Plasma Polymerization in Industrial Applications

e$^-\rightarrow$ film-forming species $\downarrow$ deposition

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Motivation

Plasma polymerization

Conversion of ‘monomer’ gas molecules into film-forming species via gas phase processes yielding plasma polymer films (PPFs) involving surface processes.

\[ C_2H_4 \text{ plasma} \]
\[ \text{at 250 Pa} \]
\[ (n_{\text{max}} \approx 6 - 10) \]

→ highly branched PPF

J.M. Tibbitt et al.,

Succeeds in polymerizing monomer units also at low pressure, including organic molecules characterized by saturated bonds – unlike conventional (chain-growth) polymerization.

\[
\left[ \begin{array}{c}
\star \text{CH}_2 \text{CH}_2 \star \cdots \star \text{CH}_2 \text{CH}_2 \cdots \star \text{CH}_2 \text{CH}_2 \cdots \\
\text{C}_2\text{H}_6 \\
\text{C}_4\text{H}_9 \\
\text{C}_9\text{H}_{13} \\
\end{array} \right]_n
\]

linear low density polyethylene (n ≈ 10’000 - 100’000)
Motivation

Plasma polymerization – gas phase + surface processes

### Motivation

Field of industrial applications for plasma coatings

#### Diamond-like carbon (DLC) coatings

<table>
<thead>
<tr>
<th>process</th>
<th>type of DLC</th>
<th>hardness</th>
<th>surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>cathodic arc deposition</td>
<td>ta-C: ta-C:H</td>
<td>20-55 GPa</td>
<td>rough</td>
</tr>
<tr>
<td>sputter deposition</td>
<td>a-C: a-C:H:Me</td>
<td>15-30 GPa</td>
<td>smooth</td>
</tr>
<tr>
<td>plasma polymerization</td>
<td>a-C:H, a-C:H:Si</td>
<td>5-25 GPa</td>
<td>smooth</td>
</tr>
</tbody>
</table>

→ higher deposition rates by plasma polymerization

H. Tamagaki, PSE2016
Motivation

Field of industrial applications for plasma coatings

PLASMA APPLICATIONS @ BOSCH
PROCESS STEPS OF DLC COATING

► Loading the vessel with components and evacuation
► Plasma Etching  Cleaning process by low pressure plasma
► Adhesion Layer  PVD (Physical Vapor Deposition)
► Transition Layer  Combination of PVD and PECVD (Plasma Enhanced Chemical Vapor Deposition)
► Functional Layer  PECVD: Mainly ion bombardment determines the DLC properties
► Venting of vessel and unloading

(≈1-2 μm)

Matthias Müller, ROBERT BOSCH MANUFACTURING SOLUTIONS GMBH
PLASMA GERMANY Frühjahrssitzung April 2019, Karlsruhe
Motivation

Field of industrial applications for plasma polymer films (PPFs)

hard coatings / semiconductors / optical coatings / barrier coatings / functional coatings

→ predominantly inorganic coatings (dominated by conditions at film growth)

→ control of gas phase and surface conditions required

DLC 

c-Si

GaN

solar cells

SiO₂

PET bottles

C:H:O

contact lenses

blood filtration

engine parts

TiO₂/SiO₂

ICs LEDs

SiO₂/SiO:CH

AR coatings

barrier foils

‘polymer-like’ PPFs
Outline

Plasma Polymerization in Industrial Applications

- Plasma polymerization mechanism
  - coupling of microscopic and macroscopic parameters
  - specific energy input and energy transfer
  - production of film-forming species

- Gas phase and surface processes
  - control of film properties

- Monomers: HMDSO, hydrocarbons (+ reactive gases)
  - plasma polymer films for industrial applications

- Economic robust processing for diverse industrial applications
  - ’simple’ process optimization and control
Plasma Polymerization

Involved steps and some related governing equations

- activation of monomer
  - excited species
  - ions
  - radicals
  - low molecular reaction products

- diffusion flow
  - discharge current
  - gas flow

- surface processes
  - adsorption
  - desorption
  - recombination
  - reaction
  - chain-branching
  - solution of products in film

- process of film growth
  - (substrate)

