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 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.\textsuperscript{1-5} Photoelectrochemical (PEC) water splitting is potentially sustainable for large-scale conversion of solar energy into storable hydrogen source.\textsuperscript{6-9} A technoeconomic report revealed that an STH efficiency above 10% is required for practical application of PEC technology.\textsuperscript{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.\textsuperscript{12-16} For the former, two fundamental losses are linked with the low photobasorbance. On one hand, most of the photon energy is lost with incident photons possessing energy lower than the bandgap ($E_b$); on the other hand, photons containing higher energy in comparison to $E_b$ are partially wasted by emitting phonons.\textsuperscript{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.\textsuperscript{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.\textsuperscript{20,21,22} 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.\textsuperscript{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 Figure 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.\textsuperscript{21,22}

In particular, high transparency and efficiency of the front photoanode are critical prerequisites for achieving satisfied STH efficiency.\textsuperscript{22} The photoanode has to transmit sunlight with a wavelength longer than its absorption edge to the rear side for reutilization by the photocathode (Figure 1). The extensively exploited TiO$_2$, ZnO, BiVO$_4$-based photoanodes have been assembled to fabricate PEC tandem cells with diverse photocathodes.\textsuperscript{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.\textsuperscript{10}

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.\textsuperscript{24} Recently, a relatively high STH efficiency was recorded using a TaN$_5$ photoanode-involved tandem cell.\textsuperscript{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.\textsuperscript{25} One key advantage of quaternary metal oxynitrides over TaN$_5$ is their theoretically higher light absorption due to narrower band gaps, such as those found for SrTaO$_2$N or SrNbO$_2$N.\textsuperscript{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.\textsuperscript{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).\textsuperscript{27,28} Reactive radio frequency (RF) magnetron sputtering,\textsuperscript{29-32} and
spin-coating in conjunction with post-ammonolysis. Although several TCL substrates have been tested, including MgO, Al₂O₃, and SrTiO₃, 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. 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.

For TCL substrates, a current collector overlayer, e.g. GaN and TiN, is required to enable transport of photogenerated electrons. The high electron mobility of the former makes it a key material in advanced AlGaN/GaN high electron mobility transistors (exceed 1000 cm² V⁻¹ s⁻¹). Insertion of an interlayer between the photoanode films and the TCL could also mitigate the charge recombination by energetic alignment of the band edges. This was observed when a 150 nm GaN layer was deposited between a Ta substrate and Ta₂N film by plasma-enhanced chemical vapor deposition (PCVD), which led to a 1.8 fold enhancement in water oxidation efficiency. 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. Furthermore, high temperatures (600–1000 °C) are often used for CVD-GaN, which is unsuitable for heat sensitive films (e.g. InN, decomposes at 500 °C).

Deposition of thin films with excellent uniformity and conformity, and controlled thickness is essential for the fabrication of solar devices with complex surface architecture. These pre-requisites, however, cannot be fulfilled by CVD, especially for three dimensional (3D) TCL substrates. A thick coating on the surface is prone to fill the trenches and/or holes (Figure 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. It should be noted that GaN layers with thicknesses less than 100 nm were also demonstrated in several reports to be capable for charge transfer in solar energy devices. 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 (Figure 2b). 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. Examination of thickness influence of GaN is meaningful to understand the critical limit required for 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 SrTaO₃N oxynitride thin film photoanodes. The oxynitride layers prepared on GaN exhibited significant transparency in almost the whole solar spectrum. A very negative onset potential was found in the photoanode with 30 nm GaN interlayer.

2. EXPERIMENTAL SECTION

2.1. Preparation of SiC/GaN Transparent Substrate.
GaN thin films were deposited epitaxially on polished single-crystal 4H–SiC (0001) substrates by ALD. A highly volatile tris(1,3-diisopropyltriazenido)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). The detailed synthetic procedure of the Ga(III) triazenido precursor is provided in our previous reports.

