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White light-driven photo response of TiO_2 thin films: Influence of substrate texturing

Ranveer Singh[a,b], Mohit Kumar[a,1], Mahesh Saini[a,b], Biswarup Satpati[c], Tapobrata Som[a,b,*]

[a] SUNAG Laboratory, Institute of Physics, Bhubaneswar 751 005, Odisha, India
[b] Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400 085, India
[c] Surface Physics and Materials Science Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700 064, India

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ABSTRACT

In this work, the role of film thickness on white light-driven photo response and electrical properties of TiO_2/Si heterojunctions is investigated. Two types of substrates, viz. pristine- and chemically prepared pyramidally textured-Si are used for simultaneous growth of TiO_2 films using radio frequency (RF) magnetron sputtering technique. X-ray diffraction study reveals the amorphous nature of as-grown TiO_2 thin films. In addition, it is observed that the surface reflectance of conformally grown TiO_2 overlayers on textured-Si substrates can be brought down to 0.73% for 5 nm and 0.77% for 20 nm, whereas in case of *pris*-Si substrates it is 40% for 5 nm and 30% for 20 nm-thick films (in the wavelength range of 400–800 nm). Further, TiO_2/Si heterostructures exhibit diode-like rectifying behavior under both dark and white light illumination. The 5 nm-thick films exhibit very low photoactivity in terms of photocurrent, whereas 20 nm-thick films show a remarkable enhancement in the photocurrent up to 10.25 and 78.68 μA (under reverse bias) when grown on *pris*-Si and *txt*-Si substrate, respectively. In addition to the transient photocurrent, the responsivity and sensitivity are also higher for 20 nm-thick films. These results are explained in terms of change in their optical and electrical properties. The present finding will be certainly important for fabricating high speed optoelectronic devices based on reverse biased TiO_2/Si heterojunctions.

1. Introduction

Oxide semiconductor-based heterojunctions have attracted tremendous attention as a driving element for the next-generation display devices such as high speed (> 250 Hz) and large scale (> 50 in.) liquid crystal displays (LCDs), flexible displays, photodetectors, and light-emitting diode (LED) displays because of their unique optical and electrical properties (Ahn et al., 2015; Hosono, 2006; Martins et al., 2007). For example, Xie et al. (2015) have demonstrated SnO_2/CuO-based visible-blind ultraviolet photodetectors (PDs) with peak responsivity of 10.3 AW^{-1} at a low bias of 0.2 V. Likewise, ultraviolet–visible (UV–Vis) photo detectors (PDs) based on transition metal oxides are very important devices which offer a lot of versatile applications (Hosseini et al., 2016; Hsu et al., 2012). Among various transition metal oxides, TiO_2 has attracted the attention of researchers for generation of solar hydrogen and photocatalysis by virtue of its photo stability, chemical stability, high photo conversion efficiency, and non-toxicity (Chang et al., 2012; Fujishima and Honda, 1972; Maeda et al., 2007; Singh et al., 2017; Wang et al., 2011). However, due to its wide band gap, it is able to absorb only 5% light out of the whole solar spectrum, albeit by doping and/or making a heterojunction with narrow band gap materials (e.g. Si) it is possible to extend the absorption of light even in the visible region (Hsu et al., 2012). A heterojunction between two different materials is found to be present in a variety of nanostructures such as core-shell nanowires (Chueh et al., 2007; Goldberger et al., 2006; Mieszawska et al., 2007), bilayered composite nanoribbons (Yang et al., 2016), etc. and exhibits huge potential for applications in solar cells (Yang et al., 2016), photodetectors (Hosseini et al., 2016), charge storage devices (Padilha et al., 2016), and light-emitting diodes (Gudiksen et al., 2002). For instance, in order to improve the photo- to dark-current ratio and achieve fast response of a photodiode, a combination of different materials such as Cu_2O/TiO_2, TiO_2:N/C, TiO_2:Cr/ZnO, and TiO_2:Nb/Si are used (Chang et al., 2012; Dao et al., 2013; Gautam et al., 2016; Tsai et al., 2011; Wang et al., 2012).

For the growth of TiO_2 thin films, several physical vapour deposition techniques are in commonplace such as pulsed laser deposition,

* Corresponding author at: SUNAG Laboratory, Institute of Physics, Bhubaneswar 751 005, Odisha, India.
E-mail address: tsom@iopb.res.in (T. Som).
[1] Present address: Department of Electrical Engineering, Incheon National University, 119 Academy Rd. Yeonsu, Incheon 22012, Republic of Korea.

