Modification de surface par procédés plasmas

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1879
W. Crookes defines the state of a ionized gas as “... a world where matter may exist in a 4th state ...”.

1927
Irving Langmuir first used this term to describe an ionized gas in 1927--Langmuir was reminded of the way blood plasma carries red and white corpuscles by the way an electrified fluid carries electrons and ions.

Irving Langmuir (1881-1957)
Nobel Laureate in Chemistry in 1932... for his discoveries and investigations in surface chemistry ...
Langmuir uses the word Plasma to define a neutral partially or fully ionized gas, containing neutral (atoms, molecules, radicals) and charged (ions, electrons) species.
AN ELECTRIC FIELD IS IMPOSED TO A GAS.

ELECTRONS AND OTHER CHARGED SPECIES ARE ACCELERATED AND GAIN ENERGY.

COLLISIONS AND ENERGY EXCHANGE PROCESSES OCCUR, MORE IONS AND ELECTRONS ARE FORMED, THE IONIZATION DEGREE INCREASES, MOLECULES ARE FRAGMENTED, HOMOGENEOUS AND HETEROGENEOUS REACTIONS OCCUR.

THE PLASMA IS SUSTAINED BY A BALANCE BETWEEN PRODUCTION (ionizations) AND LOSS (recombinations) OF CHARGED SPECIES.

Reactive species: Ions, electrons, radicals, Excited species, photons...
Three classes of plasmas...

« Hot plasmas »
Millions of degrees

Sun

« Thermal plasmas »
Few thousands of degrees

Tokamak

Welding, Metallurgy, Plasma spray deposition, ICP spectroscopy, Waste abatement

→ ITER: International Thermonuclear Experimental Reactor

« Cold plasma »
Few hundreds of degrees

→ Surface treatment of thermosensitive materials
70’s
• First plasma etching processes
• Plasma processes started to be applied for surface modification of materials, in the field of microelectronics and semiconductors

80’s
• deposition processes for semiconductor thin films for solar cells (α-Si:H)

90’s
• Polymers, textiles, packaging, biomaterials, paper, ceramics, metals, MEMS, composites, etc. fully exploit plasmas

Consider PLASMA a tool to engineer materials
Plasma/surface Interaction?

Plasma processing of materials?

Positive and negative effects of plasma processing?
SURFACE MODIFICATION PROCESSES IN COLD, LOW PRESSURE PLASMAS

1. Etching
   - CO, CO2, H2O, NO...
   - volatile products
   - cold burning process
   - Cleaning of a silicon surface (Ar/H2)
   - Cleaning of a fluorinated surface (+H2)
   - Etch rate: Few hundred nm/min

2. Treatment
   - Adhesion, wettability...
   - Non polymerizable gas: O2, Ar/O2
   - Non polymerizable gas: O2, N2, NH3...
   - Polymerizable gas

3. PE-CVD (coatings)
   - Food packaging, Corrosion protection,
     Biomolecule immobilization in biomaterials and sensors;
   - 100 Å - 100nm typical size
   - Few tens of Å
SURFACE MODIFICATION PROCESSES IN COLD, LOW PRESSURE PLASMAS

1. Etching

2. Treatment

3. PE-CVD (coatings)

Volatile products

Plasma/Surface?

Polymerizable gas

100 Å - 100nm typical size

Food packaging, Corrosion protection, Biomolecule immobilization in biomaterials and sensors;

Adhesion, wettability...
Applications:
- Textile (stain resistant...)

Non adhérence:
- Hydrophobic material, non wettable

Adhésion:
- Hydrophilic surfaces, wettable

Applications:
- metal/polymer adhesion, ink/polymer
Plasma surface modifications of PE with NH3 plasma

Untreated PE

**C_{1s}**

(C-C, C-H) 285 eV

Binding energy, eV

NH3 Plasma treated PE

**C_{1s}**

(C=N, C=O) (287.1 eV)

(C-C, C-H) 285 eV

COOH

CONH₂ (288.3 eV)

(C-NH₂, C-OH) (286.1 eV)

Binding energy (eV)

Adhesion
PLASMA TREATMENTS OF POLYMERS

Ions, metastables

Plasma

1. Creation of radicals (activation)

2. Grafting

3. Volatilization of LMWOF (C, H, O)

4. Etching

Elimination of LMWOF (CO$_2$, CO, H$_2$O)

Boundary layer

Inert gas (He, Ar…)

COOH
CONH$_2$
OH
CHO

Substrate

Ar, He: Cross-linking by ion bombardment, VUV

O$_2$, air, CO$_2$…: Increased surf. energy & wettability, sterilization, etching occurs.

