Semi-Transparent Quaternary Oxynitride Photoanodes on GaN Underlayers

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ABSTRACT: Quaternary oxynitrides AB(O,N)₃ are promising photoactive materials for solar energy-driven water splitting, but it remains challenging to manufacture them as semi-transparent thin films for the construction of a tandem photoelectrochemical (PEC) cell. In this letter, we develop a generalized approach by chemical solution deposition (CSD) in conjunction with conductive gallium nitride (GaN) on sapphire substrate towards the synthesis of a semi-transparent quaternary oxynitride thin films. Additionally, conformal atomic layer deposition (ALD) technique is employed to make semi-transparent Ta₅N₅, providing the possibility to build semi-transparent oxy(nitride) heterojunction photoanodes on conductive substrate. The present work demonstrates a synthetic route for quaternary oxynitride-based wireless tandem PEC cells beyond semi-transparent Ta₅N₅ photoanodes.

A sustainable solution for storing the solar energy in principle can be achieved by PEC technology, which is based on splitting of earth-abundant water into the renewable energy carrier hydrogen and oxygen.¹ Connecting the photoanode and the photocathode in a stacked configuration enables the devices to maximize sunlight harvesting by using narrow band gap semiconductors in tandem.² Thus, the photovoltage generated in each photoabsorber can be summed to drive water splitting at high efficiency. In the tandem geometry, the photoanode as first photoelectrode absorbs photons of higher energy while the photocathode absorbs the transmitted photons to drive water reduction.³ Figure 1 depicts a wireless tandem PEC cell configuration, in which the solar photons not absorbed by the semi-transparent photoelectrode at the front side will pass through the intermediate transparent conductive substrate (TCS). Subsequently, the remaining photons can be harvested by the second photoelectrode with a smaller band gap energy (Eₒ).⁴

FIGURE 1. Schematic illustration of a wireless artificial leaf tandem cell configuration for overall water splitting. The n-type and p-type semiconducting photoelectrodes are serially connected with a transparent conductive layer.

Additionally, the other advantages of the wireless PEC tandem cell are the i) flexibility in materials selection, ii) low resistance losses and iii) high proton conductivity,⁵,⁶ which target for high solar-to-hydrogen (STH) conversion efficiency.⁷ Furthermore, the wireless configuration is more suitable for industrial manufacturing in comparison to the wired tandem configuration in which the photoabsorbers are connected via external circuit.⁸ With respect to the TCS materials required for a PEC tandem cell, the most commonly used substrates are transparent conductive oxides (TCOs) such as fluorine/indium doped tin oxide (FTO/ITO) and aluminum doped zinc oxide (AZO).⁹ These TCS materials, however, cannot be applied to materials that require synthetic conditions including ammonia at elevated temperatures (>873 K). As such, common TCS materials are limited in their implantation for nitrogen-containing photoelectrode materials.¹⁰,¹¹

For commercialization of PEC technology, it is widely accepted that the STH efficiency needs to be greater than 10%.¹² Among the often studied metal oxide-based photoanodes such as TiO₂, WO₃, ZnFe₂O₄ and BiVO₄, the most representative one is the latter,¹³ exhibiting the highest STH conversion efficiency of 3.7% in a bias-free tandem cell for PEC water splitting.⁷ To achieve higher STH efficiency, the front photoanode in wireless tandem PEC cells has to be semi-transparent. Thus, it must absorb photons with energy larger than its band gap and transmit the remaining photons to the photocathode behind it, avoiding scattering or parasitic absorption of the transmitted light.