Prior to the deposition, the 4H–SiC substrates were cleaned in solutions of 1:1:5 solution of H₂O₂: (30%), NH₃ (25%), and H₂O and [1:1:5 solution of H₂O₂ (30%), HCl (37%), and H₂O] 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 flowing with N₂ (99.999%, 300 mL min⁻¹) was heated at 450 °C for 2 h to remove the trace amount of residual H₂O and O₂ in the deposition chamber due to the air contaminant during substrate exchange. Inside a N₂ filled glovebox, ∼1.0 g of the Ga(III) triazenido 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 at 130 °C. A dried gas mixture containing NH₃ (99.999%) and Ar (99.9997%) in ratio of 75/100 was introduced as NH₃ 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 NH₃ plasma were used for each cycle of deposition, separated by a 10 s pulse of N₂. 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. The obtained substrates were finally diced into 1 × 2 cm² pieces and well stored for further use.

2.2. Fabrication of SrTaO₅N Thin Film on SiC/GaN Transparent Substrate. Quaternary SrTaO₅N thin films were prepared by ammonolysis of the corresponding metal-oxide layer 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. In a typical synthesis, 200 mg TaCl₅ (Sigma-Aldrich, 99.8%) and 858 mg citric acid (Sigma-Aldrich, 99.8%) were dissolved in 2 mL deionized water, ultrasonication, was then slowly injected into the aforementioned complex solution and the setup was kept at 70 °C during the process. The suspension was subsequently heated to 100 °C and magnetically stirred for 30 min. The resultant viscous suspension 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 ramping rate of 7 °C min⁻¹. The transparent SrTaO₅N film on GaN/SiC substrate was finally obtained after cooling down to room temperature.

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 Kα 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 transmission spectra were recorded by using a UV–vis spectrophotometer (Shimadzu, UV-2600).

The GaN films were fully comparable to the previously reported films by this ALD process, 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-AA 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 SrTaO₅N/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. The applied potentials were ultimately converted into the scale of reversible hydrogen electrode (RHE) with Nernst equation (\(E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 V \times \text{pH} \)). Linear sweep voltammetry (LSV) at a scan rate of 10 mV s⁻¹ and Chronoamperometry (CA) at 1.23 Vₚᵣₑₜ were measured with a potentiostat (PalmSens4, PalmSens BV) under interrupted AM 1.5G illumination with an interval of 5 s.

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 1). A hexacoordinated Ga–N bonded precursor we synthesized recently, Ga(triaz)₅, was employed as the Ga source. This precursor was demonstrated to be an excellent ALD precursor for high-quality GaN. ALD of GaN was implemented on SiC substrates by using an ALD cycle with alternating pulses of the Ga(III) triazenide precursor and NH₃ plasma separated by N₂ 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 2). The complex sol was prepared by a PC method due to the homogeneity of the metal species inside the organic network. After a calcination in air and subsequent nitridation in NH₃ atmosphere, stoichiometric SrTaO₅N 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 3a) and confirmed the single-phase crystallographic purity of SrTaO$_2$N. The diffraction peaks are in agreement with the ICSD entry 130056.55

Panels b and c of Figure 3 correlate the digital photos of the GaN/SiC substrates overlayed with metal 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 image of the prepared SrTaO$_2$N thin film on GaN/SiC shows a smooth surface (Figure 3d). A close shot image further discloses the occurrence of numerous closely packed irregular nanoparticles with an average diameter lower than 100 nm (Figure 3e). 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.21,56–58

The prepared SrTaO$_2$N thin films on GaN (30 and 60 nm thickness) exhibit high transparency (Figure 4). The UV-vis measurement indicates that the transmittance of the photoanodes is greater than 60% in almost the whole solar spectrum. Only a slightly 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 potential to allow for the construction of a dual photoanode cell or a tandem PEC cell by integrating with another photoanode.17,21,25

![Figure 3](image_url) **Figure 3.** (a) PXRD patterns of SrTaO$_2$N. (b) and (c) Digital photos of oxide-precursor film and SrTaO$_2$N film, respectively. Panels (d) and (e) are SEM images of the SrTaO$_2$N film. The substrate with 30 nm film of GaN was used.