CF$_4$, CF$_4$/O$_2$…: Etching occurs, Textile (stain resistant…)

H$_2$: For pre-treatments, F-abstraction, cleaning, surface reduction. Limited polymer degradation, mild treatments.

N$_2$, NH$_3$…Grafting N-groups, increased surf. energy & wettability, limited etching, poor selectivity, sensitive to ageing
Drawback 1: Poor selectivity of the plasma treatment process
Drawback 1: Poor selectivity of the plasma treatment process

Untreated PE

NH\textsubscript{3} Plasma treated PE

Poor selectivity of the process
SOLUTION???
1. NH3 Plasma

2. H2 Plasma

H₂* → 2H
Selective grafting of \(-\text{NH}_2\) groups on PE by means of plasma treatments in \(\text{NH}_3\) and \(\text{H}_2\)

P. Favia et al, Plasmas & Polymers; 1, 91, 1996

\[\begin{align*}
\text{NH}_2 & \quad \text{NH}_2 & \quad \text{NH}_2 & \quad \text{NH}_2 & \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{NH}_2 & \quad \text{NH}_2 & \quad \text{NH}_2 & \quad \text{NH}_2 \\
\end{align*}\]

H2 plasma treatment time (s)

\[\begin{align*}
\text{NH}_2 / \text{N} & \\
\end{align*}\]

efficiency / selectivity after H2 discharge

\[\begin{align*}
\text{efficiency} & \quad \text{selectivity} \\
\end{align*}\]

H2 plasma treatment time (s)

\[\begin{align*}
100 \% \text{ H}_2 \text{ feed} & \\
10 \text{ sccm} & \\
10 \text{ Watt} & \\
500 \text{ mtorr} & \\
\end{align*}\]
Drawback 2: Plasma treated polymeric materials aged quickly…
Ageing of plasma treated materials

Freshly treated material

3-5 days

Ageing time

WCA

untreated polymer

hydrophobic polymers, grafted with polar (hydrophilic) groups, loose properties with time in air (= hydrophobic recovery)
The physical problem = ageing

HYDROPHOBIC RECOVERY

plasma treatment

time
Mécanisms

Adsorption by atmospheric contaminants

Reorientation

Diffusion of additives or low molecular weight fragments

To avoid superficial degradation of the topmost surface layer
To reinforce the cohesive strength of the compost surface layer via CASING process
How to limit ageing?

To limit the chain mobility by crosslinking reactions

Chain Reorganisation

He Pretreatment + \( \text{NH}_3 \)
Other solution??
How to decrease the ageing of PT polymers?

1. Immobilization of adherent immediately after the treatment

2. To avoid the rearrangement of grafted polar groups

3. To crosslink the topmost surface layer by He pretreatment

Other solution → Plasma deposition of a thin coating
Aging of a plasma treated PS-surface

contact angle (water)

50° C
20° C
-9° C

Plasma treated PS
Coatings
SURFACE MODIFICATION PROCESSES IN COLD, LOW PRESSURE PLASMAS

1. Etching

Plasma/Surface?

volatile products

2. Functionalization

Adhesion, wettability...

Polymerizable gas

100 Å - 100nm typical size

3. PE-CVD (coatings)

Food packaging, Corrosion protection, Biomolecule immobilization in biomaterials and sensors;

SURFACE MODIFICATION PROCESSES IN COLD, LOW PRESSURE PLASMAS

1. Etching
2. Polymerisable gas → PECVD

PE-CVD PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

Inorganic (SiO$_2$, DLCs...) and organic (silicone-, PEO- teflon-like...) coatings can be deposited. PLASMA POLYMERIZATION is jargon name for PE-CVD of organic coatings;
Mechanisms of Plasma Polymerization?

