Applied Surface Science xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

A facile method to fabricated UV–Vis photodetectors based on TiO_2/Si heterojunction

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ARTICLE INFO

Article history:
Received 25 October 2017
Received in revised form
15 November 2017
Accepted 17 November 2017
Available online xxx

Keywords:
Heterojunction
Photodetector
Nanoparticle
Spin coating

ABSTRACT

Spin coating was used to prepare TiO_2/Si heterojunction photo-detector using anatase TiO_2 nanoparticles modified with 1,4-butanediol. The heterojunction was formed between the spin coated TiO_2 nanoparticle films (200 nm) and the Si substrates. The heterojuncted structures will facilitate the separation of photo-generated carriers. The large surface-to-volume ratio of TiO_2 nanoparticles will improve the lifetime of photo-generated carriers. Our results show that the photocurrent has a linear relationship to the intensity of UV/visible light when negatively biased at −2 V. The quantum efficiency can reach 137% and 190% at 350 nm and 550 nm, respectively. The response/recovery time is very short (t_r and t_d <0.05 s), which promising a potential use in rapid detection and multi-band imaging.

1. Introduction

With the rapid development in semiconductors and technology, heterojunction devices based on wide/narrow bandgap semiconductors have attracted considerable attention due to their unique properties. Photo-detectors based on heterojunction could extend their detection range to dual-band or multi-band which have a wide applications in multi-color imaging [1,2], medical treatments [3,4] and military applications [5]. A lot of heterojuncted structure has been designed and investigated such as NiO/Si [6–8], ZnO/Si [9], SnO_2/ZnO/GaN [10] and TiO_2/Si [11]. However, these detectors generally suffer from low quantum efficiency and low photocurrent. To enhance quantum efficiency and photocurrent, wide-band semiconductor materials are commonly prepared into nanostructures, such as nanoplates and nanorods, etc. [12,13] . But, most growth processes for nanostructured wide-band semiconductors reply on expensive vacuum epitaxial growth technology, which exacerbated the production cost of the detection devices.

Titanium oxide (TiO_2) is a wide-bandgap (anatase, 3.2 eV) semiconductor with high refractive index and transparent to visible light, and become an ideal ultraviolet (UV) detection semiconductor in photoelectric detectors [11,14–18]. Various nanostructures of TiO_2 have been prepared by chemical vapor deposition [19], pulsed laser deposition [20], sputtering [21] and hydrothermal method [11,15–17]. However, Si-based TiO_2 heterojunction devices still have a problem of low quantum efficiency in UV detection. Sol-gel method is a facile and economic method to synthesize inorganic materials under low temperature, which is also the most commonly used method for preparing TiO_2 nanoparticles.

In this work, 1,4-butanediol was used as a modifier and binder to prepare high density TiO_2 nanoparticle films on Si substrate by spin coating. Under the ultraviolet (UV) and visible (Vis) light irradiation, the quantum efficiencies are greater than 100% (∼137% at 350 nm, ∼190% at 550 nm). Also, the device has high stability with the photocurrent almost linearly changed with light intensity, and the response and recovery times (t_r and t_d) are all less than 0.05 s. The device is expected to be widely used in fast and low light detection.

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https://doi.org/10.1016/j.apsusc.2017.11.144
0169-4332/