![Figure 4](image_url) **Figure 4.** UV-vis transmittance spectra of GaN/SiC and SrTaO$_2$N/GaN/SiC films. The insets exhibit the photographic images of the films.

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 5a). LSV curves measured at 10 mV s$^{-1}$ were recorded under interrupted illumination with increasing potential bias (Figure 5b). 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 potential. The detected net photocurrent densities for this electrode are comparable in the wide potential range, i.e. 0.2–1.4 $V_{RHE}$ despite the consecutive increment in the applied potentials. A similar phenomenon was also identified in a 500 nm Ta$_2$N$_3$ 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 We attributed this result mainly to the limited thickness of the oxynitride thin film on the substrate confining the availability of sufficient active sites.30,59 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 SrTaO$_2$N thin film was approximately 6 µA cm$^{-2}$ at 1.23 $V_{RHE}$ (Figure 5c). 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 SrTaO$_2$N film photoanode grown on Ta sheet by reactive RF magnetron sputtering.\textsuperscript{30} In this report, the enhanced photocurrent was clearly observed upon expanding the film thickness by adjusting the sputtering duration.\textsuperscript{30} This photocurrent density is also higher than a 162 nm LaTiO$_2$N and a 177 nm GaNbO$_3$N 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 $\mu$A cm$^{-2}$ was recorded at 1.23 $V_{\text{RHE}}$.\textsuperscript{59} In this regard, the present result is promising and the performance is likely to be further improved through 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 SrTaO$_2$N thin film was grown identically on a 60 nm epitaxial GaN on the 4H–SiC substrate (Schemes 1 and 2). Except for a slightly higher net photocurrent density in the negative potential range, this electrode displays a very similar performance to the SrTaO$_2$N photoanode with a 30 nm GaN underlayer (Figure 5b and c) in both LSV and CA. The emerged dark current density contribution is a common phenomenon for a pristine metal-based oxynitride photoelectrode, which is linked with the photocorrosion and the recombination of photocharges.\textsuperscript{21,51,60} 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 an thin GaN film between the photoanode material and the SiC substrate is critical to supplying the pronounced photoresponse (vide infra).\textsuperscript{25,37} We have recently introduced a 2 $\mu$m GaN layer on sapphire substrates by MOVPE, which was used for SrTaO$_2$N and LaTiO$_2$N thin film deposition.\textsuperscript{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 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.\textsuperscript{25,37,61,62} 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.\textsuperscript{63,64} The introduced GaN that can afford hole-blocking potential barrier is prone to suppress the backward holes migration from the photoabsorber, due to its deep position on the top of the valence band (Figure 5d). 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.\textsuperscript{59}

![Figure 5](image)

**Figure 5.** (a) Scheme of the PEC water splitting cell. (b) LSV and (c) CA curves at 1.23 $V_{\text{RHE}}$ of SrTaO$_2$N/GaN/SiC photoanodes and bare substrate recorded under interrupted AM 1.5G illumination in 0.1 M NaOH electrolyte. (d) Schematic band view of the laminated structure of SrTaO$_2$N and GaN on SiC, this view is described on the basis of the two previous reports.\textsuperscript{51,65}
CONCLUSION
In summary, we have demonstrated ALD grown GaN on SiC can be used as transparent substrates for constructing semi-transparent SrTaO₃N/GaN/SiC photoanodes. The absence of a buffer layer for initial GaN film growth, the high-quality GaN, and the ease of the SrTaO₃N thin film displays the practicability of this process for large-scale manufacture. 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 photoelectrode in constructing stand-alone tandem PEC devices. Despite the low photocurrent of the planar photoanodes with respect to the theoretical value, which is partially due to the lack of applied catalyst and low specific surface area, 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.

ASSOCIATED CONTENT

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All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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Deposited by Reactive Sputtering.


Based Tandem Cells for Self


