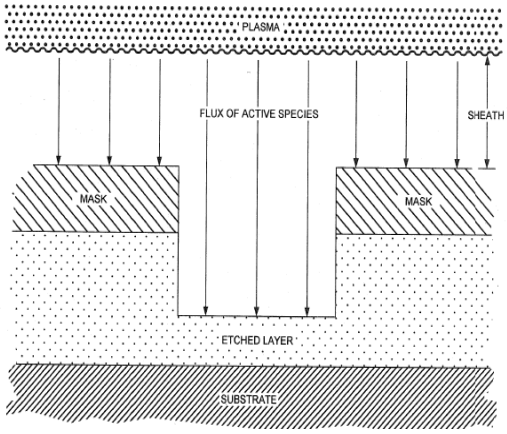
Chemical Etching

(Isotropic & poor resolution)



Plasma Etching

(Anisotropic & better resolution)



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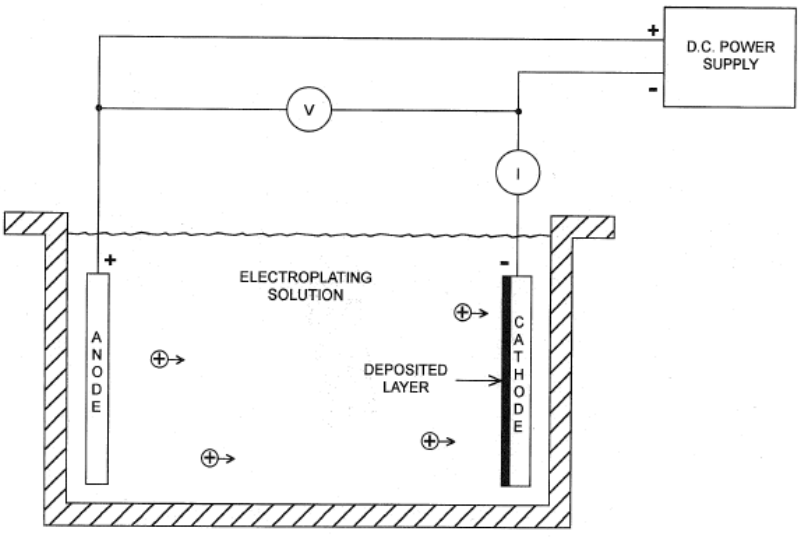
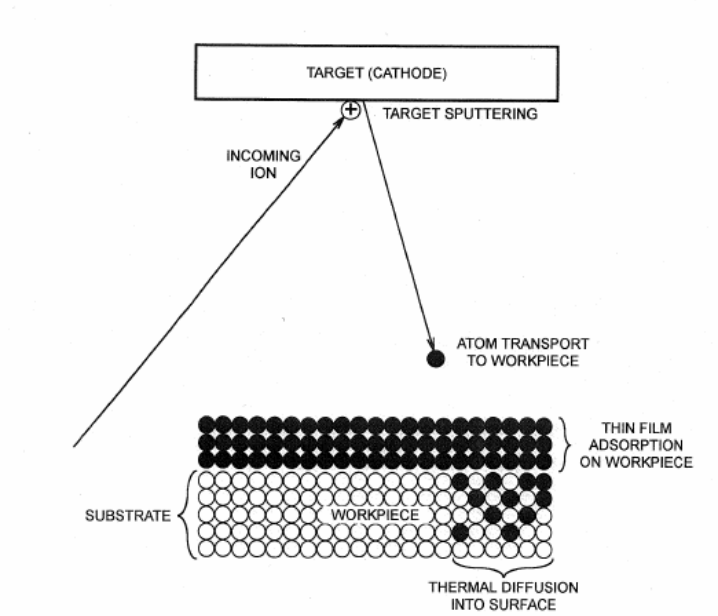
Conventional Technique for Film Deposition



