High Ion Flux Plasma Nanostructures for Electrochemical Applications

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Electrochemical Energy Applications

Photo-electrochemical water splitting

Progress in performance is required \(\rightarrow\) large surface area
The Importance of Large Surface Area

- Higher performance per projected area
- Miniaturization

Projected length

→ higher performance per projected area
→ miniaturization

Real length
Fabrication of Large Surface Area Thin Films

**Top down**

- E-beam lithography
- Soft lithography
- Ion beam sputtering

**Bottom up**

- Vapor methods
- Sol gel
- Self-assembly

**References**

- Thesis Tanyeli (2016)
High Ion Flux He Plasma Nanostructuring: Nanofuzz in Fusion

New method of making nanostructured surfaces: High Ion Flux Plasma Exposure


Mechanism of Nanostructuring

Example: Photoelectrode for water splitting
High Ion Flux He Plasma Exposure

Typical plasma treatment parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>He</td>
</tr>
<tr>
<td>Electron density</td>
<td>0.4–30*10^{22} m^{-3}</td>
</tr>
<tr>
<td>Ionisation energy</td>
<td>Few eV-60 eV</td>
</tr>
<tr>
<td>Ion flux (max.)</td>
<td>10^{25} m^{-2} s^{-1}</td>
</tr>
<tr>
<td>Magnetic field</td>
<td>&lt; 1.6 T</td>
</tr>
<tr>
<td>Temperature</td>
<td>~ 1000°C</td>
</tr>
<tr>
<td>Discharge current</td>
<td>150-250 A</td>
</tr>
<tr>
<td>He flow rate</td>
<td>1.4-2 slm</td>
</tr>
</tbody>
</table>

High ion flux plasma exposure of thin films → parameter evaluation

Challenges for Thin Films

- **Substrate – thin film interface**
  - Thermal stability
  - Delamination
  - Interdiffusion
  - Penetration depth

- **Substrate**
  - Thermal stability
  - Undesired nanostructuring of substrate

*Bieberle-Hütter, Tanyeli, Lavrijsen, Koopmans, van de Sanden*  
DC Sputtering of Fe Thin Films

Before annealing

After annealing

Plasma Exposure of Thin Films

- Using bulk plasma conditions (high T, high current)
  → samples break
- Using mild plasma conditions → no imprint
- Never found delamination of the thin films
- Strong interplay of many exposure parameters: T, t, current, bias, He flow rate
Plasma Nanostructured Iron Oxide Films

Nanostructure Formation

Before annealing, top view SEM

No nanostructuring for light imprint.

Nice nanostructure for strong imprint.

No nanowires.

Stable Microstructure After Annealing


Stable nanostructure after annealing; no nanowires.
Spatial Distribution of Nanostructure Formation

- Best nanostructure formation in the middle of the sample.
- No significant difference due to annealing.

• Same features seen as in top view.
• No thickness change due to plasma exposure.
• No delamination at the Fe$_2$O$_3$-FTO interface.
• Damage of FTO?
• Low overall photocurrent due to very thick films.
• 2-5 times increase in photocurrent after plasma exposure.
• Less structured material has a higher performance.

Sinha, ABH et al., under preparation.
Summary

Fe/Fe-oxide model system on glass substrate (water splitting):

*Thin films on glass* can be nanostructured by high ion flux plasma.

*Highly porous* and *stable* structure with *small features* formed.

Nanostructure is *electrochemical active.*

Transfer to other applications?
Transfer to Other Applications: Opportunities and Challenges

Electrodes for fuel cells

+ large surface area needed
+ interconnected structure → impregnation?
- plasma nanostructuring of complex oxides?
- impact on electrochemical performance?

Metal oxide sensors

+ large surface area of up to 90%
- impact of impurities on sensing performance?

Large surface area substrates

+ large surface area of up to 90%
- reachable surface area?
Investigate direct nanostucturing of oxide materials
- Relate structure and performance
- Study the impact of impurities from the plasma exposure process
- Other applications?
  - Large porosity (up to 90%)
  - Large surface area
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