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Water splitting TiO_2 composite material based on black silicon as an efficient photocatalyst

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ABSTRACT

We attempt to evaluate Black Silicon (BSi) substrate loaded with water splitting (WS) semiconductor and Au particles as an efficient WS composite material. Further, thermal annealing was performed to study the effect of the WS photocatalyst microstructure evolution on optical properties, crystallinity, photo-response and the hydrophilicity. The thermal annealing was carried out at 450–850 °C range in ambient environment. The WS crystal structure analysis by X-ray Diffraction, shows that TiO_2 turns after annealing at 450 °C to anatase phase known for high photocatalytic behavior. This transformation increases the optical reflection (%R) of the WS material in UV–Vis–Near IR region for both substrates (Si and BSi), however this increase about 1–5% is insignificant for the BSi due its morphology consisting of needles and wells. Nevertheless, this transformation decreases the hydrophilicity of the material surface of BSi due to its inherent structure. In addition, we showed that the photo-response after annealing is associated with lower resistance and higher photocurrent emission compared to non-annealed sample. This result suggests that BSi used as a substrate to receive WS semi-conductor has a great potential to be used as an efficient WS materials compared to Si.

1. Introduction

Alternative forms of renewable energy are needed to combat our excessive use of the limited fossil fuels resources. One of the viable and sustainable forms of alternative energy production comes from the use of fuel cells, which employ hydrogen gas to produce power, with the only waste product being H_2O. One of the problems within the fuel cell economy, is the production of sufficient and clean forms of hydrogen. Hydrogen generation through the water splitting (WS) process is being considered as a growing route to increase the hydrogen fuel production. WS typically involves the separation of H_2O molecules into its constituent parts of H_2 and O_2. This is a viable and renewable approach considering water is an abundant and sustainable resource. After achieving an efficient and clean manner to produce H_2, the hydrogen fuel economy becomes more desirable [1]. Many methods are developed for efficient H_2 production via WS such as, using electron donor/sacrificial agents to assist in the propagation of the WS [2–6], dye sensitization [7–9], and Nobel metal loading [10,11].

WS is highly dependent on efficient photocatalyst materials, with high optical properties as well as an affinity for water molecules. Exploring modified silicon substrate for instance, black silicon (BSi) has shown an enhancement of optical properties; this material is obtained by various etching methods of flat silicon and was found to possess high aspect ratio in the use for MEMS [12]. BSi also showed a great potential for photoluminescence applications [13], and Photodetector applications [14]. Mainly, the purpose of using BSi instead of Si is to increase the optical absorption of the material for a broad range of wavelengths. Although, Si is used in various applications related to microelectronic industry, Si suffers from high reflectance of about 40% in certain optical ranges. Therefore, etching the Si surface is one of the ways to obtain significant increase in the absorption of photons for applications requiring high optical absorbance such as, photocatalytic applications. Because of its inherent structure, BSi exhibits on its surface pillars with different sizes and different spacings (wells). This provokes multiple interactions with incoming photons [15], which gives several opportunities for the photons to be trapped and then absorbed. The well-like structure of BSi allows for the entrapment of photons; this is due to the higher energy of the incident photons entering the wells, but the scattered photons leaving the wells do not have sufficient energy to escape back. Along with this, the refractive index is slightly changing along the height gradient of the pillars, respectively from top to bottom with a refractive index of about 1.3 at the top of the tips to about 3.0 and higher towards the bottom of the well. This change in refractive index allows for multiple scattering lines of wavelengths of different wave phases, leading to an entanglement of various waves creating destructive wave interference; hence, lowering the amplitude of the

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photons and making it difficult for the light to escape and easier to be absorbed by the BSi [16].

This study is aimed at characterizing BSi comparatively to flat Si as a suitable WS composite materials, both substrates are loaded with TiO_2 and Au particles. BSi has an exceptional optical absorption due to the increase of Si light trapping ability and Au is considered here to extend the optical absorbance to visible region [17]. We evaluate these two aspects of the composite material along with other physical properties such as microstructure, photocurrent and wettability to assess the potential use of this composite as an efficient WS material.

2. Materials and methods

2.1. Fabrication of BSi using DRIE

The BSi was fabricated from N-type silicon wafers by Deep Reactive Ion Etching (DRIE) tool (Oxford™ Instruments) using medium density plasma, with fluorine as an etchant. No masks were used, the natural oxides along with the dust that may have been on the surface of the wafer were used as an intrinsic mask for the silicon [18].

2.2. Deposition of TiO_2

TiO_2 serves as a photocatalyst for the WS composite. A thin film of 40 nm was grown using an Oxford™ FlexAL ALD tool at 250 °C with a growth rate of 0.3 Å/cycle (11 s/cycle). TDMAT precursor was used under O_2 plasma and Ar flow using the bubbling delivery method at pot temperature of 70 °C and pressure range of 15–40 mTorr.

