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Fabrication of semi-transparent SrTaO$_2$N photoanodes with a GaN underlayer grown via atomic layer deposition

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ABSTRACT

Quaternary metal oxynitride-based photoanodes with a large light transmittance are promising for high solar-to-hydrogen (STH) conversion efficiency in photoelectrochemical (PEC) tandem cells. Transparent substrates to support PEC water-splitting were fabricated using atomic layer deposition (ALD) to synthesize 30 and 60 nm GaN on SiC substrates. A generalized approach was used to grow a quaternary metal oxynitride, i.e. SrTaO$_2$N thin film on the GaN/SiC substrates. The transparency above 60% in the wide solar spectrum highlights its availability of transmitting visible light to the rear side. A photocurrent onset at ca. −0.4 V vs. reversible hydrogen electrode (RHE) was achieved by the SrTaO$_2$N/GaN/SiC photoanodes in a 0.1 M NaOH electrolyte under simulated solar irradiation. This paves the way for the construction of hierarchically nanostructured tandem PEC cells. This work demonstrates the viability of integrating ALD in constructing substrates for semi-transparent quaternary metal oxynitride photoanodes.

1. Introduction

The development of effective solar-to-hydrogen (STH) systems is considered essential to alleviate the energy problem and establish a carbon-neutral society (1–5). Photoelectrochemical (PEC) water splitting is potentially sustainable for large-scale conversion of solar energy into storable hydrogen source (6–9). A technoeconomic report revealed that an STH efficiency above 10% is required for the practical application of PEC technology (10, 11). While efficiencies have been improving over the past decades, enhanced sunlight utilization and circumvention from applying external voltage remain pressing issues, in addition to durability problems (12–16). For the former, two fundamental losses are linked with low photoabsorbance. On one hand, most of the photon energy is lost with incident photons possessing energy lower than the bandgap ($E_g$); on the other hand, photons containing higher
energy in comparison to $E_g$, are partially wasted by emitting phonons (17, 18). The driving force for the latter is the required photovoltage (the potential difference between the quasi-Fermi levels of photogenerated electrons and holes), which is generally insufficient for a single photoelectrode to surmount the barriers associated with the kinetics needs (19). In this regard, a self-biased PEC tandem cell powered only by solar energy is an ideal photoabsorber system to minimize the energy loss of the solar spectrum (3, 17, 20). Sufficient photovoltage can be obtained to fulfill the energetic requirements, and higher potential states can be populated by both the excited electrons and holes to promote redox reactions (10). A wireless tandem PEC cell, in which the photoanode and the photocathode are grown back to back, and separated by a visible-light-transparent and electrically conductive layer (TCL) are depicted in Scheme 1. Fabrication of this type of PEC device is desired due to its advantages in low photon and photovoltage losses and flexibility for industrial manufacture (21, 22).

In particular, high transparency and efficiency of the front photoanode are critical prerequisites for achieving satisfied STH efficiency (22). The photoanode has to transmit sunlight with a wavelength longer than its absorption edge to the rear side for reutilization by the photocathode (Scheme 1). The extensively exploited TiO$_2$, ZnO, BIVO$_4$-based photoanodes have been assembled to fabricate PEC tandem cells with diverse photocathodes (22, 23). To achieve the STH efficiency of 10%, however, transparent photoanodes are required to spread their optical absorption spectra to the visible region, which accounts for a large portion of the solar spectrum (10). It should be noted that the first photoanode in the optical pathway with high transparency for illumination below its band gap is also a prerequisite for dual-photoanode cells, which have advantages in achieving complementary light absorption and improving the STH efficiency (17).