Metal nitrides and oxinitrides exhibit narrower band gaps than the best-performing oxidic photoanode candidates. An example is Ta₅N₅ with a bandgap of 2.1 eV and that can be obtained by ammonolysis of Ta₂O₅. This synthetic
approach makes it challenging to produce semi-transparent metal (oxy)nitrides on FTO, because the transparent SnO$_2$ becomes metallic Sn under the nitridation conditions.\textsuperscript{14} It should be noted that fabrication of semi-transparent photoanodes by means of electrophoretic deposition of powder samples displays significant worse mechanical stability under operating conditions. Recently, the groups of Hamann\textsuperscript{10,14} and Domen\textsuperscript{15-17} have demonstrated alternative methods to fabricate semi-transparent Ta$_3$N$_5$ photoanodes. Although Ta$_3$N$_5$ has a high theoretical STH, it suffers from a high onset potential of 0.3-0.8 V versus reversible hydrogen electrode (RHE),\textsuperscript{14,18,19} which then must be generated by the tandem photocathode for overall water splitting to occur.\textsuperscript{20}

The quaternary metal oxynitrides ATa(O,N)$_3$ display a photocurrent onset at smaller applied potentials and, for several compounds, can potentially exhibit a higher theoretical STH efficiency than the binary Ta$_3$N$_5$.\textsuperscript{21,22} This is due to the narrower band gaps of quaternary metal oxynitrides, depending on the chemical composition and being tunable within the range of 1.7 and 2.4 eV.\textsuperscript{22-24} This renders semi-transparent quaternary metal oxynitrides generally as very promising photoanode candidates for PEC tandem cells, which could outperform Ta$_3$N$_5$-based devices. So far, semi-transparent quaternary metal oxynitride films have been mainly fabricated by means of reactive radio-frequency (RF) magnetron sputtering\textsuperscript{25-28} or pulsed laser deposition (PLD)\textsuperscript{29,30} on MgO or Nb: SrTiO$_3$ substrate. In case of the RF approach, the oxynitride sputtering targets have to be made first with multi-step processes and harsh conditions (usually up to 1073 K for film deposition) are required, too.\textsuperscript{27} The development of photoelectrode materials with more narrow band gaps than Ta$_3$N$_5$ and hematite is mainly motivated by the higher theoretical light absorption capacity.\textsuperscript{11} Recently, Domen et al. have demonstrated a core-shell heterojunction photoanode of Ta$_3$N$_5$-nanorods/BaTaO$_3$:N$_5$ generating a stable photocurrent owing to efficient generation and extraction of charge carriers.\textsuperscript{31} For the reproducible fabrication of thin films exhibiting controllable thickness on the atomic scale and conformal features, Atomic Layer Deposition (ALD) is a promising technique for the deposition of oxidic precursor layers for subsequent nitridation.\textsuperscript{32}

In this letter, we demonstrate the synthesis of semi-transparent quaternary photoanodes on the examples of SrTaO$_3$N and LaTiO$_3$N. First, ALD was explored to obtain semi-transparent Ta$_3$N$_5$ thin films on conductive n-type GaN substrate. GaN was selected as the substrate because it can maintain chemical stability at high temperature in NH$_3$ without degradation\textsuperscript{12} and under ambient conditions.\textsuperscript{33} Low pressure metalorganic vapor phase epitaxy reactor (MOVPE) was employed to grow unintentionally-doped GaN epitaxial film on double-sided polished Al$_2$O$_3$ (sapphire) substrates (see Experimental Methods in the Supporting Information for details).

The ALD cycle procedure for Ta$_2$O$_5$ deposition is illustrated in Figure 2a (see Experimental Methods in the Supporting Information for details). The Ta$_2$O$_5$ thin films were converted to Ta$_3$N$_5$ by nitridation at 1148 K for 2 h.\textsuperscript{34} The sample after nitridation is depicted in the inset of Figure 2c. The transmittance of the prepared thin film was evaluated by means of Ultraviolet-visible spectroscopy (UV-vis) as a function of the wavelength (Figure 2c). After depositing Ta$_2$O$_5$ onto Al$_2$O$_3$/GaN substrate, the transmittance only decreased slightly because of thin Ta$_3$N$_5$ layer and its wide band gap. After nitridation, the transmittance of the resulting Al$_2$O$_3$/GaN/Ta$_3$N$_5$ thin film decreased to around 70% at wavelengths above 600 nm.

