Influence of CIGS Surface Conditioning on GDOES Depth Profile Measurement Results

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Why CIGS?
• CIGS (Cu(In,Ga)Se₂) is the most promising thin-film solar cell material. Cell efficiencies up to 21.7 % for single cell (0.5 cm²) and 16.5 % on module could be demonstrated. A further increase of cell efficiency to higher values is possible.
• Total cell thickness around 3 to 4 μm CIGS enables use in flexible solar cells with stainless steel or polyimide substrates.

Structure of CIGS
• A 500 nm thick Mo layer is sputtered as the back contact on soda lime glass.
• Semiconductor consists of coevaporated CIGS (2 μm) and chemical bath deposited CdS (60 nm) layers.
• Front contact is sputtered i-ZnO+AZO (1 μm). Small cells are coated with a Ni/Al/Ni grid. For modules a monolithic design is used.

Why GDOES?
• Fast depth profiling; no waiting time for sample transfer; depth profile comparable with SNMS and SIMS

Important Values for CIGS depth profiling
• GGI: Ga/(Ga+In) ratio corresponds to band alignment and band gap \( E_g \)
• CGI: Cu/(Ga+In) ratio is related to stoichiometry

Na content in CIGS: strong influence on cell efficiency; reason for efficiency improvement is still under discussion.

Treatment

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>water rinse:</td>
<td>normally used for removing particles</td>
</tr>
<tr>
<td>Na₂S etching:</td>
<td>removing of oxidized CIGS surface layer</td>
</tr>
<tr>
<td>CdS bath deposition:</td>
<td>protection against surface oxidation</td>
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<tr>
<td>CdS etched:</td>
<td>removing of CdS by hydrochloric acid</td>
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</tbody>
</table>

Water and CdS remove Na totally from CIGS surface (1), confirmed by XPS and SIMS measurements (not shown). CdS, Na₂S and plasma are the best choices for removing C from CIGS surface (2). Water sometimes increases C amount at surface (3b, also confirmed by XPS). A combination of treatment methods could improve surface cleaning properties for each method. For instance, water removes Na (3a) and plasma C (3b). The order of treatment is thus important.

Influence on sputter rate

Some surface treatments (Na₂S, KCN, CdS etched) have a diminishing effect on sputter rate (1). A lower sputter rate generates a smaller Ga depletion in the measurement signal near surface (≤ 0.10 normalized CIGS depth) (2) and a corresponding enrichment towards the Mo back contact (0.95–1.0 normalized CIGS depth) (3). But in contrast fast sputter rate leads to a decreased signal intensity and significantly reduced depth resolution.

Ga depletion could also be detected in GGI ratio (4). This effect is not observable for CGI. But sometimes a Cu peak is apparent near the surface (0.01–0.02 of normalized CIGS depth) (5). This effect is not related to surface conditioning and can be observed for all treatment methods and sputter rates (6).

Summary
• Best cleaning effect with CdS treatment, but cleaning effect could also be achieved by combinations of other methods.
• Surface conditioning influences sputter rate and sputter rate influences Ga distribution during measurement
• Best measurements obtained with CdS-coated samples — constant surface conditioning of CIGS sample.
• Appearing of a Cu peak at surface is not correlating to surface conditioning

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