Compared with the best-performing oxidic photoanodes, i.e. BIVO$_4$, nitrogen-containing compounds, such as metal nitrides and metal oxynitrides (1.7 –2.4 eV), exhibit narrower bandgaps (24). Recently, a relatively high STH efficiency was recorded using a Ta$_3$N$_5$ photoanode-involved tandem cell (25). The transparent Ta$_3$N$_5$ on GaN/Al$_2$O$_3$ demonstrated high transparency of greater than 70% at wavelength above 600 nm, and gave an initial STH efficiency above 7% when combined with serially-connected dual-CuInSe$_2$-based photocathodes for hydrogen production (25). One key advantage of quaternary metal oxynitrides over Ta$_3$N$_5$ is their theoretically higher light absorption due to narrower band gaps, such as those found for SrTaO$_2$N or SrNbO$_2$N (19). The occurrence of more cathodic photocurrent onsets is also generally observed in oxynitride-driven systems, which makes them being very attractive photoanode candidates for tandem PEC cell (19, 21, 26).

Nonetheless, the fabrication process of transparent oxynitride thin films is demanding in comparison to oxides. Transparent quaternary oxynitride films have been previously obtained by pulsed laser deposition (PLD) (27, 28), reactive radio frequency (RF) magnetron sputtering (29–32), and spin-coating in conjunction with post-ammolysis (21). Although several TCL substrates have been tested, including MgO, Al$_2$O$_3$, and SrTiO$_3$ (21, 32), the limited choices hamper the widespread application of transparent oxynitride-based photoanodes in tandem cell. This is because of the high temperatures and reducing atmosphere required in these processes. The frequently used indium tin oxides (ITOs) and fluorine-doped tin oxides (FTOs) substrates are not stable under ammonolysis and lose transparency, i.e. tin oxide is reduced to metallic tin (33). An alternative substrate is silicon carbide (SiC), which is used for the deposition of electronic grade GaN in high-frequency electronics due to its extremely good thermal conductivity (34).

For TCL substrates, a current collector overlayer, e.g. GaN and TiN, is required to enable the transport of photogenerated electrons (25, 28). The high electron mobility of the former makes it a key material in advanced AlGaN/GaN high electron mobility transistors (exceed 1000 cm$^2$ V$^{-1}$ s$^{-1}$) (35, 36). Insertion of an interlayer between the photoanode films and the TCL could also mitigate the charge recombination by energetic alignment of the band edges (10, 37). This was observed when a 150-nm GaN layer was deposited between a Ta substrate and Ta$_3$N$_5$ film by plasma-enhanced chemical vapor deposition (PCVD), which led to a 1.8-fold enhancement in water oxidation efficiency (37). However, it is difficult to deposit GaN directly onto SiC.
by chemical vapor deposition (CVD) due to poor wetting of the film on the substrate (38). Furthermore, high temperatures (600–1000°C) are often used for CVD-GaN (39, 40), which is unsuitable for heat-sensitive films (e.g., InN, decomp. 500°C) (41).

Deposition of thin films with excellent uniformity and conformity, and controlled thickness is essential for the fabrication of solar devices with complex surface architecture (42). These pre-requirements, however, cannot be fulfilled by CVD, especially for three-dimensional (3D) TCL substrates (43, 44). A thick coating on the surface is prone to fill the trenches and/or holes (Scheme 2a), which is adverse for interfacial reactions. These aspects, therefore, highlight the importance of atomic layer deposition (ALD) due to its self-limiting growth mechanism for realizing future hierarchically nanostructured metal oxynitride photoanodes (38, 45, 46). It should be noted that GaN layers with thickness less than 100 nm were also demonstrated in several reports to be capable of charge transfer in solar energy devices (47–49). This is important for us to allow the deposition of the current collector layer to be governed readily by ALD in a low-temperature regime and to simultaneously maintain structural conformity (Scheme 2b) (50). Motivated by these conditions, we were interested to examine the viability of the ALD GaN layer on 4H–SiC for constructing transparent quaternary oxynitride photoanodes. The examination of thickness influence of GaN is meaningful to understand the critical limit required for the fabrication of quaternary oxynitride film on 3D transparent substrates.

In this work, we fabricated planar n-type GaN-coated SiC substrates using ALD and subsequently synthesized SrTaO$_2$N oxynitride thin film photoanodes. The oxynitride layers prepared on GaN/SiC exhibited significant transparency in almost the whole solar spectrum and a very negative onset potential of photoresponse.