![Figure 2](image_url)

Figure 2. (a) Schematic illustration of the ALD procedure for Ta$_2$O$_5$ on substrate. (b) UV-visible transmittance spectra for Ta$_3$N$_5$ film on Al$_2$O$_3$/GaN substrate and the substrate with Ta$_2$O$_5$ layer comparing with pristine substrate. The inset depicts photographic image of the Ta$_3$N$_5$ film. (c) SEM micrograph of Ta$_3$N$_5$ film on Al$_2$O$_3$/GaN substrate. (d) LSV of Ta$_3$N$_5$ film measured in 0.1 M NaOH under chopped AM 1.5G solar simulated light (100 mW cm$^{-2}$).

The light-absorbing thin film Ta$_3$N$_5$ on the Al$_2$O$_3$/GaN substrate was composed of grains with approximately size of 100 nm due to sintering at high temperature (Figure 2b). The grains are distributed uniformly throughout the substrate as observed at the low magnification scanning electron microscopy (SEM) micrograph (Figure S1).
The Al₂O₃/GaN/Ta₂N₅ photoanode, which was prepared by MOVPE and ALD, generated a photocurrent of 0.21 mA cm⁻² at 1.23 V vs. RHE in 0.1 M NaOH under AM 1.5G illumination (1 sun) as shown in the linear sweep voltammetry curve (LSV, Figure 2d). The photocurrent maintained stable during chronoamperometry (CA) (Figure S2).

![Figure 3. Schematic illustration of the fabrication procedure for semi-transparent quaternary metal oxynitride thin film photoanode on transparent conductive GaN/Al₂O₃ substrate.](image)

Given the suitability of the deposited GaN layer for electron transport of nitric light absorbers, we elucidated the possibility to fabricate quaternary metal oxynitrides on the transparent substrate Al₂O₃/GaN. Figure 3 shows the preparatory procedure of semi-transparent quaternary oxynitride thin films (see Experimental Methods in the Supporting Information for details). A spin-coating step followed to deposit a sol-gel film on the substrate from a precursor solution containing La and Ti with molar ratio of 1:1. The sol-gel was prepared by dissolving titanium(IV) butoxide and La(NO₃)₆·H₂O as Ti and La sources into the mixture containing 2-methoxyethanol, acetic acid and acetylacetone. Afterwards, the substrate was annealed at 773 K for 1 h in air to remove organics from the sol-gel to form the precursor oxide of La and Ti. The oxide was converted to LaTiO₃ by nitridation under flowing NH₃ (15 mL min⁻¹) and H₂ (5 mL min⁻¹) at 1148 K for 2 h at a ramping rate of 10 K min⁻¹.

X-ray diffraction (XRD) patterns presented in Figure 4a reveal that the grown LaTiO₃ thin film on Al₂O₃/GaN substrate is of single-phase purity. The LaTiO₃ patterns fully match the simulated powder patterns (ICSD #239555). The UV-vis spectrum (Figure 4b) also shows an absorption edge at approximately 600 nm, consistent with the LaTiO₃ band gap of 2.0-2.1 eV. The transmittance decreased from 80% on the Al₂O₃/GaN substrate to roughly 60% on the Al₂O₃/GaN/LaTiO₃ substrate for wavelengths above 600 nm. The high transparency (see inset of Figure 4b) of LaTiO₃ is above the threshold for constructing a tandem PEC cell by integration with a photocathode of smaller band gap. The damping-like feature of the spectrum is due to the interference fringes of multiple layers, i.e. Al₂O₃, GaN and LaTiO₃. The SEM micrograph in Figure 4c shows the morphology of the prepared LaTiO₃ film in the form of a microstructure comprised of nanoparticulate agglomerations that were several hundred nanometers in diameter. A similar morphology is usually obtained for other ceramic thin films prepared by CSD. The SEM at low magnification (see Figure S3) demonstrates that the film is uniform and crack-free. We also synthesized SrTaO₃N in order to verify the generality of the CSD-based synthesis for semi-transparent quaternary oxynitride photoanodes. Its XRD pattern (Figure 4d) confirms the formation of single-phase SrTaO₃N crystallizing with the tetragonally-distorted perovskite structure in space group I₄/mcm (ICSD 95373). The prepared SrTaO₃N thin film also exhibited high transparency (see inset of Figure 4e). UV-vis measurements showed transmittance of approximately 70% for wavelengths above 550 nm, which corresponds to the absorption edge of SrTaO₃N. These results prove that the CSD-based process can indeed be used for other semi-transparent quaternary oxynitride thin films on transparent Al₂O₃/GaN substrate.

