Recent Progress in Low-Temperature, Atmospheric Pressure Plasmas

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Outline

• Radio frequency, low-temperature, atmospheric plasma sources
• Discharge physics & chemistry
• Plasma applications
• Conclusions
Atomflo™ Plasma Tool

- Handheld system developed by Surfx Technologies LLC.
- Generates intense beam of radicals at low temperature.

Atomflo™ applicator
Control Unit

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High-Speed Linear Sources

- Beam widths from 1.0 to 12 inches.
- Activates plastic at up to 1.0 m/s.
- Gas temp. 150 – 300 °C.
- Treats 3D objects.

Atomflo™-500R by Surfx
Versatile Chemistry

- Atomflo™ may be fed with up to 5.0 vol.% O₂, H₂, N₂, CF₄, N₂O, NH₃, etc, in inert gas.
- Up to 20% of molecules are dissociated into atoms, O, H, N, F, etc.
- Chemicals may be injected downstream to deposit thin coatings.
Plasma Physics

• Need to determine the properties of the plasma:
  – Breakdown voltage, $V_B$
  – Electron density, $n_e$
  – Electron temperature, $T_e$
  – Neutral gas temperature, $T_n$
Helium breaks down at 170 V.

Townsend region before breakdown.

Abnormal glow discharge.
Current and Voltage Waveforms

- Smooth waveforms without spikes.
- Capacitive – current precedes voltage in time.
- Phase angle:
  - Argon $\sim 80^\circ$.
  - Helium $\sim 83^\circ$.

RF at 13.56 MHz
Electron Density

\[ J = -en_e \mu_e E \]

- \( J \) = current density, A/cm\(^2\)
- \( n_e \) = plasma density, cm\(^{-3}\)
- \( \mu_e \) = electron mobility (\( \alpha \ 1/P \)), cm\(^2\)/V.s
- \( E \) = electric field (V/d), V/cm
Electron Temperature

Power balance on free electrons:

\[ \varepsilon = n_e \frac{P}{K_BT_g} k_1 I_1 + n_e \left[ n_e \langle \sigma_{ei} \nu_e \rangle + \frac{P}{K_BT_g} \langle \sigma_{ea} \nu_e \rangle \right] \frac{2m_e}{M} \frac{3}{2} K_B \left( T_e - T_g \right) \]

- Power loss due to ionization
- Total power input
- Loss from electron-ion collisions
- Loss from electron-atom collisions
- Electron temperature

Physics of Atomflo™ Plasma Source

• Break down voltages: helium = 170 V; argon = 550 V.
• Electron density \( (n_e) = 1.0 \times 10^{12} \text{ cm}^{-3} \).
• Electron temperature = 1.2 eV.
• Neutral temperature = 150 – 300 °C.
Plasma Chemistry

• Need to determine:
  – Reaction mechanism.
  – Concentrations of radicals in plasma and afterglow.
Experimental Apparatus

Titration with NO:
\[ \text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M} \]
Oxygen Atom Density

[O] = 1.2±0.6 ×10^{17} \text{ cm}^{-3}

Gas density = 1.3×10^{19} \text{ cm}^{-3}

⇒ 1.2 vol.% O atoms!

Conditions: 5.0 L/min Ar, 6.0 vol.% O_2, 150 W/cm^3, and 300±30 °C.
Plasma Model

- Model inputs:
  - $n_e$
  - $T_e$
  - $T_g$
  - Feed gases

- Mechanism:
  - 32 rxns plasma
  - 11 rxns afterglow
Comparison of Model and Experiment

• Oxygen atoms
  – Exp.: \(1.2 \pm 0.6 \times 10^{17} \text{ cm}^{-3}\)
  – Model: \(1.0 \times 10^{17} \text{ cm}^{-3}\)

• Ozone
  – Exp. *: \(4.3 \pm 0.5 \times 10^{14} \text{ cm}^{-3}\)
  – Model: \(2.9 \times 10^{14} \text{ cm}^{-3}\)

* Determined experimentally by UV absorption.
Comparison of Atmospheric Plasmas

<table>
<thead>
<tr>
<th>Type of Discharge</th>
<th>Plasma Density (cm(^{-3}))</th>
<th>O Atom Density (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torch</td>
<td>(10^{16})</td>
<td>(10^{17} - 10^{18})</td>
</tr>
<tr>
<td>Corona</td>
<td>(10^{9})</td>
<td>(10^{12})</td>
</tr>
<tr>
<td>Dielectric barrier discharge</td>
<td>(10^{9})</td>
<td>(10^{13})</td>
</tr>
<tr>
<td>RF capacitive discharge</td>
<td>(10^{12})</td>
<td>(10^{16} - 10^{17})</td>
</tr>
</tbody>
</table>

Atomflo™ 1000x more powerful than coronas!
Applications

• Activating polymers for bonding.
• Metal etching.
• Depositing thin films:
  – SiO$_2$, Si$_3$N$_4$, a-Si:H, ZnO, DLC.
Surface Activation
Adhesion to Carbon-Fiber Composites

Without plasma, adhesive failure.

