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Enhanced photoelectrochemical performance of bridged ZnO nanorod arrays grown on V-grooved structure

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Abstract

Bridged ZnO nanorod arrays on V-grooved Si(100) substrate were used as the photoanode of a photoelectrochemical (PEC) cell for water splitting. Photolithography followed by reactive ion etching was employed to create a V-grooved structure on a Si substrate. ZnO nanorod arrays were grown via a hydrothermal method. The light trapping and PEC properties are greatly enhanced using the bridged ZnO nanorod arrays on a V-grooved Si substrate compared with those on a flat one. Increased short circuit photocurrent density (J_{SC} , 0.73 mA cm^{-2}) and half-life time (1500 s) are achieved. This improved J_{SC} and half-life time are 4 times and 10 times, respectively, higher than those

of the ZnO nanorod arrays grown on a flat substrate. The overall PEC cell performance improvement for the V-groove grown ZnO array is attributed to the reduced light reflection and enhanced light trapping effect. Moreover, V-groove ZnO showed stronger adhesion between ZnO nanorod arrays and substrate.

1. Introduction

The utilization of hydrogen as an alternative energy carrier is being greatly encouraged by its clean combustion and minimal environmental contamination. Recently, increasing interest has been directed towards photoelectrochemical (PEC) water splitting, since it is a facile and environmentally friendly approach for hydrogen generation. One of the critical components of a typical PEC water splitting system is the photoelectrode, which has the photovoltaic capability and determines the overall performance of PEC cell. Since TiO_2 was first discovered as a potential anode material for water splitting,^[1] many other metal oxides, such as WO_3 , Fe_2O_3 and ZnO, have been extensively studied.^[2-4] As a specialty, ZnO is of great interest due to its high electrochemical stability, suitable conduction and valence band edges that straddle the redox potentials of water, high electron mobility (10–100 fold higher than that of TiO_2),^[5,6] absorption occurrence in the visible light region induced by the intrinsic defects, and lower recombination of electrons and holes from longer electron lifetimes of ZnO.^[7]

Despite the superior properties of ZnO to other metallic oxides in PEC water splitting, the low photoelectron conversion efficiency and short life time of the ZnO anode are the main issues that hinder its practical application. To achieve a high conversion efficiency of ZnO-based PEC cell, many strategies have been reported. For instance, reducing the size to nano-scale to increase the specific surface area,^[4,8-12] doping with different kinds of impurities to reduce the band gap and enhance the absorption of visible light,^[13-16] sensitizing with dye or quantum dots^[17,18], solid solution of nitrides^[19-21], and modifying with noble metal nanoparticles to enhance the light

trapping ^[22]. Several typical examples include: Kwang-Soon Ahn's group prepared ZnO nanocorals via thermal oxidation to favor large surface areas and suitable electrical pathways for efficient carrier collection; ^[9] Yu-Kuei Hsu's group obtained ternary $Zn_{1-x}Cu_xO$ nanorods with high photoresponse of visible light via an electrochemical route; ^[16] Kazunari Domen's group fabricated a GaN – ZnO solid solution $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ by NH_3 treatment of a mixture of Ga_2O_3 and ZnO to achieve a stable visible-light-driven photocatalyst for water splitting. ^[23] We have recently introduced a bent photoelectrode made of Ag-decorated ZnO nanorod arrays on flexible substrate, to enhance light harvesting and charge transport. ^[22]

Improved efficiency has been achieved by all these approaches, the strengthened light trapping and stability of photoelectrode are, however, still challenging. ^[24-27] Light trapping is particularly critical in PEC cells to increase light absorption and hence overall efficiency. Typically, only a small portion of the sunlight that strikes the surface can be eventually converted into electric current, which is mainly due to the large reflective loss of incident light occurring at the interfaces. Therefore, further improvement on reducing the light reflective loss and increasing the bonding strength between the anode material and substrate is necessary. In this work, ZnO nanorod arrays with a unique architecture were grown on a specially patterned Si substrate. A V-groove structure was simply created on the substrate before growth for the purpose of enhanced light trapping/absorption and photoelectrode adhesion/stability. The geometric and morphological effects on the light trapping and PEC properties of the improved photoanode were investigated.