Film deposition by Plasma Technique



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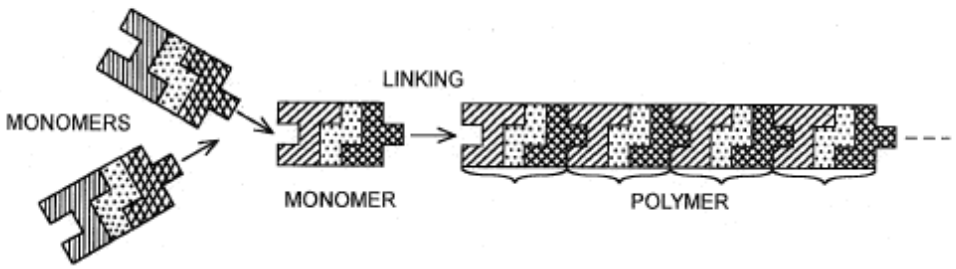
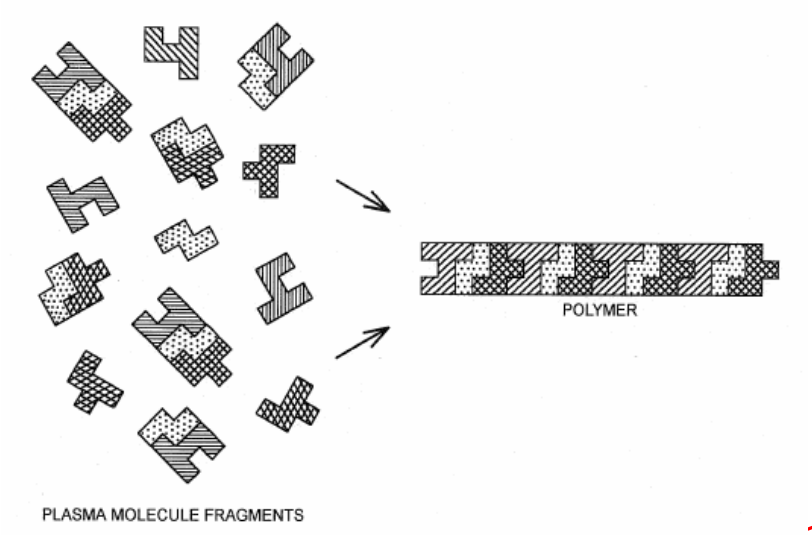
Conventional Polymerization



a) CONVENTIONAL POLYMERIZATION

Plasma Polymerization



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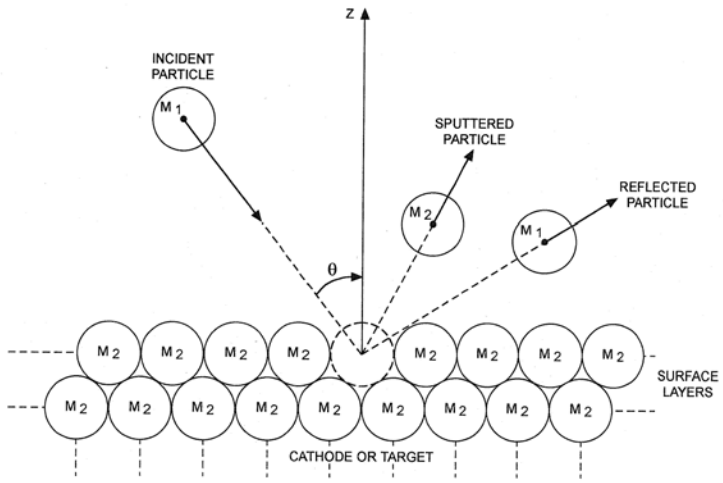
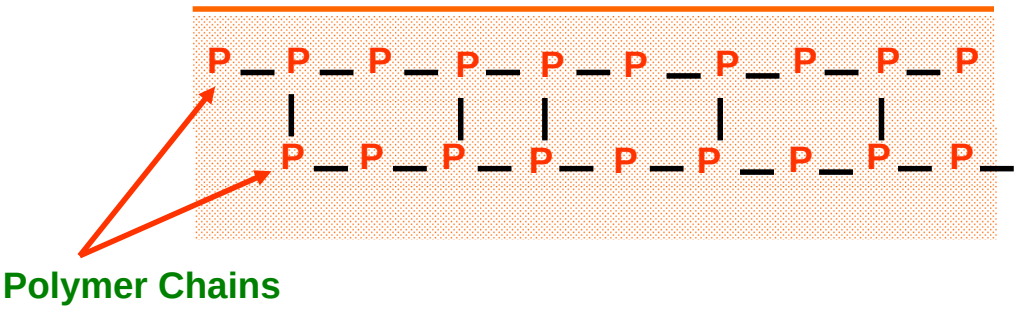
Plasma Sputtering



Plasma induced Cross-linking in polymer chain



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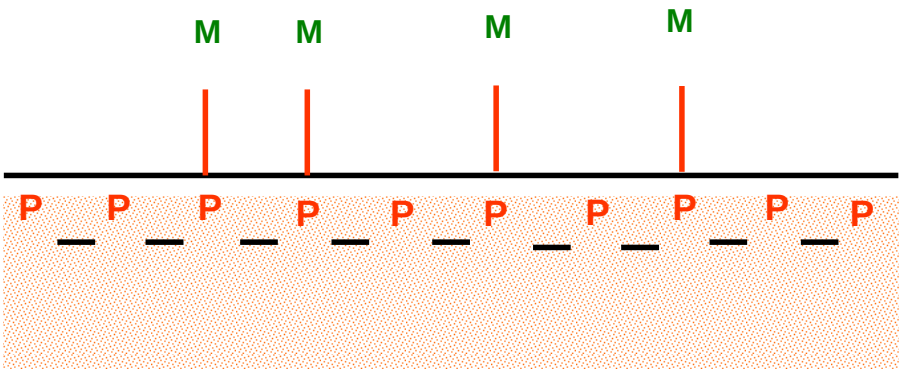
Plasma induced Functionalization