The preferred locus of plasma polymerization is a subject of controversy…

(i) In the gas phase  
(ii) Or in the layer adsorbed on the substrate
Plasma polymerisation process

Plasma

C₂F₄, C₂F₆

3D structure (depending on the degree of crosslinking)

Presence of different groupments
CF₂, CF₃, CF, C-CF, CHF, CHF₂

Specificity of plasma polymerised coatings

1. Ultra thin, pinhole-free layers of various compositions can be deposited as plasma polymers

2. Not a conventional polymerisation process: No repetition of the structure of the initial monomer

1. The physico-chemical properties of the coating are controlled by the plasma parameters (power, pressure) and not only by the starting monomer
Plasma-enhanced chemical Vapor deposition Reactor for Organic/inorganic coatings
Today:
there is a strong need to retain the monomer structure
during plasma polymerisation process

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{CH}_2=\text{CH} & \quad \text{CH}_2=\text{CH} \\
\text{Vinyl} & \quad \rightarrow & \quad \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}
\end{align*}
\]

n monomer with functional groups X

Polymer with \( n-y \) functional groups X

\( X : \text{Functional group}= \text{NH}_2, \text{COOH}, \text{SH} \ldots \)

To control the reaction selectivity
To control the stability of the coating

Use of modulated discharges (Pulsed discharges)
How to control the selectivity of the process?

Polymerization under continuous wave plasma

H. Yasuda introduced an important factor (Yasuda factor)

$$YF = \frac{W}{FM} \text{ (wattage/Molar mass x monomer flow)}$$

For the case of high values of $W/FM$, all monomer molecules are extensively fragmented into single atoms and the monomer composition and structure is barely recognizable in the resulting plasma polymer structure and composition.

$$ABCDEF + \text{ plasma} \rightarrow A + B + CD + E + F \rightarrow [\text{FCABDE}]_n$$

Yasuda proposed a new mechanistic concept in the 70's which he called « Atomic polymerization »
How to use LOW values of W/FM ??

Introduction of the pulsed-plasma technique, which corresponds to the greatest innovation in the field of plasma polymerization was ...

**POWER MODULATION**

**Modulation Parameters**

- Period = $t_{ON} + t_{OFF}$
- Duty Cycle = $(t_{ON}/\text{Period}) \times 100$

**Effective power**

$W_{eff} = W_{tot} \times DC$
Linear polymeric structures
Low degree of crosslinking

A clever choice of « monomer » must be done to produce specific characteristics
corrosion resistant coatings

(Silica coatings from Organosilanes...)

antifouling coatings
Ether rich coatings
From glycols precursors

Scratch and abrasion-resistance (DLC coatings from CH4/Ar plasmas)

Teflon like coatings… from fluorinated monomers

anti-stain clothes

anti-ice on plane wings

transparent barrier Films for food packaging

poly(vinyl alcohol) (PVA) layers

anti-fog

Super hydrophobic coatings
XPS

Decrease of the DC (low $W_{eff}$)

Increase of % $\text{CF}_2$

"teflon-like" structure

R. d’Agostino (Bari, Italie)
Plasmas Processes and Polymers, 2004
“Super Hydrophobic” Plasma Deposited Coating

PTFE  \( \text{WCA} = 118^\circ \)

\[ \text{DC} = 5\% \quad \text{Period} = 200 \text{ ms} \]
\( \text{WCA} \geq 160^\circ \)

Polyethylene PE  \( \text{WCA} = 90^\circ \)

Nanosized ribbons of crystalline teflon produced with modulated Discharges (releasing coating)

R. D’Agostino et al.
Plasma processes for cell adhesion

**INHIBITION**
PEO-like coatings

PEO \( -(\text{CH}_2\text{CH}_2\text{O})_n- \)

**PROMOTION**
Grafted N-groups
-\( \text{COOH} \) functional coatings

Key Parameter: retention of the PEO structure in the coating

Feed: glycols
1. Oligoglymes \(((\text{CH}_3\text{-O-})\text{(CH}_2\text{-CH}_2\text{-O)}\text{n-CH}_3, \text{n}=1-4)\)


Diglyme (n=2) Di(ethylene glycol) dimethyl ether ou 2-Methoxyethyl ether \((\text{C}_6\text{H}_{14}\text{O}_3)\)