- mounting of films
  - crosslinking in the near surface-region induced by energy carriers
  - interface layer with embedding of radicals
  - substrate surface dominated structure

Energy per monomer molecule (specific energy input, $SEI$)

$$E_{pl} = \left. \frac{W_{abs}}{F_m} \right|_{pl}$$

Flux of film-forming species (conversion of monomer)

$$\Gamma_{dep} = \frac{F_m}{A_{dep}} \cdot f(T_e) \cdot f(E_{pl})$$

Sticking probability

$$s = f(E_d, \tau_{surf})$$

Residence time @ surface

$$\tau_{surf} \approx \sqrt{\frac{A_{dep}}{v}}$$

Energy per condensing atom/molecule

$$E_d = \frac{E_i \Gamma_i}{s \Gamma_{dep}}$$

Plasma Polymerization

Conversion of monomer in gas phase related to deposition rates

RF CCP, ~5 Pa

‘Yasuda’ factor: $W/ FM$

observed deposition rate, $R$, in energy-deficient regime

$R = a \cdot W$

in monomer-deficient regime at saturation

$R = c’ \cdot FM$


$W$: power input; $F$: gas flow rate

$M$: molecular mass of monomer

Hirotsugu ‘Koge’ Yasuda
1930-2018
**Plasma Polymerization**

**Hydrophilic plasma polymer films on contact lenses – industrial application**

**C:H:O plasma polymer** \((\text{CH}_4 + \text{air 1:2, 5 Pa}) \rightarrow \text{ca. 20 nm}\)

on contact lenses made of silicone hydrogel

→ vertical gradient by interphase formation (ablation vs. deposition)

→ improved wettability and breathability (wearing comfort)

→ cost efficient production (compared to wet-chemical treatment):
  
  400 contact lenses per run (total processing time of 4 min)

→ 30 Mio CL per year (1 Eurocent per CL vs. 2 Eurocent wet-chemically)


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photo: Diener Electronic
Plasma Polymerization

Energy transfer via electrons in the electric field of the plasma

\[ \theta_{\text{abs}} = \frac{e^2 E_p^2 v}{2m_e (v^2 + \omega^2)} = \bar{\epsilon} \delta \nu \]

\[ T_e = \frac{2\bar{\epsilon}}{3e} \text{ (in [eV])} \]

average power absorbed per electron (in [W])

\[ \bar{\epsilon} : \text{mean electron energy} \quad \delta : \text{energy transfer coefficient} \]

average electron collision frequency

\[ \nu = N \cdot \langle \sigma (v_e) \cdot v_e \rangle \]

\[ \nu = \frac{2}{3} \frac{\epsilon}{e} \]

rate coefficient, \( k \)

N : particle density
\( \sigma \) : cross-section
\( v_e \) : electron velocity

frequency of field \( \omega \)

energy transfer coefficient \( \delta_{\text{el}} \ll \delta_{\text{in}} \)

electron temperature \( T_e \gg T_{\text{gas}} \)

mass of molecules \( M >> m_e \)

\[ P_{\text{abs}} = n_e \theta_{\text{abs}} = n_e \bar{\epsilon} \delta \nu \equiv \frac{W_{\text{abs}}}{V_{\text{pl}}} \]

total absorbed power of electrons (in [W cm\(^{-3}\)])

\[ \text{absorbed power per plasma volume} \]

Plasma Polymerization

Coupling of microscopic and macroscopic plasma parameters

Electron density proportional to absorbed power density for many monomers

\[ n_e = \left( \theta_{abs} \right)^{-1} \frac{W_{abs}}{V_{pl}} \]

\( \theta_{abs} \) only depends on \( N \) and \( T_e \) (i.e. on pressure)

- capacitive coupled discharge
- symmetric configuration
- radio frequency (13.56 MHz)

\( \theta_{abs} = \theta_l \)
Plasma Polymerization

Simplified model for the production of film-forming species in the gas phase

One averaged reaction pathway yielding activation reactions:

\[ \nu \rightarrow \bar{\nu}_a \]