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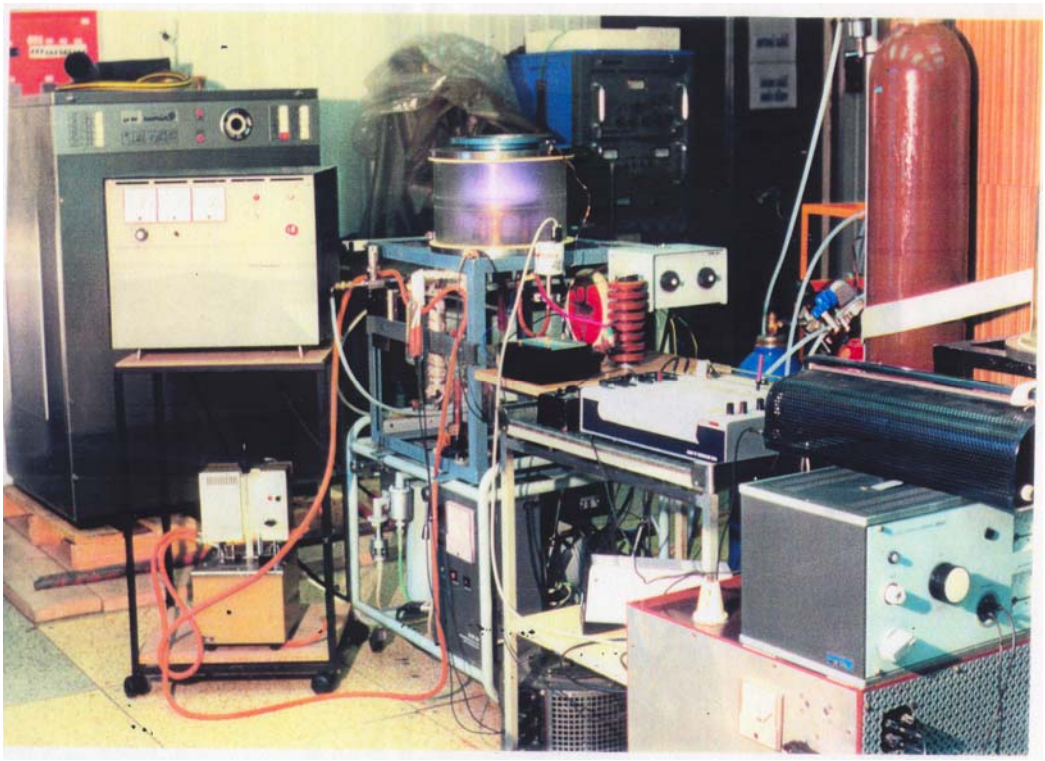
EXPERIMENTAL DESCRIPTION

A planar reactor Coupled to RF Generator

Treatment Conditions:

Reactor	**: Planar**
Working gas	**: Argon & Oxygen**
RF Power	**: 100W- 400 W**
Pressure	**: 1Pa-30Pa**
Gas Flow rate	**: 5.7-53 sccm**
Treatment time	**: 5-35 min**

