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Enhanced water splitting performance of GaN photoanode using self-assembled nickel/nickel-oxide nanoparticle catalyst

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ABSTRACT

Ni/NiOx core-shell nanoparticles were used to improve the water splitting efficiency and stability of an n-GaN photoanode. Nanoparticles were fabricated by thermal annealing and oxidizing a Ni thin film deposited on an n-GaN substrate. The performance of water splitting was investigated by varying Ni film thickness and oxidation time, which led to different nanoparticle distribution and NiOx thickness in the core-shell structure. Nanoparticles fabricated from a thinner Ni film led to a smaller particle-to-particle spacing. It allowed holes in n-GaN to diffuse to nanoparticle catalysts in a shorter distance for water splitting reaction, thereby providing higher photocurrent and better protection against oxidation corrosion. Ni/NiOx core-shell nanoparticles obtained from partial oxidation showed higher photocurrent than sole Ni or fully oxidized NiOx nanoparticles. It is attributed to the optimization between having more NiOx for reaction centers and keeping NiOx thin for easy hole transport from n-GaN across NiOx to NiOx/electrolyte interface for reaction.

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Introduction

Photoelectrochemical (PEC) water splitting has gained great research interests for its ability to directly convert solar energy to H₂ fuel, which can be stored, transported and converted back to electricity. The PEC reaction involves three basic processes: charge generation from absorbed photons, separation and transport of charges to electrodes, and water redox at electrode-electrolyte interfaces [1–9]. The first two processes can be realized by many semiconductors used for photovoltaic solar cells. The last process, however, is often challenging and has been under serious studies. To precede direct PEC process without external voltage assistance, the

band edges of semiconductor have to straddle the water redox potentials [10]. Semiconductor photoanodes often suffer serious oxidation corrosion in the PEC process, which limits the device stability. GaN semiconductor has received substantial interests for PEC water splitting because its bandgap satisfies the water redox potential requirement for direct PEC water splitting. In addition, its bandgap can potentially be tuned by alloying with InN for absorption spectrum optimization. Even though the material is relatively inert to chemical etching as compared with most semiconductors, it still suffers oxidation corrosion [11–21].

NiOx is known to be an excellent catalyst for water splitting with long-term stability [22,23]. Numerous studies using NiOx coating on a GaN photoanode as a co-catalyst have

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shown significant corrosion protection and improved photocurrent. Photogenerated holes in GaN can be rapidly consumed by NiOx for water oxidation, thereby protecting GaN from oxidation corrosion. Sparse NiOx particles spin-coated on a GaN substrate has shown improved water splitting efficiency and stability [24]. Other methods using solution based metal organic chemical decomposition or e-gun deposition have also been reported [25–29]. Depending on fabrication methods, different NiOx geometries and distributions are formed on the GaN surface, which can affect the water splitting performance. Here, we report the fabrication of self-assembled Ni/NiOx core-shell nanoparticles on an n-GaN sample, and study the effect of oxidation condition and particle spacing on water splitting performance.

Materials and method

The photoanode used in this study was a 3 μm thick n-type GaN (n-GaN) grown by a MOCVD on a sapphire substrate. The carrier concentration was $1.6 \times 10^{19} \text{ cm}^{-3}$. Ni/NiOx nanoparticles were fabricated on the n-GaN surface as co-catalysts. The fabrication steps were as follows: A Ni thin film was deposited on a n-GaN sample by e-gun evaporation and then annealed at 900 °C under 1 atm nitrogen ambient for 4 min n-GaN surface is stable under this annealing condition [30][S1]. The annealing resulted in self-assembled Ni nanoparticles. The sample was subsequently oxidized at 500 °C under 1 atm oxygen (O_2) ambient. Different NiOx shell thickness could be formed using different oxidation time. When the nanoparticle size was small and the oxidation time was long enough, Ni nanoparticles could be fully oxidized to NiOx nanoparticle. Otherwise, the process only oxidized Ni into Ni/NiOx core-shell nanoparticles. In this study, when the thickness of the deposited Ni film was over 30 Å, the height of the self-assembled nanoparticles was around 40–60 nm. At this thickness, the nanoparticles could not be fully oxidized even the oxidation time was over 40 min. In contrast, when the Ni thin film thickness was 15 Å, the nanoparticle height was 10–20 nm and a 40-min oxidation time would fully oxidize the Ni nanoparticles. The extent of oxidation could be seen from the change of sample appearance from opaque to semi transparent to transparent due to the reducing thickness of Ni and the increasing thickness of NiOx, which was transparent [S2].