→ reaction rate:

\[ \frac{dn_a}{dt} = n_e \bar{\nu}_a = n_e n_m k_a \]

residence time in plasma:

\[ \tau_{act} = \frac{V_{pl}}{F_m} n_m \frac{kT_0}{p_0} \]

\[ n_e \theta_{abs} = \frac{W_{abs}}{V_{pl}} \]

Conversion of monomer into film-forming species:

\[ c_a = \frac{\tau_{act}}{n_m} \frac{dn_a}{dt} = \tau_{act} \frac{n_e}{n_m} \bar{\nu}_a = \tau_{act} n_e k_a \]

Specific Energy Input (SEI):

\[ E_{pl} = \frac{kT_0}{e p_0} \frac{W_{abs}}{F_m} \]

available energy * number of molecules converted per energy

fraction of transferred energy to activation channels with threshold energy \((E_{pl} \leq E_{th})\):

\[ \theta_{l,a} = \alpha \theta_{abs} \approx \alpha \sum_m \nu_m eE_m = \bar{\nu}_a \ eE_{th} \]

sum of excitation/dissociation reactions

\[ c_a = \alpha \frac{E_{pl}}{E_{th}} \]

\[ \alpha(T_e) = \frac{\theta_{l,a}}{\theta_{abs}} < 1 \]

(operational parameters)
Plasma Polymerization

Conversion of monomer in gas phase related to deposition rates

\[
\frac{R}{F_m} = s \frac{M_{dep}}{N_A A_{dep} k T_0} c a = s \frac{M_{dep}}{N_A A_{dep} e e E_{th}} \frac{\alpha W_{abs}}{F_m} = a(T_e) \frac{W_{abs}}{F_m}
\]

for \( E_{pl} \leq E_{th} \)

s: sticking probability; \( M_{dep} \): mass of deposited species; \( A_{dep} \): deposition area

RF CCP, \( \sim 5 \) Pa

Yasuda (1976-1985)

\[
R = a \cdot W
\]

observed deposition rate, \( R \), in energy-deficient regime

‘Yasuda’ factor:
\( W/FM \)

slope: \( a \)

‘plasma-state polymerization’
activation in the plasma is considered as the essential step (reaction kinetics-limited)
Plasma Polymerization

Involved steps and some related governing equations

- **energy per monomer molecule** (specific energy input, SEI)
  \[ E_{pl} = \frac{W_{abs}}{F_m} \left|_{pl} \right. \]

- **flux of film-forming species** (conversion of monomer)
  \[ \Gamma_{dep} = \frac{F_m}{A_{dep}} \cdot f(T_e) \cdot f(E_{pl}) \]

- **sticking probability**
  \[ s = f(E_d, \tau_{surf}) \]

- **residence time @ surface**
  \[ \tau_{surf} \approx \frac{\sqrt{A_{dep}}}{v} \]

- **energy per condensing atom/molecule**
  \[ E_d = \frac{E_i \Gamma_i}{s \Gamma_{dep}} \]
Surface Processes

Sticking probability $s$ – depending on residence time and deposited energy

Surface Processes

Sticking probability depending on deposited energy

AGM (ion-) Activated Growth Model’

\[ s = \text{const.} \]

sufficient energy flux + time

sufficient binding energy

deposited energy

\[ E_d = \frac{E_i \Gamma_i}{s \Gamma_{dep}} \]

e.g. \( \sim 7 \text{ eV} \) for a-C:H

etching effects

surface loss probability

reduced deposition rate

Reduced deposition rate required that film-forming species get stuck in the growing film

Etching affects film growth (more surface-dominated)

\( \rightarrow \) hard coatings (for >25 eV)

’induced plasma polymerization’

activation at the surface is considered as the rate-limiting step


Riccardo d’Agostino 1942-2018

Sufficient nucleation sites
Surface Processes

Deposited energy – kinetic energy yielding non-equilibrium conditions

\[ \varepsilon = E_i \cdot \Gamma_i / R \]  
(energy flux / deposition rate)

\[ n_{atom} = \rho \left( \frac{N_A}{M_{atom}} \right) \frac{C_{atom} M_{atom}}{C_{atom} M_{atom} + C_i M_i} \]

e.g. a-C:H (DLC)  
\[ \rho = 2.1 \text{ g/cm}^3, \ 25 \text{ at}\% \ H \ (C_i = 0.25, \ C_{atom} = 0.75) \]
\[ \rightarrow \sim 100 \text{ C atoms per nm}^3 \]
\[ \rightarrow \text{for } \varepsilon = 3000 \text{ eV/nm}^3: \sim 30 \text{ eV per C} \]