A Capacitively coupled planar reactor



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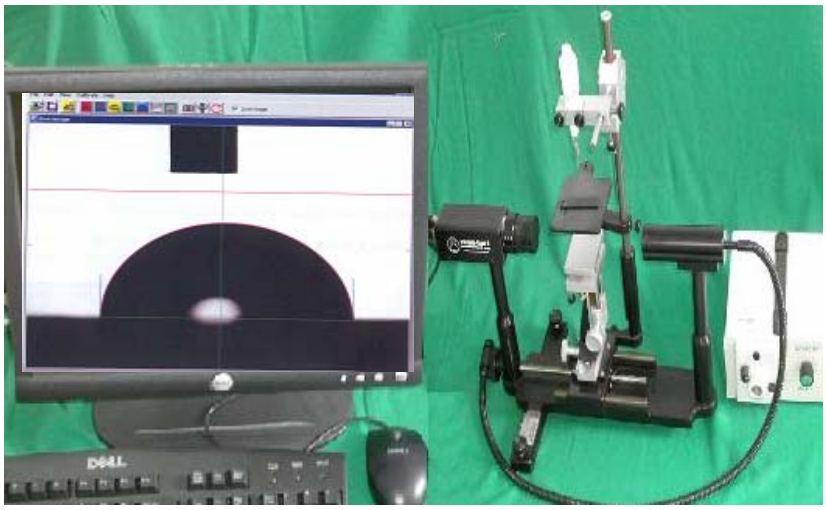
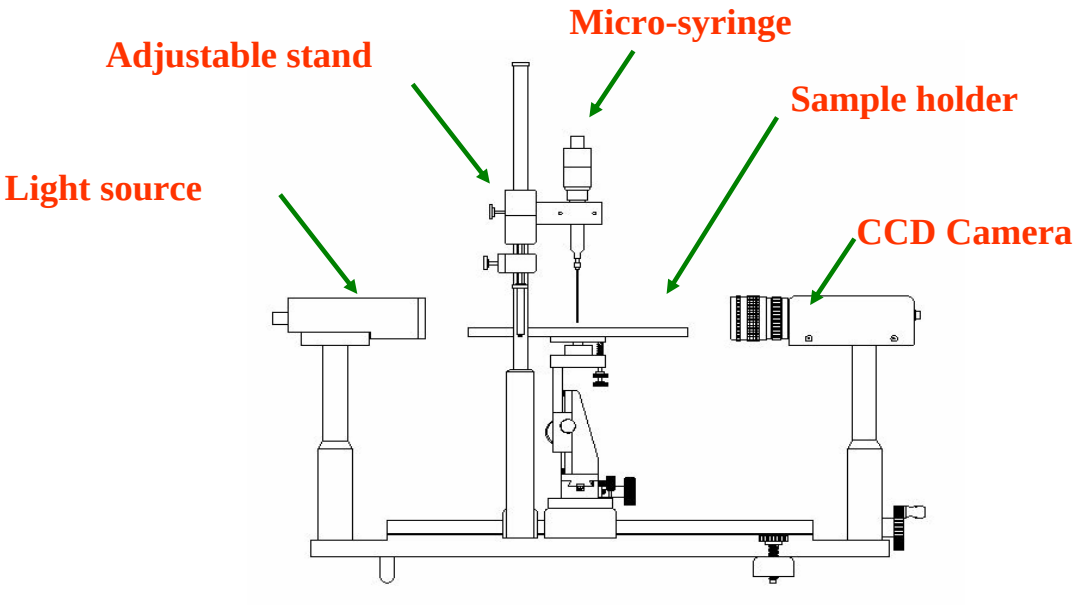
Contact Angle Goniometer



Contact Angle Measurement System



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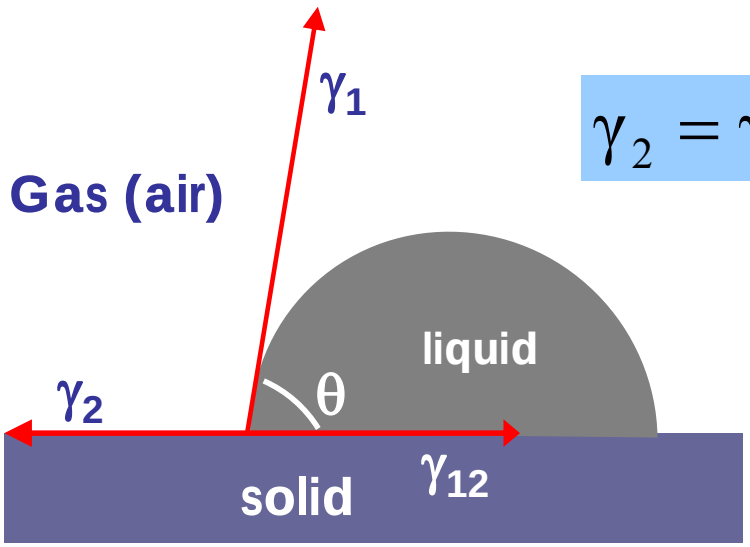
Contact Angle Measurement



$$\gamma_2 = \gamma_{12} + \gamma_1 \cos\theta$$

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Effect of Treatment in Wettability (Hydrophilicity)

Untreated sample
(Hydrophobic surface)

Sample after treatment
(Hydrophilic Surface)

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Methods of Surface Characterization

1. X-ray Photoelectron Spectroscopy (XPS): For the analysis of Chemical composition

2. Atomic Force Microscopy (AFM) : For the analysis of surface roughness

3. Contact angle measurement (CA): For the estimation of surface wettability of plasma treated materials

4. Gravimetric method: For the analysis of etching and sputtering

XPS Analysis of RF Plasma Treated PC

Gas	Power [Watt]	C (%)	O (%)	Si (%)	N (%)
Untreated	___	84.3	15.7	0	0
Ar	100	76.4	20.3	0.4	2.2
Ar	400	76.0	19.9	1.3	2.8
O_2	100	74.0	24.0	0.4	1.7
O_2	400	72.6	24.7	1.6	1.2

