Supporting Information

Towards zero bias photoelectrochemical water splitting: onset potential improvement of Mg:GaN-modified Ta₃N₅ photoanode

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Abstract: Tantalum nitride (Ta₃N₅) based photoanodes were overlaid with magnesium-doped gallium nitride (Mg:GaN) thin films by plasma-enhanced chemical vapor deposition (PCVD) technique, and subjected to photoelectrochemical activity tests, aiming for a negative shift of onset potential for O₂ evolution. A remarkable negative shift of the onset potential was observed after annealing Mg:GaN in N₂ gas, reaching 0 V vs RHE, despite a lower photocurrent than that on bare Ta₃N₅. Mg:GaN annealed in NH₃ exhibited an improvement of the photocurrent. A detailed study of the photoelectrochemical performance for various samples and a thorough characterization have revealed the effects of N₂/NH₃ post annealing over Mg activation/Ta₃N₅ damage recovery, controlling the onset potential shift and the current density improvement. N₂ post annealing shifted the onset potential to 0 V vs RHE but decreased the current density. On the other hand, NH₃ post annealing slightly shifted the onset potential and increased the current density largely. Albeit the current density loss, this onset potential shift unlocks the prospect of unassisted photoelectrochemical water splitting on Ta₃N₅.

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Figure S1. XRD patterns of a) Mg:GaN/Ta$_3$N$_5$ with different Mg:GaN thickness, b) Mg:GaN/Pyrex glass with different Mg concentration.
Table S1. EDS elemental analysis of Mg:GaN/Ta₃N₅ sample before and after post annealing in N₂ or NH₃.

<table>
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<tr>
<th>Elements</th>
<th>Concentration, wt%</th>
<th>As-prepared</th>
<th>N₂-post annealed</th>
<th>NH₃-post annealed</th>
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<tbody>
<tr>
<td>Mg</td>
<td>2.2</td>
<td>2.0</td>
<td>0.7</td>
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<tr>
<td>Ga</td>
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<td>76.6</td>
<td>70.4</td>
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<tr>
<td>N</td>
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<td>14.9</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>3.9</td>
<td>3.2</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>3.2</td>
<td>3.5</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
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</tr>
</tbody>
</table>
Figure S2.

a – f : XPS elemental peaks of Mg:GaN/Ta₃N₅ sample surfaces as prepared, post-annealed in N₂, and post-annealed in NH₃.

g – i : XPS elemental peaks for standard Mg materials. Mg 1s, Mg 2p and O 1s signals on MgO and Mg metal (Ar-bombarded for 15 min and 30 min for cleaning).

The Ga 2p3/2 peaks in d are positioned at 1117.5 eV of the binding energy, closely to that of typical GaN films grown by thermal CVD.²³

Mg 1s peaks in a and b are positioned at that of oxidized Mg²⁺ (compared to g and h).
Figure S3. XPS of a) Mg 2p, b) Mg 1s, c) Ga 3d, d) Ga 2p, e) O 1s, f) N 1s on depth profiling of N$_2$ post annealed-Mg:GaN/Ta$_3$N$_5$. 
Table S2. EDS elemental analysis of Mg:GaN area in Mg:GaN/Ta3N5 sample after N2 post annealing.

<table>
<thead>
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<th>Elements</th>
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<td>Ga</td>
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<td>N</td>
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<tr>
<td>O</td>
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<tr>
<td>Ta</td>
<td>8.7</td>
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<tr>
<td>Total</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Figure S4. a) Dark- and b) bright-field cross-sectional STEM images of as-prepared Mg:GaN/Ta3N5 and STEM-EDS mapping of c) Mg, d) Ga, e) N, f) Ta, and g) O for the same observing area. Scale bar = 50 nm.
Figure S5. EDS line scan of the Mg:GaN/Ta$_3$N$_5$ after N$_2$ post annealing. The abscissa of each viewgraph corresponds to the position on the yellow line in the SEM image. The coordinate of each viewgraph indicates EDS counts (in an arbitrary unit).
Figure S6. HRTEM image at interface of Ta₃N₅ (dark, right side) and Mg:GaN (bright, left side) after N₂ post annealing. The spacing of 0.25 nm in the striped pattern in the GaN side matches the (002) plane spacing of wurtzite GaN. This part of GaN agrees with the XRD pattern (Fig. 2) involving the intense peak at 2θ = 34.5°.
Figure S7. Tauc’s plot of Mg:GaN/Al₂O₃ a) before and after post annealing, and b) with different Mg concentration. The Tauc’s plot are used to determine the bandgap energy of the corresponding samples.
Figure S8. PESA spectra of a) Au, b) Ta₃N₅, c) Mg:GaN/Al₂O₃ with different Mg concentration, d) commercial n-GaN/sapphire and p-GaN/sapphire, and e) Mg:GaN/Al₂O₃ before and after post annealing.
Figure S9. MS plot of a) Ta$_3$N$_5$, b) GaN/Al$_2$O$_3$, c) as-prepared Mg:GaN/Al$_2$O$_3$, d) N$_2$ post annealed Mg:GaN/Al$_2$O$_3$, e) NH$_3$ post annealed Mg:GaN/Al$_2$O$_3$.

Figure S10. Magnification of background-subtracted LSV curve in Figure 5a, showing the onset potentials of Ta$_3$N$_5$ and Mg:GaN/Ta$_3$N$_5$ after N$_2$ and NH$_3$ post annealing.
Figure S11. LSV of a) Si:GaN/sapphire, GaN/Ta₃N₅, Mg:GaN/Ta₃N₅ and Mg/Ta₃N₅, under full-light irradiation by solar simulator, b) Mg:GaN/Ta₃N₅ in solar simulator full light and solar simulator+L42 (visible light, λ>420 nm). All the experiments were done using 100 mL of 0.5 M K₂HPO₄ solution at pH 13 (KOH adjusted) electrolyte, with CoPi cocatalyst addition.
**Figure c**

- Voltage: 1 mA cm$^{-2}$, 10 mV/s
- Temperature: 1000 °C, 900 °C, 800 °C, As-prepared
- Current density vs Potential V vs RHE

**Figure d**

- Voltage: 2 mA cm$^{-2}$, 10 mV/s
- Concentration: 3.0 wt% Mg, 2.3 wt% Mg, 1.2 wt% Mg
- Current density vs Potential V vs RHE
Figure S12. LSV of 100 nm Mg:GaN/Ta$_3$N$_5$ a) after N$_2$ post annealing with different temperatures, b) after N$_2$ post annealing at 800 °C with different Mg concentration, c) after NH$_3$ post annealing with different temperatures, d) after NH$_3$ post annealing at 1000 °C with different Mg concentration, e) 300 nm Mg:GaN/Ta$_3$N$_5$ after NH$_3$ post annealing.

Figure S13. LSV of bare Ta$_3$N$_5$ exposed to PCVD chamber followed by N$_2$ or NH$_3$ post annealing.
Figure S14. LSV of Mg:GaN/Ta$_3$N$_5$ subjected to a) N$_2$ post annealing, b) N$_2$ post annealing followed by NH$_3$ post annealing, c) NH$_3$ post annealing, d) NH$_3$ post annealing followed by N$_2$ post annealing.
Figure S15. LSV of NH$_3$ post annealed-Mg:GaN/Ta$_3$N$_5$ sample followed by rapid thermal annealing (RTA) at different temperature in static N$_2$. 