HMDSO Plasma Polymerization

Versatility, mechanism and applications

hexamethyldisiloxane
$\text{SiO}_2\text{C}_6\text{H}_{18}$

PDMS-like coatings

nanoporous SiO:CH coatings

drug delivery

quartz-like coatings

water repellence

barrier coatings

biomaterials / protein adsorption / microfluidics / sensors / packagings
HMDSO Plasma Polymerization

Evaluation of mass deposition rates, $R_m$, in energy- and monomer-deficient regime

RF CCP symmetric large (pure HMDSO)

RF CCP symmetric small (pure HMDSO)

$E_{pl} = \frac{kT_0}{e p_0} \frac{W_{abs}}{F_m}$

$T_0 \approx 1.6 \text{ eV} \approx \text{const.}$

$\alpha \approx 0.04$

$\alpha \approx 0.15$

conversion of monomer into deposit

$R_m/F_m = s \frac{M_{dep}}{N_A A_{dep}} \frac{p_0}{kT_0} c_\alpha$

$s$: sticking probability  $M_{dep} \leq 74 \text{ amu}$


modified Arrhenius approach

$c_\alpha(E_{pl}) = \begin{cases} 
\alpha \cdot \frac{E_{pl}}{E_{th}}, & E_{pl} \leq E_{th} \\
\alpha \cdot \exp \left( \frac{E_{pl} - E_{th}}{E_{pl}} \right), & E_{pl} > E_{th} 
\end{cases}$

$\alpha \approx 0.04$

$\alpha \approx 0.15$

$T_e \approx 1.6 \text{ eV} \approx \text{const.}$
HMDSO Plasma Polymerization

HMDSO – conversion, mass deposition rates, and energy threshold, $E_{th}$

RF CCP asymmetric (HMDSO + Ar)

$T_e(p) > 2\text{ eV}$

$\alpha \approx 0.37 \text{ (max)}$

$\rightarrow$ linear increase in $R_m/F_m$ and $c_a$ up to $E_{th}$, Arrhenius behavior for $E_{pl} > E_{th}$

$\rightarrow$ max. conversion requires $s = 1$ for film-forming species (of 74 amu)

$E_{th} = 14 \pm 1 \text{ eV}$ for HMDSO independent of plasma source and pressure

DBD 20 kHz (HMDSO + 10 slm Ar)

$\alpha \approx 0.12$

$E_{th} \approx 14 \text{ eV}$

HMDSO Plasma Polymerization

HMDSO – proposed plasma chemical reaction pathway

\[
\text{vibr. ex. } \sim 0.1 \text{ eV}
\]

\[
\text{dissociative ionization pathway}
\]

mass spectroscopy

HMDSO Plasma Polymerization

Reaction rate coefficient for the combined average activation reaction

One averaged reaction pathway yielding activation reactions:

\[ \nu \rightarrow \bar{\nu}_a \]

\[ \bar{\nu}_a = n_m k_a = \alpha(T_e) \frac{\theta_{abs}}{eE_{th}} \quad \text{for} \quad E_{pl} \leq E_{th} \]

energy-deficient

\[ k_a(T_e, \frac{E_{pl}}{E_{th}}) \]

linear  Arrhenius regime

\[ \frac{1}{e} \approx 0.37 \]

Plasma Chemistry

Macroscopic description of plasma-activated reactions in the gas phase

One lumped reaction rate coefficient for activation with corresponding $E_{th}$

$\rightarrow$ use of different $k_a(T_e, E_p/E_{th})$ for different $E_{th}$

HMDSO

acrylic acid (Aac)

$\rightarrow$ Aac activation

$\rightarrow$ dissociation

Plasma Chemistry

Macroscopic description of plasma-activated reactions in the gas phase

Reaction rate coefficients $k_a(T_e, E_p/E_{th})$ according to macroscopic model

Also an interesting approach for plasma-chemical gas conversion?
→ optimize conversion and energy efficiency