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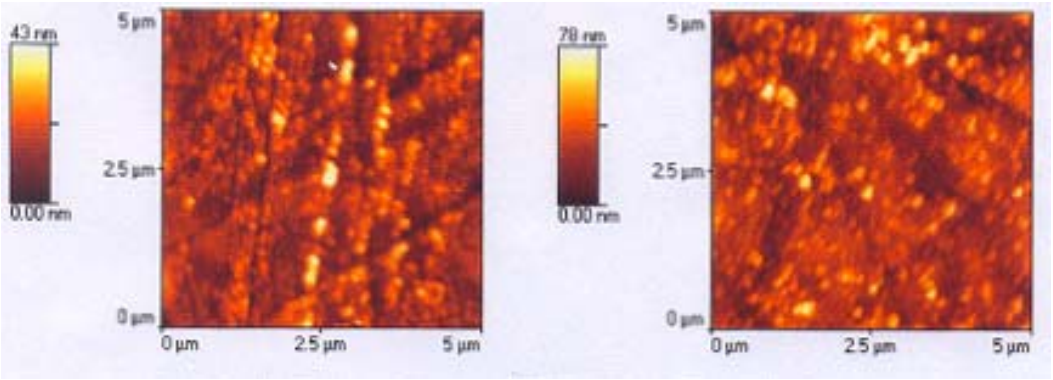
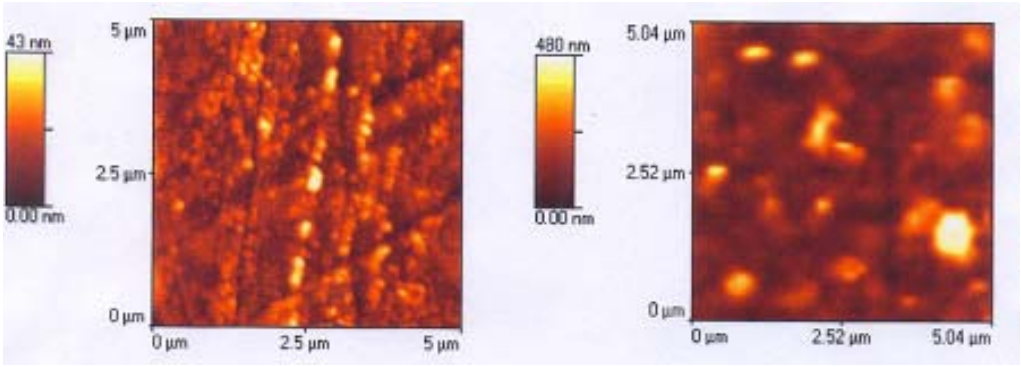
AFM Analysis of RF Plasma Treated PC



Before Treatment

After Treatment in Ar Plasma

AFM Analysis of RF Plasma Treated PC



Before Treatment

After Treatment in Oxygen Plasma

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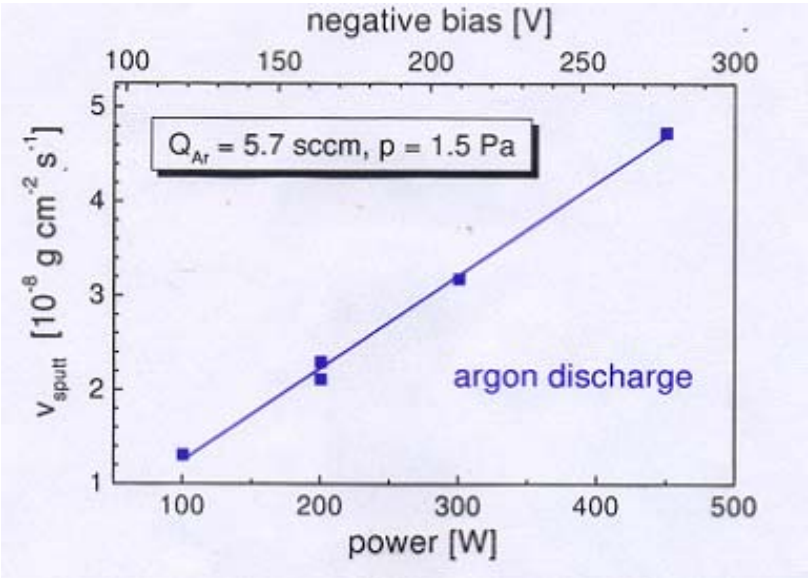
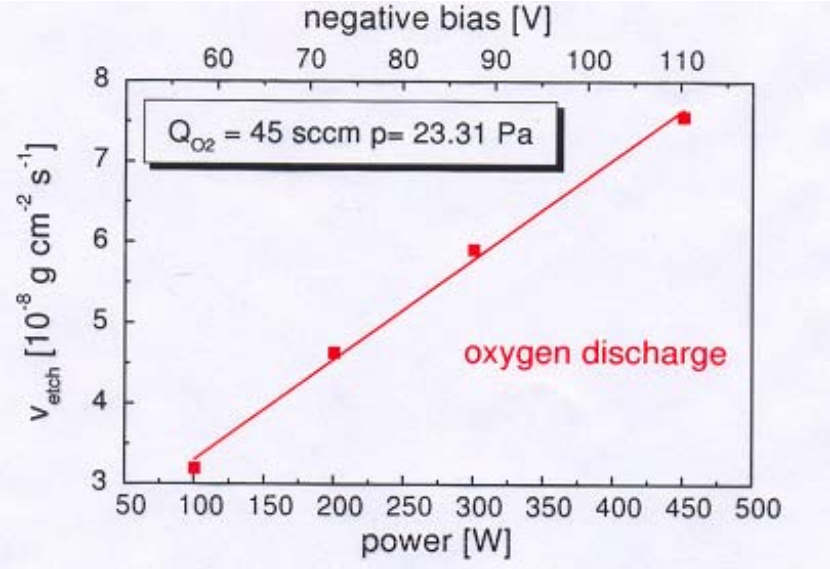
Sputtering of PC in RF Plasma



