Diamond-like Carbon Thin Film with Controlled Zeta Potential for Medical Application


**MSE 576 Thin Films & Analysis Presentation**
**Dec 4th 2008**

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Outline

- Diamond-like carbon thin films
- Zeta potential
- Discuss paper by Nitta et. al.
Diamond-like carbon

- Amorphous thin films with both graphite and diamond bonds.

- Interesting properties:
  - Low coefficient of friction
  - Wear resistance
  - Wide band gap

- Applications: Dies and automobile parts.
Diamond-like carbon

- DLC thin films are potential medical materials because:
  - biocompatibility
  - antithrombogenicity

- Reason: Medical devices that are in contact with the blood, e.g., artificial hearts and blood pumps.

- Present problem: blood clotting, performance.
Diamond-like carbon

- Present material: Polymers, but they have problems:
  - Blood compatibility is not outstanding.
  - Adhesion is not great to metallic substrate.

Solution: DLC thin film
Diamond-like carbon

- DLC thin film:
  - Chemically stable amorphous hydrocarbon thin film.
  - Smooth with atomic flatness.
  - Superior compatibility with tissue and blood.

- Problem: Not effective in all the situations.

- Account must be taken of the interactions between the cell and the DLC thin film surface.

- Important parameter: Zeta potential!!
What’s zeta potential?

- It’s an abbreviation for electrokinetic potential in colloidal systems (says Wiki).

- Theoretically, it is the electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface.

- In simple terms, it is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.
What’s zeta potential?

Source: http://www.malvern.co.uk/LabEng/technology/zeta_potential/zeta_potential_LDE.htm
What’s zeta potential?

Source: http://www.geocities.com/CapeCanaveral/Hangar/5555/zeta.htm
The significance of zeta potential

- Its value can be related to the stability of colloidal dispersions.

- It indicates the degree of repulsion between adjacent, similarly charged particles (the vitamins) in a dispersion.

- A high zeta potential: **Stability** ! (+ or -)

- A low zeta potential: **Flocculation** !
  Because attraction exceeds repulsion, and the dispersion breaks.
# The significance of zeta potential

<table>
<thead>
<tr>
<th>Zeta potential (mV)</th>
<th>Stability behavior of the colloid</th>
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<tbody>
<tr>
<td>0 to ±5</td>
<td>Rapid coagulation/flocculation</td>
</tr>
<tr>
<td>±10 to ±30</td>
<td>Incipient instability</td>
</tr>
<tr>
<td>±30 to ±40</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>±40 to ±60</td>
<td>Good stability</td>
</tr>
<tr>
<td>&gt; ±61</td>
<td>Excellent stability</td>
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</table>

**Zeta potential of colloids in water and waste water**

Cells: **Negatively charged**, and their surface potential varies depending on the individual cell.

Stimulation to the cells can be reduced by controlling the zeta potential.

Method by Nitta et. al.: Introduce functional groups such as amino (-NH$_2$) and carboxyl groups (-COOH).

Zeta potential in biological environ

- Carboxyl groups: high negative charge.

- Amino groups: high positive charge.

If the quantities of these functional groups can be controlled at the DLC thin film surface, it will be possible to control the zeta potential.
Experimental

- Plasma surface treatment in a chamber (5 Pa)

- Process chamber connected to a RF power supply with an excitation frequency 13.56 MHz at power of 300W.

- RF power of 30 W was injected to generate plasmas.

- Capacitatively Couple Plasmas (CCP) was generated by means of two parallel plate electrodes.

- Gases used: O₂, Ar, NH₃ and C₂H₂ (15 seconds).
Experimental

- DLC thin films used were prepared by ionization-assisted deposition using benzene.

- DLC thin film thickness: 40 nm.

- After plasma surface treatment:
  - XPS: Composition ratios of the DLC samples.
  - Contact angle meter: Static contact angle.
  - Zeta potentiometer: Zeta potential of the samples.

### Composition ratio: XPS results

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>N1s</th>
<th>O1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2H2+O2</td>
<td>80.6</td>
<td>0.6</td>
<td>18.8</td>
</tr>
<tr>
<td>C2H2+NH3</td>
<td>63.05</td>
<td>22.5</td>
<td>14.45</td>
</tr>
</tbody>
</table>
Results: $\text{C}_2\text{H}_2$ followed by $\text{O}_2$ treatment

XPS spectra of C1s waveform. The C1s peak assigned to the binding energy of C-C, C-O, C=O and O=C-O bonded network. The binding amounts were 71.8, 18.6, 2.9, and 6.5 atomic %, respectively.
Results: C$_2$H$_2$ followed by O$_2$ treatment

Binding amounts in an untreated DLC sample were:
82.7 (C-C), 11.7 (C-O), 3.8 (C=O), and 1.7 (O=C-O) (atomic %)

<table>
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<tr>
<th>Functional Group</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>C – C</td>
<td>82.7</td>
<td>71.8</td>
</tr>
<tr>
<td>C – O</td>
<td>11.7</td>
<td>18.6</td>
</tr>
<tr>
<td>C=O</td>
<td>3.8</td>
<td>2.9</td>
</tr>
<tr>
<td>O=C – O</td>
<td>1.7</td>
<td>6.5</td>
</tr>
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</table>

Comparing them with the XPS results of the DLC samples show that C-C bonds or C-H bonds were cleaved by radicals, electrons, and ions in the plasma.

Thereby oxidation reactions such as C-O, C=O and O=C-O were promoted.
Results: C$_2$H$_2$ followed by O$_2$ treatment

- O$_2$ or O radicals in plasma mainly drew H from C-H bonds. Amount of C-C bonds or C-H bonds in DLC thin films were dependent on functional groups introduced to DLC surface.

- Thus, it is considered that amount of functional groups introduced to DLC thin films surface can be controlled by controlling amount of C-C bonds or C-H bonds in DLC thin films.
The O=C-O peaks stem from the carboxyl groups and were three times more numerous than that of untreated DLC sample.

Carboxyl groups can be introduced efficiently onto the surface of DLC thin films by plasma surface treatment.
Results: \( \text{C}_2\text{H}_2 \) followed by \( \text{NH}_3 \) treatment

**C1s**

Binding amounts
- 79.1 (C-C)
- 11.6 (C-O)
- 7.2 (C=O)
- 2 (O=C-O)

(atomic %)

**N1s**

Binding amounts
- 20.7 (C-N=C)
- 58.7 (C-NH\(_2\))
- 16.3 (C-N)
- 1.7 (N-O)
- 2.6 (N=O)

(atomic %)
C-C bonds were larger than those of $\text{C}_2\text{H}_2+\text{O}_2$ plasma treatment.

N1s peak was remarkable compared to that of $\text{C}_2\text{H}_2+\text{O}_2$ plasma treatment.

C-H bonds or C-C bonds were cleaved by radicals, electrons, and ions in the $\text{NH}_3$ plasma, and nitrogen was introduced into the DLC thin films surface.

C-NH$_2$ peak dominated

It is possible to generate amino groups on DLC thin films surface.
Results: Contact angle measurement

- Contact angle of conventional DLC film is 70 degrees.
- C-O, C=O, O=C-O are hydrophilic
Results: Zeta potential measurement

Dependence of zeta potential on O=C-O/C

The zeta potential decreased twice as much as untreated sample with increasing in the O=C-O/C ratio.
It is possible to control the zeta potential of DLC thin films by controlling the amounts of the carboxyl groups and amino groups.

A new method discovered to develop a biocompatible material.
Questions ?
Thank You