The PEC water splitting was carried out in a custom-made Hoffman apparatus without external voltage bias. The electrolyte was 1 M aqueous NaOH. An 18-cm coiled Pt wire was used as a counter electrode. The light source was an Hg lamp with an illumination intensity of 100 mW/cm². The illumination power intensity was measured by a UV detector with a spectral filter of 40 nm linewidth centered at 360 nm. A fixture with an illumination aperture of 0.8 cm² held the sample.

Results and discussion

We used AFM to scan the nanoparticle topography. A typical AFM image of Ni/NiOx nanoparticles fabricated from a Ni thin

film of 40 Å is shown in Fig. 1. The average diameter of nanoparticles is 280 nm. The height of nanoparticles has a distribution varying from 60 nm to 120 nm. Subsequent oxidation increased particle height by 10–20 nm and formed a Ni/NiOx core-shell structure. The oxidation reaction was rapid in the first 30 s and slowed down significantly after 1 min due to the increase of NiOx shell thickness that blocked the further diffusion of oxygen into the Ni core.

A nanoparticle was selected from the sample to study the Ni/NiOx core-shell structure using TEM measurement. Fig. 2(a) is the cross-section view of the particle. An energy dispersive X-ray spectroscopy analysis (EDS, Oxford) was performed along the green line to analyze the composition, as shown in Fig. 2(b). The interface of GaN and Ni is at the distance of 20 nm. The range of Ni signal appears from 20 to 165 nm, corresponding to a nanoparticle height of 145 nm. Oxygen signal starts from 130 to 165 nm, indicating a NiOx thickness of 35 nm. The decreasing oxygen signal beyond 165 nm is due to oxygen diffusion during specimen preparation. Ga and N signal appear in the first 20 nm. The presence of Ga signal at all location is because Ga source was used in FIB for sample preparation. Fig. 2(c) explicitly shows the interface of GaN and Ni, revealing different crystalline structures. Fig. 2(d) is the EDS mapping images of Ni and oxygen. It shows a Ni core surrounded by oxygen signal at the outer region, confirming the Ni/NiOx core-shell nanoparticle structure.

To study the effect of Ni, Ni/NiOx, and NiOx nanoparticles on water splitting performance, four samples were fabricated from Ni thin film thickness of 15 Å and respectively oxidized for 0, 5, 10, and 40 min. The annealing of 15 Å Ni thin film resulted in a densely distributed nanoparticles with spacing of <30 nm. This spacing is smaller than the reported hole diffusion length of ~250 nm in n-GaN [31]. Holes therefore can easily diffuse to nanoparticles and be used by the catalytic activity of Ni or Ni/NiOx nanoparticles for water oxidation. The 5 and 10 min oxidation time formed Ni/NiOx core-shell nanoparticles with different NiOx thickness while the 40 min one produced NiOx nanoparticles as verified from its fully transparent appearance. The PEC photocurrents versus time of the four samples were shown in Fig. 3(a). The illumination was turned on for 20 min and off for 10 min three times to make sure that electrochemical activation process was stabilized and photocurrents were repeatable. For comparison, a plain n-GaN sample without any coating was also measured. It has a large decrease in the first experiment, followed by smaller decreases in the subsequent two tests. n-GaN surface showed obvious corrosion after experiment from AFM inspection [S3]. The oxidation corrosion causes large photocurrent decrease and the non-repeatable photocurrent in subsequent experiments. The photocurrents of Ni and Ni/NiOx samples in contrast are fairly repeatable. At the turn on of illumination, there is a fast rise and descendant current. This transient current occurs due to the initial separation of the photo-generated electrons and holes respectively moving toward the photoanode and counter electrode [2,32]. After the fast transient, the current settles to a steady value in a few minutes. The decay is due to the build up of diffusion layers with ions of opposite signs around electrodes, which slow down water splitting reaction.

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