DIGLYME 5W :
- antifouling +++ sur fibroblastes
- Surface de contact cellule/support minimale

R. Gristina et al.
CH₃O-(CH₂CH₂O)₃-CH₃
TEGDME monomer

PEO structure retention

C₀ = C-C/C-H
C₁ = C-O -> non fouling
C₂ = C=O
C₃ = COOR

“PEO” CHARACTER

R. d’Agostino et al.
TRANSPARENT BARRIER FILMS \( \text{SiO}_x \)

- LOW GAS TRANSMISSION RATE (food, pharmaceutical packaging)
- MW compatibility
- HARDNESS
- TRANSPARENCY
- INERTNESS
- CORROSION RESISTANCE
- DIELECTRIC PROPERTIES

In optimum conditions, \( \text{O}_2 \) GTR in industrial scale ranging between 3 and 10 cm\(^3\) m\(^{-2}\) day

**Key Parameters**
- monomer/\( \text{O}_2 \) ratio
- input power (fragmentation)

**MONOMERES**

- HMDSO
- TEOS
- HMDSN
- TMS

\[
\begin{align*}
\text{HMDSO} & : \text{CH}_3 & \text{Si} & \text{O} & \text{Si} & \text{CH}_3 \\
\text{CH}_3 & \text{Si} & \text{O} & \text{Si} & \text{CH}_3 & \\
\text{CH}_3 & \text{Si} & \text{N} & \text{Si} & \text{CH}_3 & \\
\text{CH}_3 & \text{Si} & \text{CH}_3 & \\
\text{TEOS} & : \text{CH}_3 & \text{CH}_2 & \text{O} & \\
\text{HMDSN} & : \text{CH}_3 & \text{Si} & \text{N} & \text{Si} & \text{CH}_3 & \\
\text{TMS} & : \text{CH}_3 & \\
\end{align*}
\]
SiOx film composition at different feed ratios

R. D’agostino et al.
PECVD of SiO$_2$-like films

Silanols drill holes in high density SiO$_x$
Stability??
ORIGIN OF AGEING

Water contact angle

Non treated before washing

120°

< 10°

45-50°
Use of microfluidic devices to understand the properties of plasma deposited materials

IPGGM: Pierre Gilles de Gennes Institute for microfluidic
Microfluidic device: A tool to evaluate the stability of Plasma polymerized coatings

- Elastomer, rather inert, hydrophobic
- Dedicated material for micro-fabrication

Emulsions: oil in water (O/W)

Continuous phase (Water)

Entry into the microchannel

PDMS

\[
\begin{align*}
\text{CH}_3 \\
\text{Si-O} \quad \text{Si-O} \\
\text{CH}_3
\end{align*}
\]

Modification of PDMS surface is necessary

Uncoated PDMS

120°

200 μm

10 cm

Continous phase

Elastomer, rather inert, hydrophobic

Dedicated material for micro-fabrication
After optimization of the plasma process parameters…

PDMS + dépôt AA

C-Si : 100 %

C-Si : 32 %

C-C : 42 %

COOH : 23.1 %

wettable
1. Pretreatment: Ar Plasma

2. Deposition of PAA

3. Post-treatment: He plasma

Optimization

Avoid partial dissolution of the coating

Crosslinking

Multi step process

PAA coating (Hydrophilie)

Réticulation

SUPPORT - PDMS
Evolution of the COOH/C1s ratio measured by XPS as a function of the plasma power (role of washing).

A compromise has to be found between selectivity/stability.

Use of an O2 plasma treatment

0h

36h

24h

48h

Ageing
Treatment of flat substrates is easy...
3D objects?
Plasma treatment of powders in a Fluidized Bed Plasma Reactor

Diameter: few microns to hundred of microns...