2. Experimental

2.1. Preparation of SiC/GaN transparent substrates

GaN thin films were deposited epitaxially on polished single crystal 4H–SiC (0001) substrates by ALD (38). A highly volatile tris(1,3-diisopropyltriazenide)gallium(III) precursor, (Ga(triaz)$_3$), was used as the Ga source. This is due to the low carbon impurities and high stoichiometry of the final GaN film (Ga/N ratio: 1.05) (38). The detailed synthetic procedure of the Ga(III) triazenide precursor is provided in our previous reports (38, 42).

Prior to the deposition, the 4H–SiC substrates were cleaned in solutions of [1:1:5 solution of H$_2$O$_2$ (30%), NH$_3$ (25%), and H$_2$O] and [1:1:5 solution of H$_2$O$_2$ (30%), HCl (37%), and H$_2$O] to remove potential organic and inorganic contaminants. A hot-wall Picosun R-200 equipped with a Litmas remote plasma source was used for the deposition. The system filling with N$_2$ (99.999%, 300 mL min$^{-1}$) was heated at 450°C for 2 h to remove the trace amount of residual H$_2$O and O$_2$ in the deposition chamber due to the air contaminant during substrate exchange. Inside a N$_2$-filled glovebox, $\sim$1.0 g of the Ga(III) triazenide precursor (per 1000 ALD cycles) was transferred into a glass vial and placed into a stainless steel container (bubbler). It was then assembled into the system and the temperature for the bubbler was adjusted to 130°C. A dried gas mixture containing NH$_3$ (99.999%) and Ar (99.997%) in the ratio of 75/100 was introduced as NH$_3$ plasma with a 2800 W plasma power, which was located ca. 75 cm above the SiC substrate. A 10 s pulse of Ga(III) triazenide precursor and 12 s NH$_3$ plasma were used for

![Scheme 2](https://example.com/scheme2.png)

**Scheme 2.** Schematic illustration of the crucial role ALD plays in achieving semi-transparent hierarchically structured quaternary oxynitride photoanodes. 3D substrates are covered by (a) thick and (b) conformal GaN overlayers. Previous reports using metalorganic vapor phase epitaxy deposition (MOVPE) for GaN deposition led to a micrometer coating that results in the loss of nanostructured textures. Realizing GaN fabrication via ALD on SiC would enable to maintain the high surface area.
each cycle of deposition, separated by a 10-s pulse of N₂. The base pressure of the ALD reactor under carrier gas flow is 5 hPa, while a slight increase in the reactor pressure up to 7 hPa can be seen during the precursor pulse. This process was conducted at 350°C (growth rate: 0.3 Å/cycle) to yield 30 and 60 nm of epitaxial GaN on 4H–SiC (38). The obtained substrates were finally diced into 1 × 2 cm² pieces and well stored for further use.

2.2. Fabrication of SrTaO₂N thin films on SiC/GaN transparent substrates

Quaternary SrTaO₂N thin films were prepared by ammonolysis of the corresponding metal–oxide layers at elevated temperature. A modified polymerized-complex (PC) method was applied to prepare the precursor solution with follow-up spin-coating to give metal-complex layer (51–53). In a typical synthesis, 200 mg TaCl₅ (Sigma-Aldrich, 99.8%) and 858 mg citric acid (Sigma-Aldrich, > 99%) were dissolved in 2 mL ethylene glycol (Sigma-Aldrich, > 99%) under vigorous stirring to produce the Ta-complex solution. An inert atmosphere was used during the preparation. A solution of 118 mg Sr(NO₃)₂ (Sigma-Aldrich, > 99%) in 0.2 mL deionized water, dissolved using ultrasonication, was then slowly injected into the aforementioned complex solution and the setup was kept at 70°C during the process. The mixture was subsequently heated to 100°C and magnetically stirred for 30 min. The resultant viscous solution was used to prepare the thin film on the GaN/SiC substrate by spin-coating at 2000 rpm for 3 min in air. It was baked afterwards at 150 and 300°C for 30 min each in sequence to promote polymerization. The obtained sample was calcinated at 550°C for 2 h to remove organic components and to give the metal oxide precursor. The substrate was transferred into an alumina boat and mounted in a tube furnace for nitridation at 1000°C for 2 h under flowing NH₃ (30 mL min⁻¹) and H₂ (5 mL min⁻¹), with the ramping rate of 7°C min⁻¹. The transparent SrTaO₂N film on GaN/SiC substrate was finally obtained after cooling down to room temperature.

