Supporting Information


Boosting the Performance of WO$_3$/n-Si Heterostructures for Photoelectrochemical Water Splitting: from the Role of Si to Interface Engineering

*Yihui Zhao, Geert Brocks, Han Genuit, Reinoud Lavrijsen, Marcel A. Verheijen, and Anja Bieberle-Hütter*
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Films deposition

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target power</td>
<td>100 W</td>
</tr>
<tr>
<td>Base pressure</td>
<td>$&lt;10^{-8}$ mbar</td>
</tr>
<tr>
<td>Deposition pressure</td>
<td>$10^{-2}$ mbar</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>O$_2$ flow rate</td>
<td>10 sccm</td>
</tr>
<tr>
<td>Ar flow rate</td>
<td>40 sccm</td>
</tr>
</tbody>
</table>

Figure S1 shows the flow diagram of the thin film depositions.
Figure S1: Flow diagram of WO$_3$/n-Si, WO$_3$/Ag/n-Si, WO$_3$/Ag/(IBM)n-Si (ion beam milling treated n-Si) and WO$_3$/Pt/n-Si deposition. The entire process is carried out without breaking the vacuum.

**Atomic Force Microscope (AFM) of WO$_3$/n-Si and WO$_3$/FTO**

Figure S2 shows the surface roughnesses of WO$_3$/n-Si and WO$_3$/FTO, which were measured by AFM. The surface roughnesses of WO$_3$/n-Si and WO$_3$/FTO are $R_a = 2.2$ nm and $R_a = 7.1$ nm, respectively.

Figure S2: Atomic Force Microscope (AFM) of (a) WO$_3$/n-Si and (b) WO$_3$/FTO after annealing in the Ar.
Cross-section HAADF-STEM of WO₃/n-Si and WO₃/FTO

Cross-section HAADF-STEM images confirm that an intimate contact is obtained for both WO₃/n-Si and WO₃/FTO interfaces, as shown in Figure S3.

![Cross-section HAADF-STEM images of (a) WO₃/n-Si and (b) WO₃/FTO.](image)

Figure S3: Cross-section HAADF-STEM images of (a) WO₃/n-Si and (b) WO₃/FTO.

GIXRD of WO₃/n-Si and WO₃/FTO

The GIXRD spectra of the WO₃/n-Si and WO₃/FTO after annealing in Ar at 450°C for 1 h are shown in Figure S4. The diffraction peaks agree well with monoclinic WO₃ corresponding to JCPDS No. 83-0950 indicating that monoclinic WO₃ was obtained for both electrodes after annealing.
**Figure S4**: GIXRD spectra of WO$_3$/n-Si (black) and WO$_3$/FTO (red) after annealing in Ar. The brown diamonds and the blue dots are monoclinic WO$_3$ (JCPDS No. 83-0950) and FTO (JCPDS No. 83-0950), respectively.

**Relative energy band levels**

Figure S5 shows the energy band diagrams of n-Si, WO$_3$, Ag, Pt and H$_2$O. The band gap of n-Si is $\sim$1.1 eV$^{[1]}$ and the Fermi level is about $-4.25 \pm 0.1$ eV vs vacuum level$^{[1-3]}$. The band gap of WO$_3$ is about 2.8 - 3.0 eV and the Fermi level is about $-5.25 \pm 0.1$ eV$^{[4-7]}$. The work functions of Ag and Pt are 4.5 ± 0.15 eV and 5.7 ± 0.1 eV vs vacuum level$^{[8]}$.

**Figure S5**: Diagram of relative energy band levels of n-Si, WO$_3$, Ag, Pt, and H$_2$O. The diagram is constructed from literature data$^{[1-8]}$.

**Reference**