With Atomflo™ plasma, cohesive failure.
Treatment of 3-D Parts

• Robot-mounted plasma sources scan
  – any 3-D object.
  – any size of flat panel display.
Plasma Etching Results

- Rates exceed those obtained in low-pressure plasmas.
- Chemistry selection for disparate materials:
  - Organics etched with O_2 plasma.
  - Metals etched with CF_4/O_2 plasma.
Tantalum Etching in \( \text{CF}_4/\text{O}_2 \) Plasma Afterglow

- Tantalum is a surrogate for plutonium.
- Etch rates up to 6.0 \( \mu\text{m}/\text{min} \) observed.
- Rate most sensitive to applied power.
Surface Morphology After Tantalum Etching

Surface is heavily fluorinated: TaF$_3$ and TaF$_4$ by XPS.
Plasma-Enhanced Chemical Vapor Deposition

Plasma Gas Mixture

RF Power

Plasma Zone

Metal Precursor

Ceramic Spacer

Sample Stage

Metal Precursor

Substrate

Heater
Plasma-Enhanced Chemical Vapor Deposition

RF Power

Argon & O₂

Plasma Physics

Afterglow Chemistry

Volatile chemical precursor

Thin Film Materials

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Organosilane Precursors

- TMCTS
- TEOS
- HMDSO
- TMDSO
- HMDSN
Low Porosity Glass Grown with HMDSN

Three-dimensional image of 650-nm-thick film grown at 0.24 μm/min using HMDSN.
Diamond-Like Carbon

- Process conditions:
  - 0.1 L/min C₂H₂, 0.5 L/min H₂, 30 L/min He, 180 W & 155 °C.
- Dep. rate = 0.2 μm/min
- Confirm DLC film by C¹³ NMR with magic angle spinning.

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Conclusions

• RF atmospheric plasmas are powerful tools for surface treatment.

• Ideal for automated processing of 3-D plastics.

• New processes are being developed to greatly enhance the functionality of materials.
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Numerical Model of the Plasma Chemistry

• One-dimensional “plug-flow” simulation.
• Mechanism includes 39 elementary steps among 19 species: neutrals, ions and metastables.
• Results compared to titration experiment.
Profiles of the Charged and Metastable Species

Electronegative plasma: $n_{F^-} = 5 \times n_e$.

Gas flow

$T_e = 2.5 \text{ eV}$
Profiles of the Neutral Species

Fluorine atom density: $1.3 \times 10^{15}$ cm$^{-3}$.

Good agreement with H$_2$ titration.
H$_2$ Titration of F Atoms in CF$_4$ Plasma Afterglow

F atoms = 2x10$^{15}$ cm$^{-3}$
1.2 cm downstream of electrodes.

12.8 Torr CF$_4$, 2.3 Torr O$_2$, 745 Torr He, 73 W/cm$^3$ and 100 °C.
Effect of Process Conditions on Tantalum Etch Rate

- **O₂ Partial Pressure (Torr)**: The etch rate starts at a lower value and then increases as the O₂ partial pressure increases. There is a visible trend where the etch rate increases with increasing O₂ partial pressure.

- **CF₄ Partial Pressure (Torr)**: The etch rate shows a linear increase with the CF₄ partial pressure. The relationship is linear, indicating a direct proportional increase in etch rate with the CF₄ partial pressure.
Plasma Etching of UO₂

Process conditions:

– Total Flow: 42 L/min, He/O₂/CF₄
– O₂: 6 Torr
– CF₄: 15 Torr
– RF Power: 300 W
– Temperature: 200 °C
– Nozzle-to-sample distance: 3 mm
Uranium Oxide Surface Morphology

Scanning electron micrographs of UO$_2$ film before and after etching with CF$_4$/O$_2$/He plasma:

Before | After a 2-min etch | After a 5-min etch

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Surface Composition

X-ray photoelectron spectra of UO₂ film

Counts

Binding Energy (eV)

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Dependence of U 4f Peak Intensity on Time

- Rate accelerates due to increased film porosity.
- Re-deposition may result in tail at >3 min.