Successive Ionic Layer Adsorption and Reaction for Organic/Inorganic Interfaces

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Background: Zinc Oxide and Organic Electronics
Zinc oxide is a promising material for use in organic electronics, particularly organic photovoltaics (OPVs). ZnO has a large band gap around 3.3 eV, a high electron mobility, it is non-toxic, and it can be processed using solution based methods at atmospheric and room temperature conditions. It has gathered attention in OPVs because it can be used as an electron acceptor at its interface with organic hole conducting molecules (Figure 1). ZnO can also be used as a contact layer in bulk heterojunction OPV devices to carry the electrons from a separated exciton to an external circuit. Both of these uses in OPVs require great control over the ZnO surface.

ZnO Orientations and Faces
ZnO has three possible orientations on the exposed surface: two polar (O-terminated and Zn-terminated) faces and one non-polar face (Figure 2).

Figure 2: a) Polar Zn-term b) Polar O-term c) Non-polar

Each face has distinctly different properties and reacts differently to chemical species. This in turn can affect morphology, charge transport, energetics, and the overall performance of the ZnO/OPV devices. Previous attempts have been made to control the ZnO surface by repairing defects using high temperature anneals (1100 °C), but now a low temperature, solution based approach will be considered. The chosen repair method is successive ionic layer adsorption and reaction, or SILAR.

Successive Ionic Layer Adsorption and Reaction
SILAR is a low temperature and solution based process that can deposit atomic layers one layer at a time. The traditional SILAR cycle for a substrate is 5:

Dip in cation precursor solution
Rinse with water
Dip in anion solution
Rinse with water

Chemical Reactions for ZnO SILAR Method

\[ \text{Zn}^{2+} + 4\text{NH}_3\text{OH} \rightarrow [\text{Zn(NH}_3)_4]^{2+} + 4\text{H}_2\text{O} \]

\[ [\text{Zn(NH}_3)_4]^{2+} + 4\text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 4\text{NH}_3 + 4\text{OH}^- \]

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \]

\[ \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \]

SILAR Methods Tested
An ideal SILAR cycle produces a single atomic layer and can be repeated as often as desired. Three methods of deposition, each for 20 cycles, were investigated and their processes are shown below. (Note: For repairing a surface, only a few cycles will be performed because the purpose is to repair, not to build.)

Method 1

- 20 s zinc ammonia complex
- 20 s DI water unheated
- 20 s DI water 95°C

Method 2

- 20 s zinc ammonia complex
- 20 s DI water unheated
- 20 s DI water 95°C

Method 3

- 20 s zinc ammonia complex
- 20 s DI water unheated
- 30 s DI water unheated sonicated

Results
Successful SILAR depositions were made on glass substrates for SILAR Methods 1, 2, and 3. Data from ultraviolet-visible spectroscopy (UV-VIS) was used to find where the absorbance changes for each method (Figure 3). From that data, the band gap for each sample was calculated. Profilometry was used to find the height of each deposition. Table 1 summarizes this data.

Table 1: UV-Vis Absorbance Data and Height Data

<table>
<thead>
<tr>
<th>Method</th>
<th>Absorbance Wavelength (nm)</th>
<th>Band Gap (eV)</th>
<th>Height (nm)</th>
<th>Height per Layer (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>376.22</td>
<td>3.298</td>
<td>1,574.2</td>
<td>78.71</td>
</tr>
<tr>
<td>2</td>
<td>373.33</td>
<td>3.324</td>
<td>1,094.1</td>
<td>54.71</td>
</tr>
<tr>
<td>3</td>
<td>377.93</td>
<td>3.283</td>
<td>607.08</td>
<td>30.35</td>
</tr>
</tbody>
</table>

Discussion and Future Work
There is no apparent trend in the band gap for each method; however, all of the band gaps agree with the literature values 2. All three of the methods had (002) as the preferred direction in agreement with Shei et al. 4. The main difference between deposition methods was in the height of each layer. Method 3 had the lowest height per layer, but this value is still nearly 60 times the atomic step height of ZnO, 0.54 nm. Though Method 3 does not deposit perfect atomic layers, it is the preferred method for repairing defects in ZnO surfaces. Future work will include reducing the layer height per deposition. The improved SILAR method will then be performed on ZnO single crystals, polar and non-polar, to determine if SILAR can heal defects on the surface.

References

Acknowledgements
Thank you to the Renewable Energy Materials Research Science and Engineering Center for this Research Experience for Undergraduates and to the National Science Foundation for supporting this research with grants DMR-0907409 and DMR-0820518.