Graphene Oxide-Copper Plasmonic Interfaces for SPR Biosensing

Yu.V. Stebunov¹, D.I. Yakubovsky¹, D.Yu. Fedyanin¹, A.V. Arsenin¹, and V.S. Volkov¹,²

¹ Moscow Institute of Physics and Technology, Institutsky 9, Dolgoprudny 141702, Russia
² GrapheneTek LLC, Skolkovo Innovation Center, Moscow 143026, Russia
³ University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

stebunov@phystech.edu, http://nano.phystech.edu/

27 June 2018, Dresden
## Copper and graphene oxide for plasmonic biosensing

<table>
<thead>
<tr>
<th>Copper</th>
<th>Graphene oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Good optical properties in visible range</td>
<td></td>
</tr>
<tr>
<td>• Variety of structures for plasmonic biosensors (films, WG, resonators)</td>
<td></td>
</tr>
<tr>
<td>• Low cost</td>
<td></td>
</tr>
<tr>
<td>• Compatible with CMOS</td>
<td></td>
</tr>
<tr>
<td>• Ideal material for mass-production</td>
<td></td>
</tr>
<tr>
<td>• Deposition on various substrates</td>
<td></td>
</tr>
<tr>
<td>• 2D material – high surface area</td>
<td></td>
</tr>
<tr>
<td>• Pi-stacking immobilization</td>
<td></td>
</tr>
<tr>
<td>• Easy manufacturing process</td>
<td></td>
</tr>
<tr>
<td>• Low optical absorption</td>
<td></td>
</tr>
<tr>
<td>• Oxygen-containing functional groups: COOH, OH, C=O, C-O-C</td>
<td></td>
</tr>
</tbody>
</table>
Copper-based SPR biosensing

- Biosensors format: instrument and sensor chips
- Simple theoretical description
- Thin film structures (no lithography and etching)
- Wide range of developed protocols

Stebunov et al., Langmuir 34 (15), 2018
Optical properties of thin copper films

Structures for ellipsometry measurements

| Au or Cu (25 nm) | SiO$_2$ (2 nm) | Si |

AFM images of copper films
Optical properties of thin copper films

Structures for ellipsometry measurements

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au or Cu (25 nm)</td>
<td></td>
</tr>
<tr>
<td>SiO₂ (2 nm)</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
</tr>
</tbody>
</table>

AFM images of copper films

Drude model: \( \varepsilon = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma \omega} \)

<table>
<thead>
<tr>
<th></th>
<th>( \varepsilon_\infty )</th>
<th>( \omega_p [10^{16} / s] )</th>
<th>( \Gamma [10^{13} / s] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.68</td>
<td>1.32</td>
<td>10.5</td>
</tr>
<tr>
<td>Au</td>
<td>5.08</td>
<td>1.35</td>
<td>12.8</td>
</tr>
</tbody>
</table>
Simulation of SPR excitation

**Copper-based SPR chips**

**Dielectric**
- Cu (27 nm)
- Ti
- Glass

**SPR angle changes**

**Sensitivity to RI changes**

\[ S_{RI} = \frac{\Delta P}{\Delta n} \]

\( \Delta n \) – RI change

\( \Delta P \) – resonant angle change
Simulation of SPR excitation

Angular reflection ($\text{Al}_2\text{O}_3$ coatings)

Sensitivity

**Sensitivity to RI changes**

$$S_{\text{RI}} = \frac{\Delta P}{\Delta n}$$

$\Delta n$ – RI change

$\Delta P$ – resonant angle change

**3-4 times improvement in sensitivity**

**Copper-based SPR chips**

**SPR angle changes**

**Yakubovsky et al., Optics Express 25(21), 2017**
SPR measurements – salt testing

Copper-based SPR chips

BiOptix Accolade 104SA

- Phase measurements
- 0.5% NaCl injections
SPR measurements – salt testing

- Phase measurements
- 0.5% NaCl injections

Dielectric 
Cu (27 nm) 
Glass

Ti + 

Copper-based SPR chips BiOptix Accolade 104SA

Sensitivity to RI changes

SiO\textsubscript{2} 

Al\textsubscript{2}O\textsubscript{3}

Sensitivity (V/RIU) vs. Thickness (nm)

- Red squares: Al\textsubscript{2}O\textsubscript{3}
- Blue circles: SiO\textsubscript{2}
- Dashed line: pure gold
Graphene oxide linking layers for SPR analysis

Deposition of GO films
- Electrodeposition
- Spin-coating
- Spray-coating

80% of one-atomic-layer flakes (0.3-0.7 um)

Uniform GO film
Graphene oxide linking layers for SPR analysis

**Deposition of GO films**
- Electrodeposition
- Spin-coating
- **Spray-coating**

80% of one-atomic-layer flakes (0.3-0.7 um)

Uniform GO film

Ellipsometry of GO film

Refractive index at 635 nm

Graphene: \( n_{gr} = 3, \quad k_{gr} = 1.16 \)

GO: \( n_{GO} = 1.82, \quad k_{GO} = 0.184 \)
Neutravidin-biotin interaction

- GO film with the thickness of 5 nm
- Neutravidin selectively binding the molecules with biotin residue
- D1, biotinylated 56bp oligonucleotide sequence
- D2, 50bp oligonucleotide sequence complementary to D1

Neutravidin-coated surface is used for immobilization of biotinylated ligands such as proteins, peptides, nucleic acids, etc.
Neutravidin-coated surface is used for immobilization of biotinylated ligands such as proteins, peptides, nucleic acids, etc.

- GO film with the thickness of 5 nm
- Neutravidin selectively binding the molecules with biotin residue
- D1, biotinylated 56bp oligonucleotide sequence
- D2, 50bp oligonucleotide sequence complementary to D1

Oligonucleotide interactions

Response (RU) vs. Time (s) graph showing interactions with D1 and D2 sequences.
Summary

- Copper can substitute gold in plasmonic biosensors
- Dielectric coatings protect copper from oxidation and increase biosensing sensitivity
- Biomolecule immobilization using graphene oxide linking layers
- Copper and GO-based interfaces will open the way towards the integration of biosensors into consumer electronics

Thank you for your attention!

E-mail: stebunov@phystech.edu, Web: nano.phystech.edu