Plasma-Enhanced Atomic Layer Deposition of NiCoO$_4$ for Photoanode Protection

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Introduction

Solar-driven water-splitting is a renewable technology for sunlight energy harvesting and H$_2$ production. Energy is stored in simple chemical bonds in H$_2$ and O$_2$ molecules by using photogenerated charge carriers to reduce and oxidize water, respectively, at (photo)electrode/electrolyte interfaces. Two approaches for designing stable and efficient photoanodes are using stable but typically inefficient semiconductors or efficient but unstable n-type semiconductors coated with a protective hole-permeable p-type transparent conductive material (p-TCM). Sputtered NiCoO$_4$ has already been studied as a p-TCM on silicon and InP photoanodes[1]. This project aims to protect and optimize silicon and GaAs photoanodes with NiCoO$_4$ deposited with Plasma-Enhanced Atomic Layer Deposition (PE-ALD).

Figure 1: Schematic of the band diagram of a photoanode, illuminated from the right, consisting of a n-type absorber (left) protected with a p-TCM (center). Red: Conduction Band, Blue: Valence Band, Dotted line: quasi-Fermi levels, yellow: photon with $h\nu \geq E_g$.

Figure 2: (left) Process flow for the deposition of nickel cobalt oxide with PE-ALD. (center) Proposed mechanism for the deposition of the first layer cobalt (or nickel) layer (right) Proposed mechanism for the deposition of subsequent cobalt or nickel layers. Precursors are NiCP$_2$ and CoCP$_2$.

Figure 3: Influence of plasma duration after cobalt precursor exposure on (left) optical and electrical properties and (center) stoichiometry. Horizontal dashed line is the stoichiometric composition, reached by depositing 3 Cobalt cycles per Nickel cycle instead of 2. Constant Co:Ni plasma duration ratio. (right) X-Ray Photoelectron Spectroscopy (XPS) spectrum of Cobalt 2p$_{3/2}$ and Nickel 2p$_{3/2}$ peaks.

Conclusion

1. The crystalline structure, chemical composition, optical properties, electrical properties and electronic band structure of NiCoO$_4$ deposited with PE-ALD under various conditions was studied.
2. Stable n-Si/p-NiCoO$_4$ photoanodes with very low onset voltage have been produced and optimized. ALD produces electrodes with better heterojunction but worse stability than sputtering (see [1]).
3. Fabrication of stable n-GaAs/p-NiCoO$_4$ photoanodes has been attempted.

Table 1: Summary of photoanode performance.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Current Density [mA/cm$^2$]</th>
<th>Voltage [V]</th>
</tr>
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<tbody>
<tr>
<td>n-Si/NiCoO$_4$</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>n-GaAs/NiCoO$_4$</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 4: Wide-Angle X-Ray Scattering (WAXS) spectra of n-Si/NiCoO$_4$ (left) and n-GaAs/NiCoO$_4$ (right). Peaks marked with a star likely do not belong to the sample; indexed peaks belong to NiCoO$_4$. Data collected at SSSL beamline 11-3 at SLAC National Accelerator Laboratory.

Figure 5: Cyclic Voltammetry scans (9 cycles) of n-Si and p$^+$-Si protected with two optimized layers of NiCoO$_4$ of 30nm thickness.

Figure 6: 64 h stability test of n-Si/NiCoO$_4$ heterojunction photoanode. The protective layer is not etched away.

Figure 7: (left) Cyclic Voltammetry (CV) scans (10 cycles) of n-GaAs protected with 30 nm NiCoO$_4$. (right) Atomic Force Microscope image of the electrode surface before CV.

Figure 8: Cyclic Voltammetry scans (9 cycles) of n-GaAs protected with a 1.4 nm layer of SiO$_2$ and 30 nm NiCoO$_4$.

Silicon photoanodes

GaAs photoanodes

Reference


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