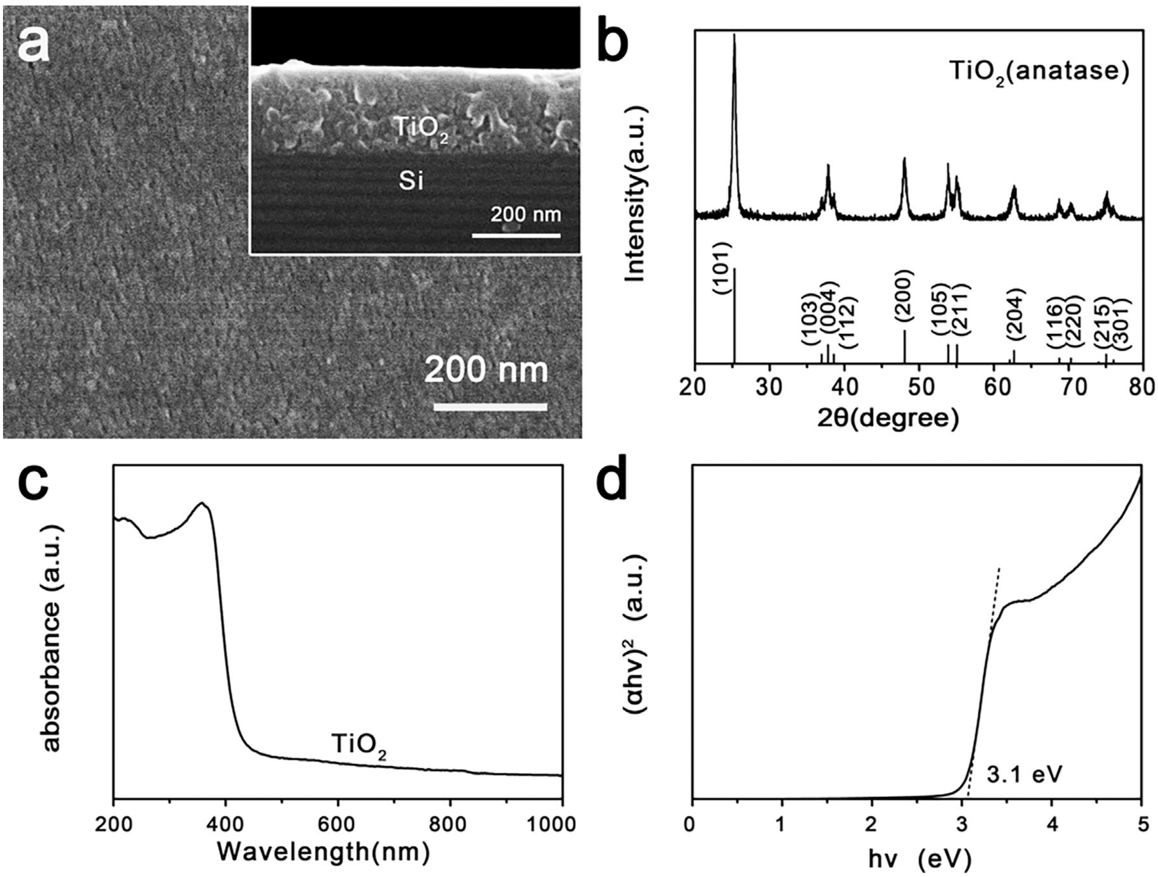

Fig. 1. (a) The front-view and cross-sectional (inset) SEM images showing the morphology of as-fabricated TiO_2/Si heterojunctions. The XRD patterns (b), UV–vis absorption spectra (c) and $(\alpha h\nu)^2$ versus hν plots (d) of TiO_2 film on glass.

2. Experimental

2.1. Synthesis of TiO_2 sol

Firstly, we added 2 mL of tetrabutyl titanate (≥98%) and 4 mL of ethanol (≥97%) to a brown glass container. The mixed solution was stirred for 30 min to form a clear solution. Then, 2 mL of 1,4-butanediol was added dropwise to the resultant solution at a rate of 0.06 mL/min, as modifier and binder. The TiO_2 sol was prepared by stirring the final solution for about 12 h.

2.2. Fabricated TiO_2 nanoparticle film on Si wafers and glass pieces

The TiO_2 sol was dropped onto pre-cleaned Si wafer and glass substrate and uniformly spin-coated on the substrates. The spin-coating process was divided into two steps. The speed was firstly keep 900 r/min for 10 s and then speeded up to 2000 r/min and kept for 20 s. The spin-coated substrate was dried in a drying oven at 150 °C for 1 h, then placed in a muffle furnace and calcined at 350 °C for 4 h. The device of Si substrate was named TiO_2/Si. The interdigital electrode was plated on the top of TiO_2 nanoparticle film of TiO_2/Si with silver. The bottom of the device was plated with silver and grounded. The bias voltage (V_B) was applied on the interdigital electrodes.

2.3. Characterizations

Powder X-ray diffraction (XRD) of the samples was conducted by a D/max-2550 PCX-ray diffractometer (Rigaku, Japan) equipped with a rotating anode and a Cu Kα radiation source (λ = 1.54056 Å). Morphology and structure of TiO_2/Si heterojunction were determined by a scanning electron microscope (SEM, S-4800). Photocurrent responses and spectra were measured by Keithley-4200. A monochromator (300150, Beijing NBET Technology Co. Ltd., Beijing, China) was used to separate UV/Vis light from a Xenon lamp (300 W). The light intensity of each wavelength is calculated according to the relative intensity of specific lights, which could be measured, such as 365 nm.

3. Results and discussion

Fig. 1a shows the top surface and cross-sectional (inset in Fig. 1a) SEM images of as-fabricated TiO_2 film on Si substrates. The TiO_2 nanoparticle films have a high-density and uniform distribution on Si wafer. The average size of TiO_2 particles was ~20 nm, and the thickness of as-formed TiO_2 film was ~200 nm. From the XRD pattern (Fig. 1b) of TiO_2 film on glass (the glass substrate accompanied with the Si wafer), the TiO_2 nanoparticles can be classified as anatase crystal phase (JCPDS No. 21–1272). The UV–vis absorption spectra of the TiO_2 are shown in Fig. 1c. And the optical band gap is determined by plotting $(\alpha h\nu)^2$ versus hν [22–24] extrapolating the linear region of the plot toward low energies, as shown in Fig. 1d. The estimated band gap of TiO_2 is 3.1 eV, which is close to the theoretical value of 3.2 eV. Ag was plated on the surface of the TiO_2 nanoparticles with an area of 0.25 cm^2 to form digitated electrodes. Ag layer was coated at the bottom of the Si wafer as ground.

The interface state characteristics of the TiO_2/Si device can be obtained from the capacitance-voltage (C–V) curve in dark at the frequencies of 50 kHz and 100 kHz at room temperature, as shown