Etching of PC in RF Plasma



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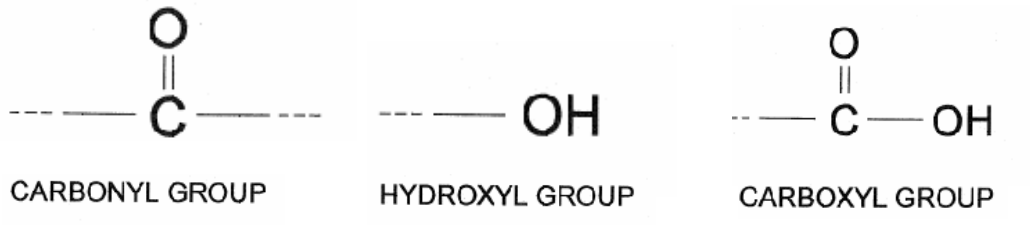
Chemical species enhancing the Wettability

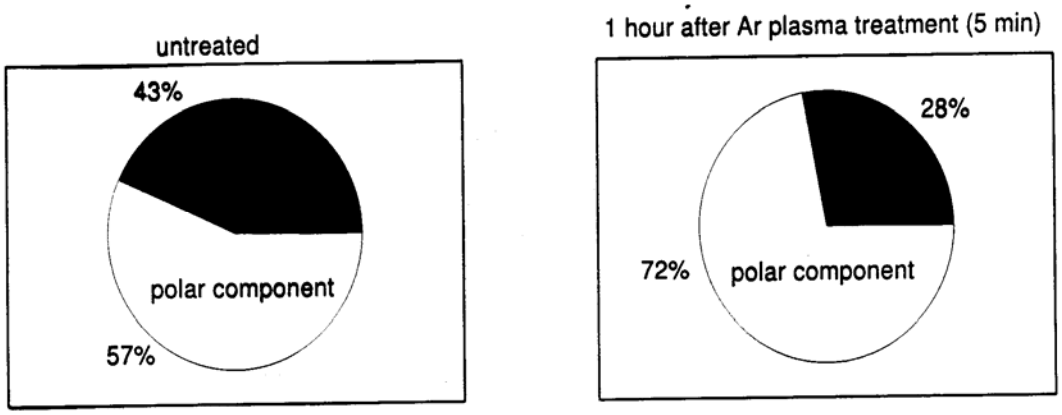


CARBONYL GROUP | HYDROXYL GROUP | CARBOXYL GROUP

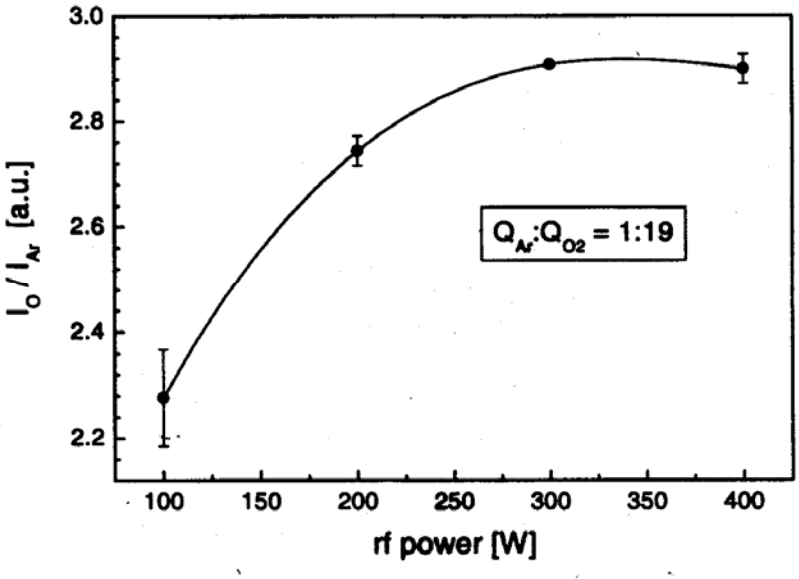
(i) **(ii)** **(iii)**

Three Chemical species which can enhance the Wettability of a hydrocarbon surface to which they attach.

