Molecular Dynamics Simulations of Plasmas-Biomolecule Interactions at Surfaces

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Outline

- Motivation
- Molecular dynamic simulation method
- Physical sputtering of lipid A by Ar$^+$ impacts
- Effects of neutrals in the Ar$^+$ flux
- Conclusions
Motivation

Inactivation of Bacteria and Biomolecules by Low-Pressure Plasma Discharges, A. von Keudell et al., Plasma Processes and Polymers, 2010, 7, 327-352

Plasma deactivation of LPS is more efficient with lower temperature than the conventional method.

E. coli on culture plate


Figure. plasma needle bacteria deactivation: a. plasma needle, b. bacteria deactivation pattern**

**Motivation**

Ar/H$_2$ microwave discharge

FTIR results show that the decrease of carboxylic acid chain in the lipid A after plasma exposure [1].

"It has appeared that the major contributing factors to endotoxicity are the number and lengths of acyl chains present and the phosphorylation state of the disaccharide backbone [2]."


Potential model

- reactive empirical bond-order (REBO) potential for C, H, and O

- repulsive Moliere potential between Ar$^+$ and C/H/O

- Newton's equation of motion is integrated numerically with velocity-verlet algorithm using a time step of 0.1 fs.

- Berendsen thermostat

- The simulation time for each ion bombardment is 0.5 ps, then the cell is cooled back to 300 K and relaxed for 0.5 ps.

- The total simulation time is defined by fluence (ion/cm$^2$).

- Plasma parameter to study: ion energy, ion/neutral type
Structure obtained according to the molecular model of E.coli LPS by N. Kato and colleagues*.
- Dimension: 3x4x7 nm
- Density: 0.8 g/cm3
- Initial surface temperature: 300 K

Blue balls – C atoms
Green balls – H atoms
Yellow balls – O atoms

Ion: Ar+
Ion energy: 5-100 eV
Ion fluence: $3 \times 10^{16}$ cm$^{-2}$

The threshold energy [1] of physical sputtering can be calculated by from the surface binding energy [2]:

$$E_{th} = 8E_{sb} \left( \frac{M_{proj}}{M_{targ}} \right)^{0.4}$$

$= 12$ eV

Caboxylic acid chain interaction with Ar⁺

Ion: Ar⁺
Ion energy: 100 eV
Ion fluence: 6x10^{16} cm⁻²

Figure 1. Carbon removal curve under 100 eV Ar⁺ ion impacts.

"HDPE (-CH₂-CH₂-)ₙ also demonstrate high etch rate."

SY_{HDPE} = 7 (SY_{acyl chain} = 11)


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<tr>
<th></th>
<th>O/C</th>
<th>H/C</th>
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<tbody>
<tr>
<td>Original film</td>
<td>0.13</td>
<td>1.9</td>
</tr>
<tr>
<td>After Ar⁺ impacts</td>
<td>0.14</td>
<td>1.8</td>
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Sputtered species during Ar$^+$ impacts

Ion: Ar$^+$
Ion Energy: 35-100 eV
Incidence Angle: normal to surface
Ion Fluence: $3 \times 10^{16}$ cm$^{-2}$

![Graph showing the number of C removed per Ar$^+$ for different energies]
Sputtered species during Ar$^+$ impacts

Ion: Ar$^+$
Ion Energy: 15-20 eV
Incidence Angle: normal to surface
Ion Fluence: $3 \times 10^{16} \text{cm}^{-2}$
Effects of H, O neutral on etching

Ion: Ar⁺  
Ion Energy: 15-50 eV  
Incidence Angle: normal to surface  
Ion Fluence: $6 \times 10^{15} \text{cm}^{-2}$

Neutral: O, H  
Neutral impact energy: 0.04 eV  
Ion/neutral ratio: 1:10

Atomic hydrogen does not effect on carbon sputtering yield, while atomic oxygen enhances sputtering yield.
Faster etching with O coupled to Ar\(^+\) flux

Ar\(^+\)/H with 35 eV impacts energy

Ar\(^+\)/O with 35 eV impacts energy
Possible mechanism of plasma-induced lipid peroxidation

Ar⁺ Ion Energy: 35 eV, Neutral Energy: 0.04 eV, Incidence Angle: normal to surface
Ar⁺/O₂ ratio: 1 :10, Ion Fluence: 3.44X10^{15} cm⁻²


Suggests a mechanism by which Ar/O₂ plasma could induce lipid peroxidation, leading to bacterial deactivation.
Conclusions

- The energy threshold of $\text{Ar}^+$ physic sputtering of simulated lipid A film is $\sim15$ eV.

- Our MD simulation results shows constant carbon sputtering yield during $\text{Ar}^+$ impacts. Film composition did not change during sputtering.

- Coupling atomic oxygen and $\text{Ar}^+$ increases carbon sputtering yield, while atomic hydrogen does not affect the carbon sputtering yield.

- $\text{Ar}/\text{O}_2$ plasma may induce peroxidation by a mechanism that combines ion-induced dangling bond formation with neutral molecular $\text{O}_2$ insertion.
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