![Figure 4. (a) XRD patterns of LaTiO₃N film on Al₂O₃/GaN substrate and simulated patterns (ICSD #239555). (b) UV-visible transmittance spectra of LaTiO₃N film on Al₂O₃/GaN substrate and the substrate before oxynitride deposition. The inset depicts a photographic image of the LaTiO₃N film. (c) SEM micrograph of LaTiO₃N film on Al₂O₃/GaN substrate. (d) XRD patterns of SrTaO₃N film on Al₂O₃/GaN substrate and simulated pattern (ICSD #95373). (e) UV-visible transmittance spectra of SrTaO₃N film on Al₂O₃/GaN substrate and the substrate before oxynitride deposition. The inset depicts photographic image of the SrTaO₃N film. (f) LSV curves of LaTiO₃N and SrTaO₃N films measured in 0.1 M NaOH under chopped AM 1.5G simulated solar light (100 mW cm⁻²).](image)

The critical feature of such prepared electrodes is the transport of electrons through the GaN pathway over the external circuit to the counter-electrode. The PEC water-oxidation performances of the prepared LaTiO₃N and SrTaO₃N films were assessed in 0.1 M NaOH electrolyte (pH 13) under simulated sunlight (1 sun, AM 1.5 G). Figure 4f displays the LSV curves measured at a scan rate of 10 mV s⁻¹ under chopped illumination. The LaTiO₃N thin film developed a net photocurrent of approximately 20 µA cm⁻² at 1.23 V vs. RHE. The photocurrent is comparable with the LaTiO₃N film deposited on MgO/TiN and Nb:Si/TiO₂ substrates via PLD and RF sputtering reported by Lippert and Domen, respectively. The dark-current contribution stems from photocorrosion of the oxynitride surface, which is a common
phenomenon for unprotected metal oxynitrides and can be suppressed with protective layers.\textsuperscript{40,41} The pristine semi-transparent SrTaO$_3$N photoanode, having a slightly larger band gap than LaTiO$_3$N, generated a photocurrent of app. 7 \mu A cm$^{-2}$ at 1.23 V vs. RHE.

In conclusion, we have successfully fabricated semi-transparent quaternary oxynitride LaTiO$_3$N and SrTaO$_3$N thin films on transparent conductive Al$_2$O$_3$/GaN substrate. PEC measurements confirmed their potential for use as the top photoanode in a PEC water-splitting cell, and the band gaps suggest that they may have higher theoretical STH than Ta$_3$N$_5$-based photoanodes. The CSD-based process can be adopted as a general method towards the manufacture of semi-transparent quaternary oxynitride thin films on large scale. Additionally, the conductive Al$_2$O$_3$/GaN substrate have been coated with Ta$_3$N$_5$ by means of ALD to yield semi-transparent thin films. Nonetheless, the photocurrent of the quaternary oxynitride thin film is far lower in comparison to their maximum theoretical values. This requires future synthetic strategies for nanostructuring of the light absorbing metal oxynitride layer and its subsequent semi-transparent catalytic coatings.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

Experimental Methods; low magnification SEM micrographs of Al$_2$O$_3$/GaN/Ta$_3$N$_5$ and Al$_2$O$_3$/GaN/LaTiO$_3$N; CA curve of Al$_2$O$_3$/GaN/Ta$_3$N$_5$.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENT

Z.M. thanks the China Scholarship Council for a Ph.D. scholarship. We thank Wenyan Wang for the access to UV-vis facility. A.S. would like to thank Vinnova (project: C1Bio 2019-03174) for financial support. R.H.C. and J.R.D. are supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC-0020301.

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