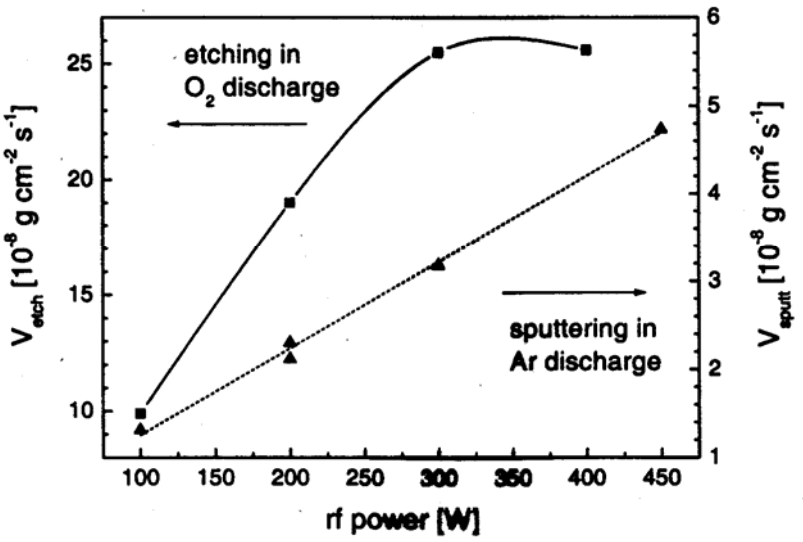
Polar and Dispersion Components



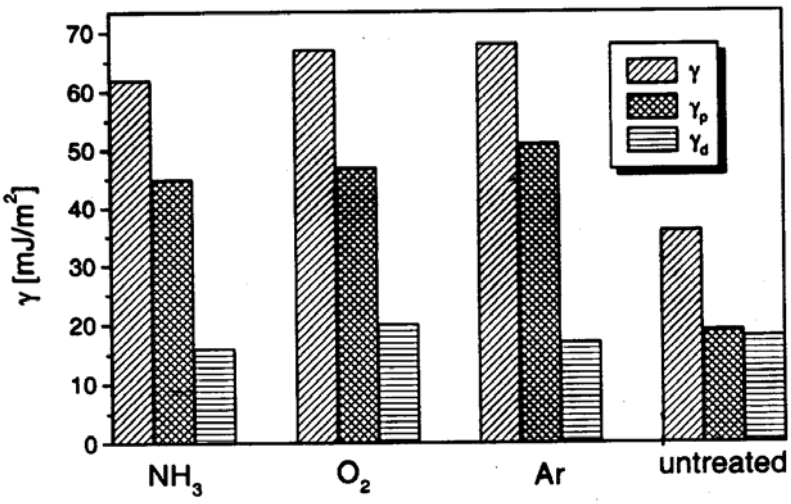
Actinometric Measurement



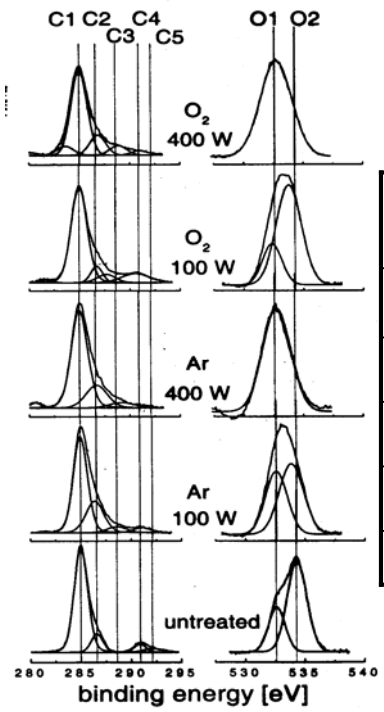
Actinometric Measurement and Etching



Polar and Dispersion components



XPS Analysis



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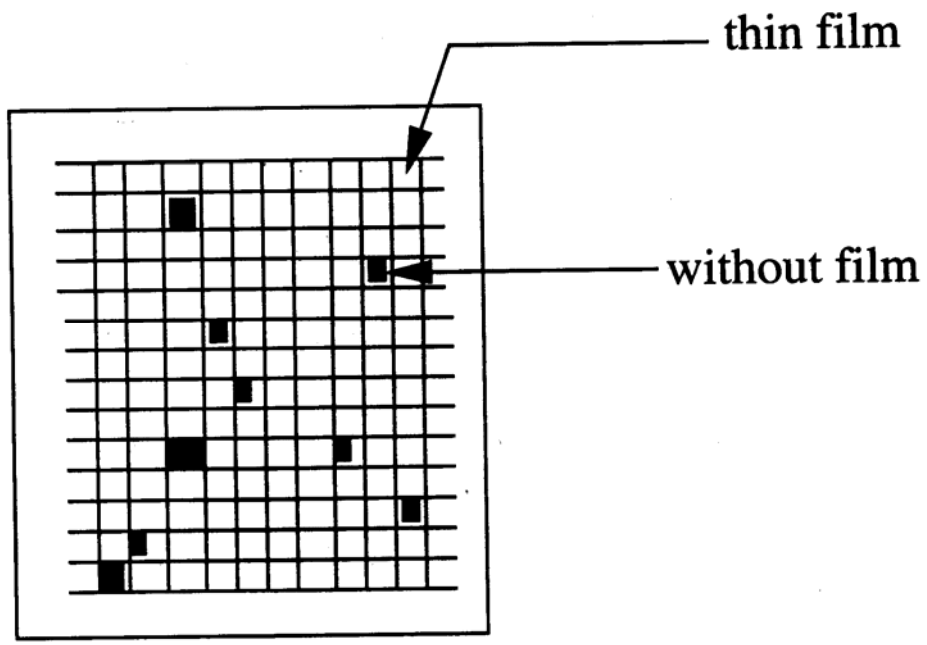
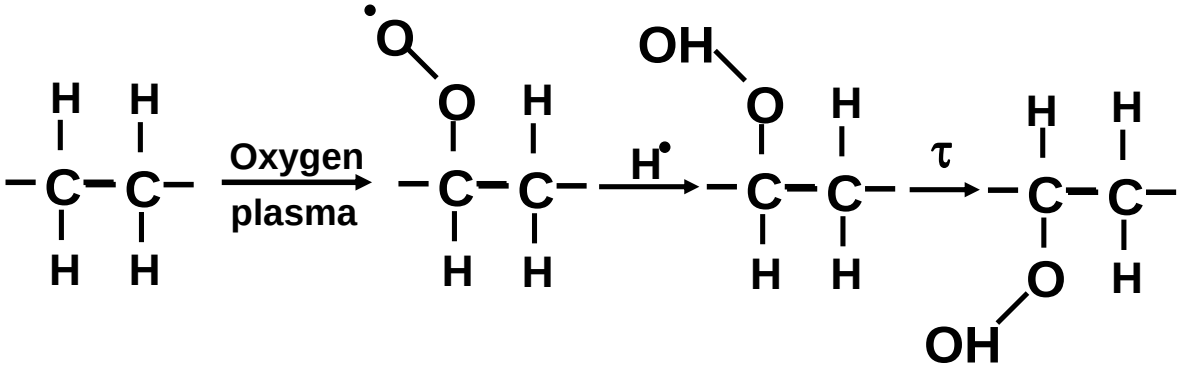
O_2	100	74.0	24.0	0.4	1.7
O_2	400	72.6	24.7	1.6	1.2

Measurement of Adhesion



Effect of Storage Time after Treatment on Wettability (Ageing Effect)



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Concluding Remark

1. Plasma treatment of PC significantly alters the O/C ratio in its composition resulting an enhanced wettability

2. An appreciable change in surface roughness after the treatment is observed which results an enhanced wettability and adhesion

3. Plasma surface modification is a reversible process

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Plasma Research Activities in Nepal

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Workshop on Low Cost Experiments on Plasma Physics, KU, Dhulikhel, 2005

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National Symposium on Plasma Physics And Material Sciences (NSPPMS), 2006, KU, Dhulikhel

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Symposium on Plasma Physics And Material Sciences (SPPMS), 2007, KU, Dhulikhel

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Symposium on Plasma Physics And Material Sciences (SPPMS), 2008, TU, Kirtipur

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Plasma Research Group at KU

1. **Dr. Deepak Prasad Subedi**
2. **Mr. Ujjwal Man Joshi**
3. **Mr. Dinesh Kumar Madhup**
4. **Mr. Ajeyandra Kumar Laghu**
5. **Mr. Raju Bhai Tyata**
6. **Mr. Devendra Rimal**

Other Collaborators

Prof. Lok Narayan Jha
Prof. C.S Wong
Mr. H. N. Poudel
Dr. Dipak Raj Adhikari
Dr. Raju Khanal
Dr. J. J. Nakarmi
Mr. Ghanashyam Shrestha
Dr. Peter Freere

Acknowledgement

I would like to express my

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THANK YOU