In addition, a particle-based SrTaO₂N photocathode was also made as contrast by the Electrophoretic deposition (EPD) method. In brief, two FTO glasses (1.5 × 3 cm²) with the distance of 1 cm were vertically immersed into 20 mL acetone solution dispersing with 20 mg SrTaO₂N powder and 7 mg iodine. The powder oxynitride was prepared via the same route to the aforementioned thin film sample, but without the spin-coating process. Constant DC bias of 20 V was applied between the FTO substrates for 3 min, after which the electrode was allowed for volatilization of iodine overnight before measurement.

2.3. Characterization

Phase structure was analyzed in transmission mode by using a calibrated STOE STADI-P powder X-ray diffractometer (PXRD) with a flat sample holder and Cu Ka₁ radiation (2θ range 5–120°, with individual steps of 0.01°). Powder sample prepared from the same precursor solution and identical ammonolysis process was used for the measurement. Scanning electron microscope (SEM, Leo Supra 35VP SMT, Zeiss) was used to scrutinize the surface morphology of the photoanodes. UV–vis transmittance spectra were recorded by using a UV–vis spectrophotometer (Shimadzu, UV-2600). The GaN films were comparable to the previously reported films by this ALD process in terms of thickness and crystallinity, detailed characterization information can be found in reference 38.

2.4. Photoelectrochemical measurements

PEC experiments were performed under simulated solar illumination, which was generated by an Air Mass 1.5 Global solar light simulator (AM 1.5G, 100 mW cm⁻², class-AAA 94023A, Newport) with an ozone-free 450 W Xenon short-arc lamp. The measurements were conducted in 0.1 M NaOH solution (pH = 13) with a three-electrode PEC cell, in which the SrTaO₂N/GaN/SiC photoanode, 1 M Ag/AgCl electrode, and Pt electrode were used as the working electrode, the reference electrode, and the counter-electrode, respectively. 0.1 M Na₂SO₃ as a hole scavenger was introduced into the electrolyte if mentioned.

CoFeOₓ as an oxygen evolution catalyst was electrodeposited on the surface of the photoanodes according to a reported protocol (54). Electrodeposition was operated in the aforementioned three-electrode cell by unidirectional sweeping voltage from 1.35 to 1.65 V_RHE for 3 cycles. The electrodeposition electrolyte was comprised of 10 mM FeCl₃-6H₂O (Sigma Aldrich, >98%), 16 mM CoCl₂ (Sigma Aldrich, >98%) and 0.1 M NaOAc (Sigma Aldrich, 99%) in deionized water, without adjusting pH.

The applied potentials were ultimately converted into the scale of reversible hydrogen electrode (RHE) with Nernst equation (E_RHE = E_Ag/AgCl + 0.059 V × pH + E_Ag/AgCl) (9). Linear sweep voltammetry (LSV) at a scan rate of 10 mV s⁻¹ and Chronoamperometry (CA) at 1.23 V_RHE were measured with a potentiostat (PalmSens4, PalmSens BV) under interrupted AM 1.5G illumination with an interval of 5 s. Mott–Schottky experiments were operated with an amplitude of 10 mV in dark condition.

3. Results and discussion

3.1. Synthesis

The GaN layer was deposited epitaxially on 4H–SiC pieces by ALD without the use of an AlN nucleation
buffer layer (Scheme 3). A hexacoordinated Ga\textsuperscript{−}N bonded precursor we synthesized recently, Ga(triaz)	extsubscript{3}, was employed as the Ga source (38). This precursor was demonstrated to be an excellent ALD precursor for high-quality GaN (38). ALD of GaN was implemented on SiC substrates by using an ALD cycle with alternating pulses of the Ga(III) triazenide precursor and NH\textsubscript{3} plasma separated by N\textsubscript{2} purges. The films were deposited at 350°C to produce 30 and 60 nm of epitaxial GaN on 4H–SiC, respectively.