→ Let’s come back to Plasma Polymerization in Industrial Applications…
HMDSO Plasma Polymerization

Film density and hydrophobicity of HMDSO-derived plasma polymer films

- Film density largely scales with energy per monomer particle in gas phase
- Plasma-state polymerization through \( \cdot (\text{CH}_3)_2 - \text{Si} - \text{O} \cdot \) bi-radicals
- Reduced hydrocarbon content
- \( \rightarrow \) CH\(_3\) abstraction in gas phase
- (post-plasma)
- O incorporation
- \( \rightarrow \) increased radical density
Industrial Applications

Hydrophobic PDMS-like plasma polymer films on textiles

hardness: ~1 GPa (crosslinked)  
→ abrasion resistance

thickness: <100 nm  
washing fastness: >30 times

→ outdoor textiles; wound bandages

1.60 m width  
15 m plasma length
HMDSO Plasma Polymerization

Admixture of oxygen to HMDSO plasma

→ addition of oxygen picks up energy, maintaining the basic reaction pathway

enhanced conversion through activation of HMDSO by O* (beside electron impact)

oxidation of hydrocarbons → CO, CO₂, H₂O

O incorporation

\[ E_{pl} = \frac{kT_0}{e p_0 F_m} \frac{W_{abs}}{0.6 \cdot F_{O2}} \]
HMDSO Plasma Polymerization

HMDSO plasma vs. O₂/HMDSO plasma

- higher Si-O coordination → denser structure
- O incorporation

\[ E_{pl} = \frac{kT_0}{e p_0 F_m} \frac{W_{abs}}{0.6 \cdot F_{O_2}} \]

→ film density largely scales with energy per monomer particle in gas phase

Industrial Applications

SiO$_2$ barrier coatings – inert barrier technology (ibt) by Greiner Packaging

O$_2$ + HMDSO 20:1, 40 mbar, MW $\rightarrow$ ca. 15 nm coating inside bottle
barrier improvement factor $>$10
$\rightarrow$ shelf life extended by 3 months
(H$_2$O + -Si-O-Si- $\rightarrow$ -Si-OH + HO-Si-)

KHS Plasmax
Hamburg / D
40’000 bottles per hour
in a continuous process
Industrial Applications

SiO$_2$ barrier coatings – OTR depending on O$_2$/HMDSO ratio and bias

$\Gamma_i = \sim10^{16}$ cm$^{-2}$ s$^{-1}$

$E_i = \sim3 / 9 / 11$ eV (A / B / C)

$R_{dep} = 0.9$ nm s$^{-1}$

deposited energy:

$\varepsilon [\text{eV nm}^{-3}] = \frac{E_i \Gamma_i}{R_{dep} [\text{nm s}^{-1}]}$

$\varepsilon = \sim330 / 1000 / 1200$ eV nm$^{-3}$ (A / B / C)

SiO$_2$ $\rightarrow$ $\sim60$ atoms per nm$^3$

$E_d = 5.5 / 16 / 20$ eV per atom

→ barrier coatings from O$_2$/HMDSO require sufficient high gas ratio and $E_d$

Industrial Applications

SiO$_2$ barrier coatings – inert barrier technology (ibt) by Greiner Packaging

→ nano-scaled multilayer coatings (adhesion + barrier)

Industrial Applications

SiO$_2$ barrier coatings – simulation of flux of film-forming species

Simplified numerical simulation model for plasma polymer deposition

1) convective flux (by pressure difference + pumping)

Comsol multiphysics

2) diffusion of film-forming species (as created in plasma according to macroscopic model)

\[ \rightarrow \text{optimization of coating uniformity (for complex geometries)} \]
Hydrocarbon PPFs

Plasma polymerization of methane, CH₄

Expectation

Experiment

Expectation

Reaction (CH₄ + e)  Excitation threshold  Eₘ [eV]