- Continuous agitation of the particles: homogeneity in the treatment of powders
- Decrease of the particle agglomeration
- Large exchange surface between the particles and the gas phase (plasma)
- Excellent heat transfer: reducing the risk of thermal degradation
Industrial plasma reactors...
With the courtesy of Prof. D’ Agostino
Industrial Coating Technologies for SiOx Barrier Material

- **Sputtering**
  - Material Source
  - Argon
  - Chill Drum

- **Evaporation**
  - Evaporation Source
  - Oxygen
  - Chill Drum

- **PECVD**
  - Disiloxane & O₂
  - Plasma
  - Chill Drum

<table>
<thead>
<tr>
<th>Process</th>
<th>Speed (m/min)</th>
<th>Thickness (nm)</th>
<th>Gas Consumption (cm³/(m² day atm))</th>
<th>Mechanical Resist</th>
<th>Heat Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering</td>
<td>200</td>
<td>40 – 50</td>
<td>3</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Evaporation</td>
<td>300</td>
<td>100 – 500</td>
<td>3</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>PECVD</td>
<td>200</td>
<td>15 – 20</td>
<td>3</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>

Tetra Pak R&D Proprietary Document
Industrial PECVD Equipment at Tetra Pak

Plain PET 12 μm
120 cm³/m²/day/atm

PET/SiOx (15 nm)
< 3 cm³/m²/day/atm

= Electrical Power + Gas mixture (Disiloxane, Oxygen)

Tetra Pak R&D Proprietary Document
Our plasma reactors...

PECVD

PECVD/Sputtering/Evaporation
Other technique:
RF SPUTTERING TECHNIQUE
The hybrid RF magnetron sputtering and expanding thermal plasma CVD setup

TEM images of Au nanoparticles prepared on carbon-coated copper grids at various RF-power settings

Nanoparticles size

1.6 nm  4.7 nm  7 nm

Microreactors!!!

μChannel:
- Width = 4 mm
- Length = 50 mm
- Depth = 500 μm
Ar discharge
7 kV – 1 kHz
Other applications…

Non-thermal plasma in air at atmospheric pressure

**Typical applications:**
- Ozone production
- Treatment of polluted gaseous effluents

*DBD device for air treatment*
The expanding pollution of drinking water sources and increasingly stringent regulations promote the development of new, innovative treatment technologies.

Conventional water treatment methods are often not effective in the removal of micro-pollutants such as Volatile Organic compounds (VOC's) because of their physical and chemical characteristics.

Henry’s law constants at 25°C (atm.m³.mol⁻¹)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Henry’s Law Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>1.21</td>
</tr>
<tr>
<td>MIB</td>
<td>1.67</td>
</tr>
<tr>
<td>NDMA</td>
<td>0.63</td>
</tr>
<tr>
<td>1,4 dioxane</td>
<td>1.24</td>
</tr>
<tr>
<td>MTBE</td>
<td>3.8</td>
</tr>
<tr>
<td>Heptanol</td>
<td>2×10⁻⁵</td>
</tr>
<tr>
<td>TCE</td>
<td>1×10⁻⁴</td>
</tr>
<tr>
<td>MIB</td>
<td>6.5×10⁻⁵</td>
</tr>
<tr>
<td>NDMA</td>
<td>3.34×10⁻⁵</td>
</tr>
<tr>
<td>1,4 dioxane</td>
<td>5×10⁻⁵</td>
</tr>
<tr>
<td>MTBE</td>
<td>6×10⁻⁴</td>
</tr>
</tbody>
</table>
The micro-structured electrode is covered by a coating exhibiting catalytic and hydrophilic properties.
CONCLUSION:
SURFACE MODIFICATION OF MATERIALS WITH LP PLASMA TECHNIQUES

PLASMA TREATMENTS: Modification of the topmost layers of materials (polymers) by grafting chemical groups

Selectivity: (-) → Controlled by gas feed
Stability: Problem of ageing → Additional pretreatment in inert gas (He, Ar…)

PE-CVD PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

High reaction selectivity: (+) → Controlled by the modulation of power input
Stability: Problem of dissolution → Control of the degree of crosslinking
CONCLUSION:
Consider PLASMA a tool for new applications

- Polymer activation for enhancing metal adhesion
- Polymer activation for enhancing color adhesion (e.g. car bumpers, plastic bags, textiles, ...)
- Stain-resistant clothings and garments
- Super-hydrophobic coatings
- Corrosion resistant coatings for alloys
- Tissue engineering and microstructuring of polymers for contact guidance of cells
- Anti-trombotic coatings for prostheses
- Bacterial resistant materials for food packaging and prostheses
- Non fouling coatings
Acknowledgements

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Thank you for your attention