A spin-coating step was conducted to homogeneously adsorb precursor sol containing Sr and Ta onto the substrates (Scheme 4). The complex sol was prepared by a PC method due to the homogeneity of the metal species inside the organic network (55). After calcination in air and subsequent nitridation in NH\textsubscript{3} atmosphere, stoichiometric SrTaO\textsubscript{2}N photoanodes with high transparency were formed.

3.2. Structure and optical property

To analyze the crystal structure of the resultant oxynitride, PXRD patterns were collected (Figure 1a) and confirmed the single-phase crystallographic purity of SrTaO\textsubscript{2}N. The diffraction peaks are in agreement with the ICSD entry 130056 (56).

Panels b and c of Figure 1 correlate the digital photos of the 30 nm GaN/SiC substrates overlayed with metal

Scheme 3. Schematic illustration of the ALD cycle used to deposit GaN on 4H–SiC.

Scheme 4. Schematic diagram of the fabrication procedure for transparent quaternary SrTaO\textsubscript{2}N thin film photoelectrode on GaN/SiC substrate. The direct synthesis was adopted by the use of the Sr–Ta-complex as the precursor solution through a spin-coating procedure and subsequent thermal treatments.
oxide precursor and SrTaO$_2$N thin film, respectively. Very thin and transparent layers were deposited on the substrate after pyrolyzing the spin-coated sample. Subsequent nitridation in ammonia atmosphere introduced a slight brownish hue on the surface while still preserving high transparency. The top-view SEM images of the prepared SrTaO$_2$N thin films on 30 and 60 nm GaN/SiC are presented in Figure 1(d) and (e), respectively, where the SrTaO$_2$N thin films composed of numerous closely packed irregular nanoparticles with an average diameter lower than 100 nm. The noticeable interspace between the oxynitride grains was most likely caused by the pyrogenic decomposition of the organic skeleton in the complex. This morphological structure has been detected in related ceramic films prepared by spin-coating with metal-complex sol in conjunction with a high-temperature pyrolysis (21, 57–59). Compared with bare GaN/SiC substrate (Figure S1), a surface morphology variation can be noticed by SrTaO$_2$N. Figure S2 correlates the cross-sectional SEM image of the SrTaO$_2$N/60 nm GaN/SiC, where the constituent layers and corresponding interfaces can be identified and the thickness of this SrTaO$_2$N film is ca. 364 nm.

The prepared SrTaO$_2$N thin films on GaN (30 and 60 nm thickness) exhibit high transparency (Figure 2a). The UV–vis measurement indicates that the transmittance of the photoanodes is greater than 60% in almost the whole solar spectrum. Only a slight difference is inspected in comparison with the pristine GaN/SiC substrate. This is ascribed to the limited deposition content of the oxynitride on the surface, which is also linked to the absence of discernible photoabsorption edge at ca. 550 nm of SrTaO$_2$N. This high transparency has the potential to allow for the construction of a dual photoanode cell or a tandem PEC cell by integrating with another photoelectrode (17, 21, 25). Due to the high transmittance of the thin film electrodes, the band gap of the SrTaO$_2$N was evaluated based on the prepared powder sample to be 2.13 eV from Kubelka–Munk-transformed reflectance spectrum, as presented in Figure 2(b). Since the band edge alignment is essential for effective charge transfer across the interface in laminated photoelectrodes, Mott–Schottky experiments were implemented to acquire the detailed band structures (Figure 2c). The flat band potential ($E_{fb}$) of the SrTaO$_2$N electrode was determined to be ca. $-0.40$ V$_{RHE}$, being consistent with the previous reported

![Figure 1.](image-url)