→ CH₄(v₂₄) + e                      0.162
→ CH₄(v₁₃) + e                      0.361
→ CH₃ + H + e                       9.0
→ CH₂ + H₂ + e                      10.0
→ CH + H₂ + H + e                   11.0
→ C + 2H₂ + e                      12.0
→ CH₄⁺ + e + e                    12.6
→ CH₃⁺ + H + e + e                 14.3

film-forming species

Eₘ

Eₘ

CH₄  →  CH₄⁺  →  •CH₃, •CH₂, •CH

surface reactions

•CH₂ + H → •CH + H₂


RF CCP, sym., 7.5 Pa

electron impact gas phase reactions
Hydrocarbon PPFs

Plasma polymerization of further hydrocarbon gases

$E_{th,1} \approx 5 \text{ eV}$

$E_{th,2} \approx 25-30 \text{ eV}$

$E_{th,1} : \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 (\text{•CH}_2\text{–•CH}_2) + \text{H}_2$

→ double deposition rate compared to CH$_4$

$E_{th,2}$ and 4x higher $R_m$ of C$_2$H$_x$ compared to CH$_4$ indicate different plasma chemistry


Hydrocarbon PPFs

Role of plasma chemistry and deposited energy for DLC – CH$_4$ vs. C$_2$H$_2$

$\sim n_e$

$V_{pl}$

Hydrocarbon PPFs

Role of plasma chemistry and deposited energy for DLC – CH₄ vs. C₂H₂

\[ \varepsilon = \frac{E_i \Gamma_i}{R_{dep}} \]


\[ F_m = 200 \text{ sccm} \]

\[ F_m = 160 \text{ sccm} \]

→ enhanced deposition rate and hardness for C₂H₂-derived DLC
Industrial Applications

DLC on tools and engine parts

diamond-like carbon

C₂H₂ plasma, 2 Pa → ca. 1 µm

→ friction reduction and wear protection
→ adhesion-promoting interlayers required, e.g. Cr- or CrNi-based
Functional PPFs

Deposition rate of functional plasma polymers from \( \text{C}_2\text{H}_4 (+\text{CO}_2/\text{NH}_3) \)


- **I**: quasi-Arrhenius (same chemical reaction pathway)
- **II**: plasma chemically induced change → O formation (only for \( \text{CO}_2/\text{C}_2\text{H}_4 \))
- **III**: ion-assisted etching (reduced s or \( M_{dep} \))

\( \text{RF CCP, sym., 10 Pa} \)

Ed > 25 eV per atom

\[ \frac{R}{F_m} [10^6 \text{ g/min cm}^2 \text{ sccm}] \]

\[ (W/F_m) [\text{J cm}^{-3}]^{-1} \]

\[ \text{polymerizing gas} \]

\[ \text{C}_2\text{H}_4 \]

\[ \text{NH}_3/\text{C}_2\text{H}_4 (2:1) \]

\[ \text{NH}_3/\text{C}_2\text{H}_4 (1:1) \]

\[ \text{CO}_2/\text{C}_2\text{H}_4 (2:1) \]

\[ \text{CO}_2/\text{C}_2\text{H}_4 (6:1) \]

\[ \frac{[\text{O}]}{[\text{C}]} = 0.28 \]

\[ \frac{[\text{N}]}{[\text{C}]} = 0.24 \]

\[ \frac{[\text{N}]}{[\text{C}]} = 0.4 \]

\[ \frac{[\text{O}]}{[\text{C}]} = 0.35 \]
Functional PPFs

Stability issues with highly functional plasma polymer films

weakly crosslinked PPF

- reorganization
- migration
- dissolution
- water intrusion

strongly crosslinked PPF

- reorganization
- water intrusion

$\rightarrow$ vertical chemical gradient PPFs
(crosslinked base layer + 1-2 nm functional surface)

Industrial Applications

Functional C:H:O plasma polymer films

On the way from development to product…

- cutlery
- basket
- surgical sutures
- blood
- filtration
- tissue engineering
- biosensor
- electroosmosis fabrics
Conclusions

- **Plasma polymerization**
  - microscopic/macroscopic
  - energy transfer $\alpha$ and $SEI$
  - chemical reaction pathway
  - gas phase/surface processes

- **Control of film properties**
  - fragmentation/densification

- **Economic robust ’tool’ for diverse industrial applications**
  - ’simple’ process optimization and control
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- Open position for PostDoc (as well as master thesis, internships)


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