2.3. Deposition of Gold

Gold serves as a Noble metal to extend the absorption of TiO_2 from the UV region into the visible region. Hence, 40 nm of gold was sputtered by Gatan™ Model 682 Precision Etching Coating Systems (PECS) at 6 KeV at the deposition rate of ~1.5 Å/s (Table 1).

3. Characterization

3.1. X-ray diffraction

Bulk crystal orientation analyses were carried out using the PANalytical™ Empyrean X-ray diffractometer (XRD) with Cu-Kα (λ = 0.154 nm) with radiation output settings at 45 kV and 40 mA power ratings. The obtained XRD data was cross referenced to the standards in the XRD data base via the HighScore software™.

3.2. Optical absorption

Diffuse reflection (%R) and transmission were carried out in the UV–Vis–NIR in the range of 380 nm to 850 nm with a PerkinElmer Lambda™ 1050 high-performance spectrometer. The obtained spectra were used to correlate the absorbance from reflectance and by neglecting the transmission light due to Si substrate using the following relationship [19]:

$$\%\,A = 100\% - \%R$$

An integrated sphere attachment was used to collect the diffuse reflection. The reference consists of spectrolon which is a fluoropolymer.

Table 1
Nomenclature of the samples under this study and their fabrication conditions.

Sample Name	AsIs (not annealed)	Annealed at 450 °C	Annealed at 850 °C
Flat Silicon	FSi	N/A	N/A
Black Silicon	BSi	N/A	N/A
Flat Silicon 40 nm TiO_2	FSiTO-AsIs	FSiTO-A450	FSiTO-A850
Black Silicon 40 nm TiO_2	BSiTO-AsIs	BSiTO-A450	BSiTO-A850
Flat Silicon 40 nm TiO_2 + 40 nm Au	BSiTAu40	NA	NA

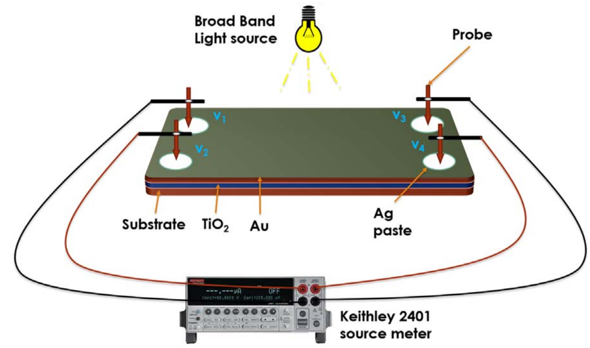

Fig. 1. Schematic showing four probe photocurrent setup used for WS material.

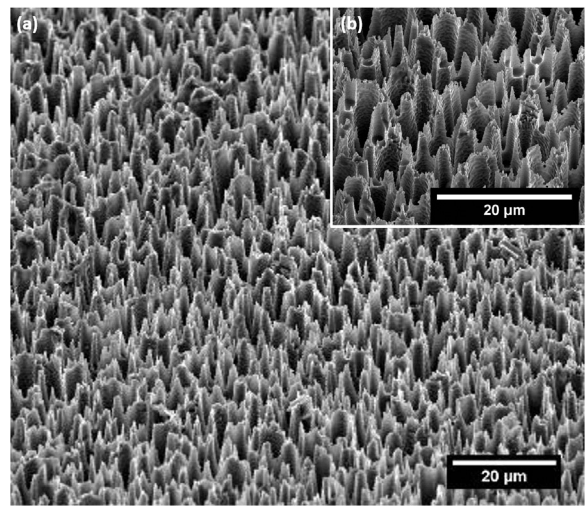

Fig. 2. BSi morphology obtained by selective etching of Si, showing pillar/grass like structure.

3.3. Morphology and Cross-sectional Assessment

FEI Quanta 250™ Scanning Electron Microscope (SEM) was used to assess the WS material microstructure. Thin lamella for cross-sectional investigation in Transmission Electron Microscope (TEM), was prepared following the standard Focused Ion Beam (FIB) milling recipe and in-situ lift off procedure using a dual beam FEI Helios NanoLab™ 650 system [18]. TEM lamella of less than 80 nm thick was then obtained for further HRTEM inspection which was carried out using a FEI™ Titan G2 TEM system operating at 300 kV.

3.4. Wettability Assessment

The wettability of the material was assessed by measuring the static contact angle obtained from a sessile drop test. The static contact angle was measured using 2 μL droplet by a Kyowa™ Interface Science Co. Ltd goniometer model Dm-501. Multiple droplets were placed onto the sample; the static contact angle of each droplet was measured and averaged over 5 measurements. [20].

3.5. Heat Treatment

The heat treatment for thermal annealing was done using a