(a) PXRD patterns of SrTaO$_2$N. (b) and (c) Digital photos of oxide-precursor film and SrTaO$_2$N film, respectively. SEM images of the SrTaO$_2$N films on (d) 30 nm GaN/SiC and (e) 60 nm GaN/SiC.
potential range (51, 60). The n-type nature of the film is also confirmed by the positive slopes of the Mott–Schottky curves (61, 62). Given that the bottom potential of conduction band ($E_{CB}$) is generally considered to be 0.2 V above the $E_{FB}$ (63), the $E_{CB}$ is therefore populated at ca. $-0.60 \, V_{RHE}$ for the SrTaO$_2$N. Based on the documented band gap value, the band edge positions of the SrTaO$_2$N photoanode are depicted in Figure 3. In addition, the electronic band structure of the underlying GaN layer is also scrutinized according to the recorded band gap of 3.41 eV in our earlier report and the detected $E_{FB}$ of $-0.31 \, V_{RHE}$ by complementary Mott–Schottky measurement (Figure 2d). Due to the staggered band edge structures, a type II heterojunction interface is therefore established by depositing SrTaO$_2$N on GaN. The driving force afforded by the gradient band energy structure is qualified to allow for spatial charge separation, during which the holes accumulated on the oxynitride film can participate in water oxidation on surface, whereas the electrons are driven backward to the counterelectrode (64).

### 3.3. Photoelectrochemical water oxidation

The PEC water oxidation performance was evaluated in alkaline media (0.1 M NaOH solution) with a three-electrode configuration (Figure 4a). LSV curves measured at 10 mV s$^{-1}$ were recorded under interrupted illumination with increasing potential bias (Figure 4b). The generated electronic current in the presence of irradiation is the photocurrent, which is proportional to the amount of H$_2$ and O$_2$ produced (28). The discernible anodic photocurrent of SrTaO$_2$N thin film on 30 nm GaN layer emerges at ca. $-0.4 \, V_{RHE}$, indicative of a very negative onset of photoresponse. The detected net photocurrent densities for this electrode are comparable in the wide

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**Figure 2.** (a) UV–vis transmittance spectra of the samples (insets exhibit the photographic images of the films). (b) Kubelka–Munk-transformed reflectance spectrum of SrTaO$_2$N. Mott–Schottky plots of (c) SrTaO$_2$N and (d) GaN. For Mott–Schottky measurement, the SiC side and the edge of the substrate were insulated with insulation paste to eliminate the potential interference from SiC.

**Figure 3.** Schematic illustration of the electronic band structures of SrTaO$_2$N and GaN layers.
potential range, i.e. 0.2–1.4 VRHE, despite the consecutive increment in the applied potentials. A similar phenomenon was also identified in a 500 nm Ta3N5 thin film photoanode, which was fabricated from RF magnetron sputtering of Ta precursor on 4 μm Si-doped GaN fixed on a sapphire substrate (25). This result is mainly attributed to the limited thickness of the oxynitride thin film on the substrate confining the availability of sufficient active sites (30, 65). The photocurrent density derived from photoexcited charge carriers is therefore already saturated at low potential bias during the LSV measurement. The net photocurrent density generated by this SrTaO2N thin film was approximately 6 μA cm−2 at 1.23 VRHE (Figure 4c). This photocurrent density is expected due to the incompatibility between high transparency and immense photocurrent density for a single-component photoelectrode. Nevertheless, it is commensurate with the values reported for a 150-nm SrTaO2N film photoanode grown on Ta sheet by reactive RF magnetron sputtering (30). In this report, the enhanced photocurrent was observed upon expanding the film thickness by adjusting the sputtering duration (30). The PEC performance of as-prepared photoanode is compared with some representative references in Table 1, the recorded photoresponse onset (−0.4 VRHE) highlights the advantage of the obtained photoanode. Given that this photocurrent density is also higher than a 162 nm LaTiO2N and a 177 nm CaNbO2N thin film photoanodes prepared by a modified PLD method on a TiN layer with (001)-oriented supporting MgO, in which photocurrent density less than 1 μA cm−2 was recorded at 1.23 VRHE (Table 1) (65). In this regard, the present result is promising and the performance is likely to be further improved by extending the oxynitride film thickness and to apply to porous 3D substrates. It is noteworthy that these post modifications would inevitably reduce the transmittance in varied degrees and an equilibrium that maintains luminousness while allows for high photocurrent density deserves further research.