2. Experimental details

2.1 Photoanode preparation

A p-type Si(100) wafer was used as the substrate. A layer of SiO_2 with a thickness of 300 nm was grown on the Si wafer through a wet oxidization process, which was

carried out at 1100 °C for 23 min using a Tystar three-zone atmosphere-pressure tube furnace. A photoresist (AZ 5214) line arrays pattern was formed via photolithography and used as a mask to etch the exposed SiO₂ layer. Reactive ion etching was then used to remove the SiO₂ exposed with a flow rate of 25 sccm for both CHF₃ and Ar with RF power of 150W. After that, the etched substrate was immersed into a KOH solution with a concentration of 30 wt% at 80 °C for 10 minutes to yield the V-shaped grooves with certain dimensions, as demonstrated schematically in figures 1(a1)–(a3). The growth of ZnO nanorod arrays on V-grooved substrate was carried out through hydrothermal process. In a typical experiment, Zn(CH₃COO)₂/ethanol solution (0.005 M) was spin-coated onto the as-prepared substrate. After heating at 500 °C in air for 1 h, the coated V-grooved substrate was kept in Zn(NO₃)₂·6H₂O aqueous solution (0.04 M), which has been neutralized by ammonia, at 90 °C for 24 h. The obtained ZnO nanorod arrays grown on V-grooved substrate was denoted as ZnO-V-P (figure 1(b)). For comparison purpose, ZnO nanorods grown on a flat oxidized Si substrate were also prepared following the same procedure and denoted as ZnO-Flat (figure 1(c)).

2.2 Photoanode characterization

The morphology of ZnO nanorod arrays was investigated using a field-emission scanning electron microscope (FESEM, JEOL-7600F). The reflectance was studied using a UV – Visible – NIR microspectrophotometer (GRAIC, 20/20 PV™). The spot size of the beam was carefully adjusted using the aperture to ensure the light is projected on the trench or ridge area. The PEC properties were studied using a three-electrode system with prepared ZnO nanorod arrays as working electrode. Pt foil and standard Ag/AgCl were used as counter and reference electrode, respectively. Na₂SO₄ aqueous solution (0.5 M) was used as electrolyte and purged with N₂ for 5–10 min before testing. During the test, the working electrode was fully exposed to a UV spot light source (Lightingcure™, model LC-5, Hamamatsu Photonics, France, for the light spectrum refer to figure S1). The full wavelength range (250–850 nm) of the light source has been used in the

measurement. The yielded illumination power density is 18 mW cm^{-2} . A potentiostat (Model 263A, EG&G Princeton applied research) and a sourcemeter (Keithley 4200) were used as potential source and current-voltage data recorder, respectively.

3. Results and discussion

3.1 Morphological analysis

The morphologies of the ZnO nanorod arrays grown on the flat and V-grooved Si substrates were shown in figure 2. Compared with the ZnO nanorod arrays on flat substrate, which is of total coverage as shown in figure 2(a1), the growth of ZnO nanorod arrays on the V-grooved substrate was restricted to the trench and edge area of V-grooves (figure 2b(1)). The enlarged image, figure 2(a2), shows the uniformity of the grown ZnO nanorod arrays. The growth of ZnO nanorod arrays is always perpendicular to the surface of substrates, as shown in figure 2(a3). This indicates that ZnO nanorod arrays grow upward in the direction perpendicular to the trench surface of the V-grooved substrate and intersect across the groove, forming a bridged morphology which straddles the trench (figure 2(b2) and (b3)).

