Applied Surface Science 422 (2017) 354–358

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Improvement of efficiency in graphene/gallium nitride nanowire on Silicon photoelectrode for overall water splitting

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ARTICLE INFO

Article history:
Received 22 March 2017
Received in revised form 19 May 2017
Accepted 24 May 2017
Available online 26 May 2017

Keywords:
Graphene
Gallium nitride
Hydrogen generation
Water splitting
Photoelectrochemical
Nanowire

ABSTRACT

Gallium nitride (GaN) nanowires are one of the most promising photoelectrode materials due to their high stability in acidic and basic electrolytes, and tunable band edge potentials. In this study, GaN nanowire arrays (GaN NWs) were prepared by molecular beam epitaxy (MBE); their large surface area enhanced the solar to hydrogen conversion efficiency. More significantly, graphene was grown by chemical vapor deposition (CVD), which enhanced the electron transfer between NWs for water splitting and protected the GaN NW surface. Structural characterizations of the prepared composite were performed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The photocurrent density of Gr/GaN NWs exhibited a two-fold increase over pristine GaN NWs and sustained water splitting up to 70 min. These improvements may accelerate possible applications for hydrogen generation with high solar to hydrogen conversion efficiency.

1. Introduction

Water splitting with semiconductors is a popular method for achieving high solar to hydrogen (STH) conversion efficiency with photoelectrode stability [1–6]. The overall photoelectrochemical (PEC) water splitting reaction for n-type semiconductor photoelectrodes can be described as:

$$4H^+ + 4e^- = 2H_2 \quad (1)$$

$$2H_2O + 4h^+ = O_2 + 4H^+ \quad (2)$$

which is an uphill reaction, due to the positive change in Gibbs free energy ($\Delta G^0 = 237$ kJ/mol at 25 °C). Therefore, the semiconductor properties must be considered for generating hydrogen without extra energy.

Gallium nitride (GaN) displays outstanding capabilities, such as: 1) overall water splitting under visible light, 2) tunable band gap energy and band edge potentials with InN and AlN, and 3) stability in aqueous solution, such as acidic and basic electrolytes [7–9]. However, several hurdles remain before GaN-based photoelectrodes could be employed for commercial use.

Recent efforts to achieve high STH mainly focused on enlarging the surface area using nanostructures, such as nanowires, nanodots, and nanotubes [10–13]. These structures enhance the STH by using shorter diffusion lengths, large surface-to-volume ratios, rapid charge carrier separation, and enhanced optical absorption. Kibria et al. reported ~13% internal quantum efficiency and one hour of photo-stability with a nanowire structured InGaN/GaN photoelectrode [14].

One drawback of such structures is their inability to resist degradation due to photo corrosion. Thus, previous efforts to prevent photocorrosion focused on post-synthetic modifications, such as the incorporation of a co-catalyst (Ni, Cr, Rb, Pt), doping with metal ions, or using it in combination with other semiconductors [15–19].

Recent studies have demonstrated the effectiveness of graphene as a protection layer, transparent electrode, and catalyst due to its outstanding mechanical, thermal, optical, and electrical properties [20–22]. For these reasons, graphene has been applied in various fields, such as photonics, fuel cells, sensors, energy conversion, and storage devices. In particular, Kim et al. employed graphene as a barrier layer for forming an electrical junction between high density vertically aligned silicon (Si) nanowire arrays, since graphene has high carrier mobility, extremely high mechanical strength,

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http://dx.doi.org/10.1016/j.apsusc.2017.05.215
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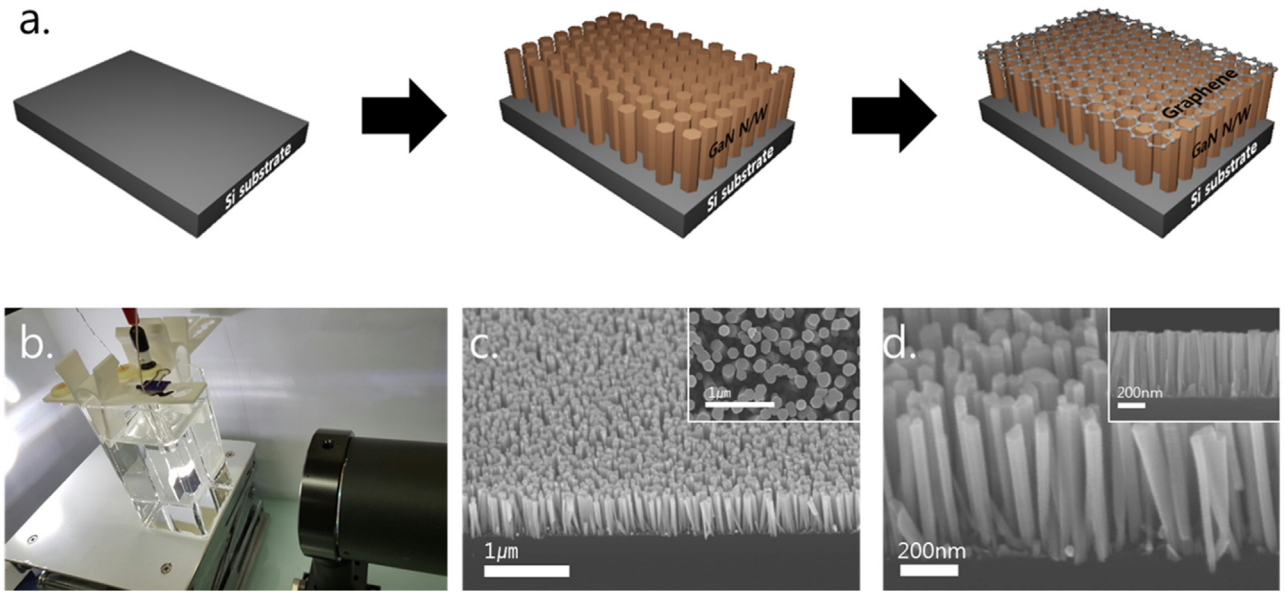