To elucidate the photoelectrode performance based on the thickness of the GaN layer, the SrTaO2N thin film was grown identically on a 60-nm epitaxial GaN on the 4H–SiC substrate (Schemes 3 and 4). This electrode displays a very similar performance to the SrTaO2N photoanode with a 30 nm GaN underlayer in
both LSV and CA (Figure 4b and c). This means that 30 nm GaN is already adequate to allow for effective charge transport. Since a bare GaN/SiC substrate does not present noticeable photoresponse, it excludes the photocurrent contribution from the substrate in the SrTaO$_2$N photoanodes. Nevertheless, the insertion of a thin GaN film between the photoanode material and the SiC substrate is critical to supplying the pronounced photoresponse (vide infra) (25, 37). A particle-based SrTaO$_2$N photoanode was also prepared by the EPD method, which is compared with the SrTaO$_2$N thin film in Figure 5. In comparison with the particle-based electrode, SrTaO$_2$N thin film photoanode demonstrates substantially higher photocurrent and lower dark current, which indicates the better PEC behavior of the latter.

We have recently introduced a 2-μm GaN layer on sapphire substrates by MOVPE, which was used for SrTaO$_2$N and LaTiO$_3$N thin film deposition (21). Although the fabricated photoanodes demonstrated comparable photocurrent density with the present SrTaO$_2$N thin film, the pronounced cathodic shift of the onset potential and the far smaller thickness of the GaN highlight the significance of the Ga(III) triazenide precursor and ALD technique in producing high-quality GaN conductive layer. In addition, the SrTaO$_2$N/60 nm GaN/SiC and SrTaO$_2$N/30 nm GaN/SiC photoanodes exhibit 1.9- and 1.7-fold improvements, respectively, in photocurrent density at 1.23 V$_{RHE}$ by introducing Na$_2$SO$_3$ as hole scavenger into the electrolyte (Figure S3). Surface modification with CoFeO$_x$ catalyst also leads to a 1.7- and

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**Table 1. Comparison to previously published thin film-based quaternary oxynitride photoanodes.**