3.2 Reflectance

The effect of geometric modification on light reflection is investigated. Compared with that from bare flat Si substrate (figure 3(a)), the reflectance from the trench area of the bare V-grooved Si substrate is largely reduced within the wavelength range of 300–850 nm. As an indication, the reflectance peak at around 370 nm, which is derived from interference effects of light reflected on the surface of SiO_2 layer and that on the SiO_2/Si interface (to verify the effect, simulated reflectance from the flat SiO_2/Si substrate was fitted according to the Fresnel equations, figure S2),^[28] as shown in curve (a) and (b) of figure 3, is as high as 80% for the bare flat Si substrate, while it is only 15% for bare V-grooved Si substrate. The significant reduction is due to the geometric

confinement. For normally incident light, the reflectivity at the V-grooved surface with tilt angles between 45° and 54° is approximated by squared reflectivities.^[29] In our case, the tilt angle is 54.7° . As shown in scheme (a) and (b) of figure 3, compared with that on the flat substrate, the incident light reflects once or twice on the surface of the trench depending on lighting spot, which helps reduce the reflectivity.

Curve (c) and (d) in figure 3 show the reflectance of ZnO nanorod arrays grown on the flat and V-grooved Si substrates, respectively. Compared with the reflectance from the bare flat Si substrate (curve (a)), that obtained from flat Si substrate covered with ZnO nanorod arrays was distinctly decreased (curve (c)). The same trend can be observed for that from V-grooved Si substrate (curve (b) and (d)). The reduction is attributed to the strong light absorption of ZnO nanorod arrays.^[30] The reflectance of ZnO nanorod arrays grown on the V-groove patterned substrate (curve (d)) was the lowest among all samples, indicating the strongest light absorption for both the UV and visible wavelength ranges. For ZnO nanorod arrays, the absorption from the incident light with energy higher than the bandgap energy of ZnO (UV range) is most efficient and useful for photocurrent generation (figure S3, curve (a)). While the light absorption from the incident light with energy below the bandgap (visible range) also contributes to the photocurrent generation, though much smaller (figure S3, curve (b))^[8,31], which arises from the intrinsic oxygen vacancies and zinc interstitials.^[32] With different morphologies, the bridged ZnO nanorods grown on V-grooved substrate have a smaller reflection compared to the nanorods grown on the flat Si substrate (curve (c) and (d)). Thus stronger photoresponse is expected for the bridged ZnO nanorods on V-grooves. For visible light (absorption by ZnO is small), besides smaller reflection caused by morphology, the light trapping function of V-grooves plays an added role in obtaining larger photo responses, as shown in scheme (d) of figure 3.

3.3 PEC properties

The photocurrent density – voltage curves of ZnO nanorod arrays on different substrates under illumination are shown in figure 4, note that the potential was applied with respect to the Ag/AgCl reference electrode. The photocurrent density is defined as the current divided by the ZnO nanorods-covered effective contact areas, which are denoted as S1 and S3 for ZnO-V-P and ZnO-flat, respectively. As a reference, the photocurrent density, by taking into account the whole consumptive area denoted as S2, was calculated. In detail, S1 is the ZnO-covered trench area of the substrate, S2 is the sum of ZnO-covered trench area and the bare flat area of the V-grooved substrate, and S3 is the ZnO-covered flat area of the substrate (the colored region shown in the upper right inset of figure 4). It is shown clearly that ZnO nanorod arrays grown on the V-grooved Si substrate exhibit significantly higher photocurrent density than those on the flat Si substrate. For instance, the photocurrent density is 0.15 mA cm^{-2} for the ZnO nanorod arrays grown on flat substrate (ZnO-Flat-S3) at the potential of 0 V, while it is as high as 0.73 mA cm^{-2} for those on the V-grooved substrate (ZnO-V-P-S1), which is more than 4 times higher (the upper left inset in figure 4). As a reference, the photocurrent density obtained from the ZnO nanorod arrays grown on V-grooved substrate, with respect to area S2 (ZnO-V-P-S2), is also higher than that from ZnO-Flat-S3 as well. The increase of the photocurrent density of the ZnO nanorod arrays on V-grooved substrate is due to the bridged ZnO nanorod arrays formed from the V-grooved structure. As verified by the above-stated reflectance results, the bridge-like network that is built from the ZnO nanorod arrays in the trench area of the V-grooves could harvest more light and provide more interaction sites for light–ZnO and water–ZnO. More electrons and holes are generated by absorbed light and drift to the counter electrode and the photoelectrode. Therefore, the designed structure which features both a bridged nanorods network and large surface area facilitates diffusion of charges to the surface of the photoelectrode, leading to a higher effective surface area for water splitting reaction sites and the ease of charge transport among ZnO nanorods. Despite the low illumination power density that used (only 18 mW cm^{-2}), the photocurrent density in this work is comparable to reported values which used much higher power density. ^[10-12,16]