Fig. 1. a) Schematic illustrations of the fabrication processes for a Gr/GaN NW array heterostructure. b) Experimental set up for PEC water splitting. c) SEM image of Gr/GaN NWs at 45° tilt. d) High magnification SEM images of Gr/GaN NWs.

and chemical stability. As a result, graphene coated Si nanowire heterostructures fabricated for molecular sensing displayed high sensitivity. In this regard, graphene played a key role in preventing the tips of vertical Si nanowires from becoming bundled, thereby making Si nanowires stand on the Si wafer separately from each other under graphene [23].

Xu et al. also reported that the photocatalytic hydrogen reaction using polymer-supported graphene was enhanced. Graphene served as an electron acceptor and hydrogen evolution site that promoted the separation of photo-induced charge carriers. More studies are required to realize the full potential of graphene-based composite catalysts for photocatalytic hydrogen production [24].

Herein, we have coated graphene layers onto GaN nanowires (GaN NWs) as a surface protection layer and electron transfer medium between GaN NWs, for water splitting. GaN NWs were grown by molecular beam epitaxy (MBE), and graphene was grown by large-scale chemical vapor deposition.

2. Experimental

Pristine GaN NWs were grown on n-type Si (111) substrates using radio-frequency plasma-assisted MBE. The GaN NWs were grown at 800 °C for 1 h, without using any external metal catalyst. Catalyst-free growth was selected to avoid catalyst-induced contaminations that might alter the electronic properties of the material.

High quality graphene films were fabricated using previously reported procedures [25]. They were grown onto Cu foil by chemical vapor deposition (CVD), and then the front side of graphene was coated by a thin layer of polydimethylsiloxane (PDMS). The back side of graphene was eliminated by O_2 plasma, and the Cu layer was then etched with ammonium persulfate, leaving only the PDMS/graphene film. The film was cleaned with deionized (DI) water, and then transferred onto a GaN NWs. After evaporating the water vapor, PDMS was removed by acetone, leaving a graphene film atop of a GaN NW. The graphene-coated GaN nanowires (Gr/GaN NWs) were then heated at 70 °C in a hot plate for 1 h, in order to eliminate any residual water and facilitate adhesion.

Morphological analysis of Gr/GaN NWs was performed by high-resolution transmission electron microscopy (HR-TEM) and scanning electron microscopy (SEM). The TEM images were recorded at 200 kV using an FEI Tecnai F20 at the Korea Basic Science Institute (KBSI, Gwangju center). In order to further confirm the existence of graphene, we performed energy dispersive X-ray (EDX) analysis. Raman spectroscopy measurements were also conducted using a JASCO Laser Raman Spectrometer NRS-5100 series (KBSI, Gwangju center), with an excitation laser wavelength of 532 nm at a power density of 5.6 mW/cm^2.

A three-electrode configuration was used to evaluate the photoelectrochemical properties, with a Ag/AgCl/NaCl reference electrode (RE), Pt wire counter electrode (CE), and Gr/GaN NWs working electrode (WE) in 1 M NaOH electrolyte. Indium was deposited on the backside of the Si substrate and annealed to form the ohmic contact. Subsequently, Si surface was covered with epoxy resin to avoid dissolution to electrolyte. A 500 W Xenon lamp with an neutral density filter (100 mW/cm^2) was used as an irradiation source for PEC measurements.

3. Results and discussion

Fig. 1(a) illustrates GaN NW growth on Si a substrate. Subsequently, a single-layer CVD-deposited graphene was transferred atop vertically-aligned GaN NWs, and then dried on a hot plate at 70 °C for 1 h to fabricate Gr/GaN NW heterostructures. Fig. 1(b) describes our experimental set up for PEC water splitting using a three-electrode configuration. The bias is applied between the WE (GaN NWs) and CE (Pt). GaN NWs are displayed in Fig. 1(c) with 45° tilted SEM. In order to see more features, Fig. 1(c) was magnified to Fig. 1(d). From this, we observed that GaN NWs had good alignment vertical to the substrate; the wires were on average 450–500 nm long, and the diameters were about 50–70 nm.

The morphology and structure of the Gr/GaN NWs were further investigated by TEM. TEM (Fig. 2(a)) clearly reveals a graphene layer contact on top of GaN NWs. In order to confirm graphene loading on the surface of GaN NWs, a selected region of Fig. 2(a) was magnified in Fig. 2(b). Based on these results, we confirmed that the surface of the GaN NW was entirely covered with graphene. The EDX results (Fig. 2(c) and (d)) indicate the presence of carbon and gallium, reconfirming that the nanostructure is GaN, and that the coated layer is a carbon material.

Before and after graphene transfer, a Raman spectrum was obtained to identify a single layer graphene. Graphene has three