| Compound       | Current collector layer | Substrate | Light source | Electrolyte | Current density at 1.23 V$_{RHE}$ | Photoresponse onset potential | Ref. |
|----------------|--------------------------|-----------|--------------|-------------|-----------------------------------|-------------------------------|------|
| CoP/Ni(OH)$_2$/TiO$_2$/SrTaO$_2$N$^a$ | /                        | Ta sheet  | AM 1.5G      | 0.1 M NaOH  | ~0.27 mA cm$^{-2}$                | b                             | (1)  |
| LaTiO$_3$N     | 2 μm GaN                 | Al$_2$O$_3$ sapphire | AM 1.5G      | 0.1 M NaOH  | ~0.20 mA cm$^{-2}$                | 0.0 V$_{RHE}$                | (21) |
| SrTaO$_2$N     | 2 μm GaN                 | Al$_2$O$_3$ sapphire | AM 1.5G      | 0.1 M NaOH  | ~0.07 mA cm$^{-2}$                | 0.85 V$_{RHE}$               | (21) |
| BaTaO$_2$N$_x$ | 106 nm TiN               | Single-crystal MgO (001) | AM 1.5G     | 0.5 M NaOH  | ~0.60 mA cm$^{-2}$                | b                            | (27) |
| LaTiO$_3$N$_x$ | 120 nm TiN               | Single-crystal MgO (001) | AM 1.5G     | 0.5 M NaOH  | ~0.20 mA cm$^{-2}$                | b                            | (27) |
| CaNbO$_2$N$_x$ | 70 nm TiN                | Single-crystal MgO (001) | AM 1.5G     | 0.5 M NaOH  | ~0.20 mA cm$^{-2}$                | b                            | (27) |
| LaTiO$_3$N$_x$ | TIN                      | MgO (001) substrate | AM 1.5G      | 0.5 M NaOH  | ~1.30 mA cm$^{-2}$                | ~0.5 V$_{RHE}$               | (28) |
| SrTaO$_2$N$_x$ | /                        | Ta sheet  | AM 1.5G      | 0.1 M NaOH  | ~1.20 mA cm$^{-2}$                | ~0.3 V$_{RHE}$               | (30) |
| LaTiO$_3$N$_x$ | /                        | Single-crystal Nb: SrTiO$_3$ (001) | λ > 420 nm (300 W xenon lamp) | 0.5 M Na$_2$SO$_4$ (pH 4.5) | ~8 μA cm$^{-2}$ | ~0.1 V$_{RHE}$ | (31) |
| LaTiO$_3$N$_x$ | 146 nm TIN               | Single-crystal MgO (001) | AM 1.5G     | 0.5 M NaOH  | ~0.19 μA cm$^{-2}$                | b                            | (65) |
| CaNbO$_2$N$_x$ | 60 nm TiN                | Single-crystal MgO (001) | AM 1.5G     | 0.5 M NaOH  | ~0.15 μA cm$^{-2}$                | b                            | (65) |
| CoP/BaTaO$_2$N$^a$ | Ta/Ti                  | Glass plate | AM 1.5G      | 0.2 M KPi$^c$ (pH = 13) | ~4.2 mA cm$^{-2}$ | ~0.1 V$_{RHE}$ | (66) |
| SrTaO$_2$N     | 30 nm GaN                | single crystal 4H – SiC (0001) | AM 1.5G     | 0.1 M NaOH  | ~6 μA cm$^{-2}$                  | ~0.4 V$_{RHE}$ | This work |

$^a$CoP represents cobalt phosphate.

$^b$The onset potential was not measured.

$^c$KPi represents potassium phosphate.

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**Figure 5.** LSV curves of (a) SrTaO$_2$N/60 nm GaN/SiC and (b) particle-based SrTaO$_2$N photoanodes.
1.5-fold improvements in photocurrent density for SrTaO$_2$N/60 nm GaN/SiC and SrTaO$_2$N/30 nm GaN/SiC photoanodes, respectively (Figure 54).

In addition to the mitigation in conductivity, the GaN layer inserted between the SrTaO$_2$N and SiC also sustains hole-blocking effect to alleviate carrier recombination (25, 37, 67, 68). This effect is similar to a reported SnO$_2$ layer for BiVO$_4$ thin film, and a Lu$_2$O$_3$ film deposited on a BiVO$_4$ photoanode (69, 70). The introduced GaN that can afford hole-blocking potential barrier is prone to suppress the backward holes migration from the photo-absorber, due to its deep position on the top of the valance band (Figure 4d). The relative thin thicknesses of GaN and SrTaO$_2$N are also conductive to mitigate the recombination of photogenerated electrons and holes, owing to the short transfer path to the interfaces of SrTaO$_2$N/GaN and electrolyte/SrTaO$_2$N, respectively (65).

4. Conclusions and outlook

In summary, we have demonstrated ALD grown GaN on SiC can be used as transparent substrates for constructing semi-transparent SrTaO$_2$N/GaN/SiC photoanodes. The absence of a buffer layer for initial GaN film growth, the high-quality GaN, and the ease of the SrTaO$_2$N thin film displays the practicability of this process for large-scale manufacture. The formation of alternative semi-transparent quaternary metal-based oxynitride photoanodes, especially for semi-transparent hierarchically structured photoanodes, would be feasible with this new process.

The excellent light transmittance and remarkably negative onset potential validated the potential of the synthesized photoanodes to work as front photocathode in constructing stand-alone tandem PEC devices. Despite the low photocurrent of the planar photoanodes with respect to the theoretical value, the GaN underlayer grown via ALD paves the way toward the fabrication of hierarchically-ordered three-dimensional semi-transparent quaternary oxynitride photoanodes. Work toward this direction is currently on-going in our laboratory.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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