CONTROLLING SURFACE PROPERTIES OF METAL OXIDE TO IMPROVE SOLAR CELL EFFICIENCY

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Renewable Energy in West Virginia
Self-Assembled Monolayers

- A Self-Assembled Monolayer (SAM) is a monomolecular film of an organic compound on a solid surface.
- SAMs exhibit:
  - High degree of orientation
  - Molecular order
  - Close packing
- Self-Assembled Monolayers are flexible because the head or tail groups can be varied.
- SAMs have been able to control corrosion.
There are two types of films: ordered and disordered
- Ordered-C-C chains have all-trans conformations
- Disordered-C-C chains have some gauche conformations

A long alkylic chain, greater than 12 carbons, is commonly used in SAMs
- Longer chain lengths tend to form all-trans conformations in the alkylic chain

Several factors affect the formation and packing density of monolayers
- Nature and roughness of substrate
- Head group
- Tail group
- Solution concentration
Film Deposition Method

- SAMs provide one of the easiest ways to efficiently obtain closed packed films
  - *Small Concentration of the solute*
  - *Easy deposition methods*

http://marvin1.pc.ruhr-uni-bochum.de/
Self-Assembled Monolayer Applications

- Corrosion barrier
  - Biomaterial
- Pharmaceutical applications
  - Polymorph
- Solar cells
  - Work function
Solar Cells

- The most common solar cells are made of silicon
  - 20% energy efficiency
  - Expensive

- Research in solar cells
  - Organic/polymer based solar cells
  - Dye sensitized solar cells
    - Lightweight
    - low-cost
    - Large area processability

[cnx.org](http://cnx.org)
Heterojunction Solar Cells
Heterojunction Solar Cells

- Organic photovoltaic cells are great interest of scientists
  - Low-cost generation
  - Easy processability
  - Alternative to high cost silicon based solar cells

- Polymer solar cells
  - Large scale production
  - Flexibility
  - Low-temperature operation

- Performances of organic solar cells are highly dependent of:
  - Morphology of active layers
  - Metal oxide layers

- Inverted-type bulk heterojunction solar cells can be fabricated using different ZnO interlayers
  - investigate the performances
  - Energy efficiencies

Zinc Oxide Nanoparticles

- Useful properties of zinc oxide (ZnO):
  - Wide band gap semiconductivity (~3.3 eV)
  - High electron mobility
  - Stable hexagonal wurtzite structure

- Applications in solar cells, energy-saving windows, antimicrobial textiles, chemical sensors, ultraviolet (UV) coatings, and corrosive-resistant coatings

Project Goal

- Zinc oxide nanoparticles were modified with SAMs
  - Phosphonic acids
  - Spectroscopy characterization
- Work function tuning
Organic Acids

Phosphonic Acid
- More stable on many metal oxide surfaces
  - Octadecylphosphonic acid (ODPA)
    - Methyl-terminated
  - 16 – phosphonohexadecanoic acid (COOH-PA)
    - Carboxylic acid-terminated
  - (12-phosphonododecyl)phosphonic acid (Di-PA)
    - Phosphonic acid-terminated
Thin Film Formation

- Nanoparticles: 0.35 g ZnO (100 nm size averaged) was dissolved in 30 mL tetrahydrofuran (THF) and sonicated.
- Organic acids: 0.09, 0.045, 0.02, 0.01 mmol of each acid was dissolved in THF and sonicated.
- Solutions were combined and further sonicated.
- Left stirring at room temperature for 24 hours.
- After modification, samples were rinsed, sonicated in THF for 20 minutes, and filtered.
Chemisorbed Phosphonic Acid Monolayers on ZnO Surface

Stable – resilient to solvent rinses and sonication

COOH-PA after deposition on the surface
PXRD: Presence of Organic Materials

Unmodified ZnO nanoparticles (black)
ODPA on ZnO (red)
COOH-PA on ZnO (green)
Di-PA on ZnO (blue)

Thanks to Duquesne University for allowing us to have access to this instrument
### Scanning Electron Microscope (SEM)

<table>
<thead>
<tr>
<th>Modifications</th>
<th>Average Particle Size (nm)</th>
<th>Particle Distribution (±nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>106</td>
<td>27</td>
</tr>
<tr>
<td>ZnO – ODPA</td>
<td>145</td>
<td>53</td>
</tr>
<tr>
<td>ZnO – COOH-PA</td>
<td>161</td>
<td>61</td>
</tr>
<tr>
<td>ZnO – Di-PA</td>
<td>194</td>
<td>83</td>
</tr>
</tbody>
</table>

**0.01 mmol ZnO-ODPA**

**0.045 mmol ZnO-ODPA**

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[ZnO SEM images with labels]
**$^{31}$P SS-NMR: Bonding**

- $^{31}$P chemical shifts of headgroups reflect nature of surface attachment
  - **Control:** 31 ppm
  - **Attached:** multiple broad peaks from 22-35.9 ppm
  - **Shift:** chemical bond between acid monolayer and nanoparticle surface
    - Upfield shift is associated with the chemically bonded phosphonic acid film with the ZnO surfaces
    - 0.01 and 0.02 mmol-tridentate preference
  - **Broadening:** distribution of binding sites
  - **Increased number of peaks:** different types of surface bonds and binding sites on ZnO surface
Energy-level diagrams of Metal/Organic Interfaces with metal work functions

Ultraviolet Photoelectron Spectroscopy (UPS)

- Hole-injection and electron-injection barriers are linearly dependent on an electrode’s work function.
- Surface potential is directly proportional to the effective work function.
- Organic molecules anchored on metal or oxide surfaces can produce a permanent dipole moment at the interface.
- Methyl-terminated modified samples work function ranges from 3.4 to 5.4 eV depending on surface coverage and film thickness.

<table>
<thead>
<tr>
<th>Modifications</th>
<th>Work function (Φ ± 0.1 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>4.4</td>
</tr>
<tr>
<td>0.010 mmol ZnO – ODPA</td>
<td>3.3</td>
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<tr>
<td>0.020 mmol ZnO – ODPA</td>
<td>3.9</td>
</tr>
<tr>
<td>0.045 mmol ZnO – ODPA</td>
<td>4.0</td>
</tr>
<tr>
<td>0.090 mmol ZnO – ODPA</td>
<td>4.4</td>
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<tr>
<td>0.020 mmol ZnO – COOH-PA</td>
<td>5.4</td>
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<tr>
<td>0.045 mmol ZnO – COOH-PA</td>
<td>5.6</td>
</tr>
<tr>
<td>0.020 mmol ZnO – Di-PA</td>
<td>5.6</td>
</tr>
<tr>
<td>0.045 mmol ZnO – Di-PA</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Conclusions

- Confirmation and characterization via IR, SEM, PXRD, and SS-NMR
  - Organic acids SAMs formed strongly-bound, mostly ordered monolayers that remained attach after various stability tests
  - Thin films were adsorbed on the surfaces through the phosphonate group

- The photoresponsivity is highly desired for photovoltaic applications such as in solar cells

- Treatments of the film surface by coating the ZnO nanoparticles was monitored and characterized by calculating work function for electronic purposes
Future Work

- Modification of ZnO using perfluorinated compounds
- Electrochemical measurements including band gap analysis
- Polymers modifications
Acknowledgements

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THANK YOU FOR YOUR ATTENTION

Questions??