The working life time of PEC cells using ZnO nanorod arrays grown on different substrates as photoanodes was studied under light illumination. A potential of 0.5 V was applied on the working electrode ($V_{WE}=+0.5$ V). The normalized half-life time curves of ZnO nanorod arrays grown on flat and V-grooved Si substrates are presented in figure 5. It is shown that the half-life time of PEC cells from ZnO nanorod arrays grown on V-grooved substrates is extended to 1500 s, 10 times higher than that from those grown on flat substrate. The improvement of the life time indicates the stronger adhesion between photoanode and substrate as well as the better stability of the bridged ZnO nanorod arrays on V-grooved Si substrate. Compared with the flat Si substrate without treatment, the surface of the V-grooved area is relatively rougher after the wet etching process (figure S3).^[33] The rougher surface possesses a high surface free energy, which facilitates the attachment of particles from the precursor to the nucleus and leads to faster kinetics of nucleation.^[34] It is therefore believed that a rougher surface brings stronger interfacial adhesion between the substrate and the grown nanostructures,^[35-36] which maintains the architecture of ZnO nanostructures on V-grooved substrate and results in a longer lifetime of the photoelectrode. The adhesion and structure stability is further verified by the morphological study of the ZnO nanorod arrays after a life time test. As shown in figure 5(a1), mesopores, which resulted from the anode corrosion, can be found on the ZnO nanorod arrays. The ZnO nanorod arrays were totally intact on the trench area (figure 5(a2)–(a3)), indicating better adhesion between the ZnO nanorod arrays and the V-grooved substrate. In contrast, the ZnO nanorod arrays grown on the flat substrate were partially peeled off from the substrate (figure 5(b)). Furthermore, a rougher substrate results from the KOH etching and shows better support for photocurrent generation than the flat one. This is confirmed by the higher half-life time of ZnO nanorod arrays grown on the KOH-etched substrate than that of ZnO nanorod arrays on the flat one (green and blue curves in figure 5).

4. Conclusions

In summary, ZnO nanorod arrays with a unique bridged architecture were formed on a patterned V-grooved Si(100) substrate via photolithography followed by hydrothermal growth. The growth of ZnO nanorod arrays were restricted to the trench area of the V-groove, leading to a bridge-like interconnected nanostructure. Reduced reflection of both UV and visible light, and enhanced light trapping for visible light were achieved for ZnO nanorod arrays on the V-grooved substrate. The photocurrent density and life time were significantly enhanced. The bridged ZnO nanorod arrays on patterned substrate show great potential as photoanode in PEC devices.

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Figure 5. Normalized half-life time of PEC cells from ZnO nanorod arrays grown on flat Si substrate, V-grooved Si substrate, and flat Si substrate etched with KOH. Insets show FESEM images of (a1) enlarged ZnO nanorod arrays, (a2) ZnO nanorod arrays in the trench area, (a₃) ZnO nanorod arrays on V-grooved substrate, and (b) ZnO nanorod arrays on flat substrate after water splitting.

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Figure S4. Field-emission scanning electron microscope (FESEM) images of (a) bare Si substrate, and (b) Si substrate etched with KOH (30 wt%) for 10 minutes.

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