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atomic layer deposition, electron beam evaporation, and magnetron sputtering (Chang et al., 2012; Singh et al., 2017; Tsai et al., 2011). Among these techniques, sputtering offers the advantages of large area deposition with accurate composition and uniform morphology of films (Singh et al., 2017). Generally, TiO_2 shows an *n*-type conductivity due to oxygen vacancies and Ti interstitial atoms (Aksoy et al., 2014). In recent years, it has been observed that oxygen vacancies and defects can increase the photocurrent and light absorption in oxide semiconductors (Ahn et al., 2008; Lei et al., 2014). For instance, it has been reported that *p*-type Cu_2O grown on *n*-type TiO_2 nanowires exhibit fast response of diode (Wang et al., 2012). In another report, Chang et al. (2012) have shown the effect of heterojunction (ITO/TiO_2/Si) on TiO_2 nanotubes grown by atomic layer deposition (ALD) on the photodiode characteristics. It is interesting to note that most of the existing reports show photodiode behavior in crystalline films under a forward bias. It is known that more crystalline structures have smooth charge conduction which helps to improve the photocurrent under light illumination (Chang et al., 2012; Hosseini et al., 2016), albeit it is observed that crystalline thin film based devices have higher leakage current (Singh et al., 2017). Also, the thickness of the films plays a crucial role in charge conduction. For instance, with increasing film thickness grain size increases and in turn scattering of charge carriers increases due to grains and grain boundaries Kumar et al. (2013). In a photodetector, polarity of the applied bias also affects photo response of a photodiode (Hosseini et al., 2016). In case of a forward bias, the photo response of a photodiode does not depend on the current density which means after light illumination, photo-generated charge carriers do not contribute too much in the current density. As a result, slow rise and fall time with less sensitivity and responsivity are observed by a photodiode under the forward bias (Wang et al., 2012). On the other hand, photo response of a photodiode depends on the current density under the reverse bias condition and width of the depletion region increases which leads to an improvement in the photocurrent by decreasing the recombination of charge carriers (Lin et al., 2014; Wang et al., 2012; Yu et al., 2010). Thus, to improve upon the response time and photocurrent of a photodetector it is important to explore the performance of the heterojunctions under reverse bias condition. In doing so to improve photo response, it will be useful if the substrate absorbs more light. Therefore, it is worth studying the photodiode characteristics of TiO_2/*pristine*-Si and TiO_2/*textured*-Si heterojunctions under reverse bias conditions. In addition, to the best of our knowledge, white light-driven thickness-dependent photo response studies on *n*-TiO_2/*p*-Si heterojunctions are also lacking.

In this work, we investigate the effect of TiO_2 film thickness on the photo response of *n*-TiO_2/*p*-Si heterojunctions where both *pristine*- and *textured*-Si substrates are used. Current-voltage characteristics of both types of heterojunction exhibit diode-like rectifying behavior under both dark and illuminated conditions. Surface morphology of TiO_2 thin films shows a granular nature. High-resolution transmission electron microscopy (HRTEM) results reveal the amorphous nature of the as-grown TiO_2 films. It is observed that heterojunction corresponding to a 20 nm-thick TiO_2 film shows better photo-responsivity and -sensitivity in comparison to a 5 nm-thick film grown on *textured*-Si substrates and those grown on *pristine*-Si substrates. These results corroborate well with the respective change in their optical properties. The present study will be useful to make photodiodes using TiO_2/Si heterojunctions under reverse biased conditions.

2. Experimental

A *p*-Si (1 0 0) wafer (ρ = 0.05–0.1 Ω-cm) was cut into small slices (1 cm × 1 cm) which were ultrasonically cleaned in trichloroethylene, acetone, propanol, and de-ionized water for 5 min. each to remove the organic contaminations and further air dried. Subsequently, the substrates were subject to alkaline etching for 30 min. to prepare pyramidally textured *p*-Si substrates, the details of which is reported elsewhere (Singh et al., 2017). TiO_2 thin films were grown on native oxide covered pristine-Si (identified as *pris*-Si) and pyramidally textured-Si (identified as *txt*-Si) substrates simultaneously at room temperature (RT) using an RF magnetron sputtering setup (Excel Instruments, India) under normally incident flux. Commercially available 99.99% pure TiO_2 target (50 mm dia × 6.2 mm thick) (Testbourne Ltd., UK) was used for depositing TiO_2 thin films in a vacuum chamber having a base pressure of 2×10^{-7} mbar. Ultra-pure (99.99%) argon gas was injected into the deposition chamber (base pressure: 1×10^{-7} mbar) with a flow rate of 30 sccm to maintain the working pressure of 5×10^{-3} mbar during deposition. An RF power of 100 W (Cesar, Advanced energy, USA) was supplied to the target. The substrate was rotated at a speed of 3 rpm to achieve a uniform film thickness where the target-to-substrate distance was kept as 80 mm and the deposition was carried out at an optimized angle of 0° with respect to the target normal.

Two different thicknesses of TiO_2 films (5 and 20 nm) were deposited on *pris*-Si (viz. S1 and S2, respectively) and *txt*-Si (viz. S3 and S4, respectively) substrates. Surface morphology and sample microstructure of the samples before and after the growth of TiO_2 films were examined by atomic force microscopy (AFM) (Asylum Research, USA) in contact mode and field emission gun-based scanning electron microscopy (FEGSEM) using 5 KeV electrons (Carl-Zeiss, Germany) under the plan-view geometry. For each sample, several images were collected from randomly chosen different regions to check the uniformity of films and evaluate the average grain sizes. Nature of crystallinity of the films were evaluated by x-ray diffraction (XRD) (Bruker, Germany) under the Bragg-Brentano geometry using a Cu-K_α radiation (λ = 0.154 nm) over a 2θ scan range of 20–80°. X-ray photoelectron spectroscopy (XPS) measurement was employed (PHI 5000 Versa Probe III, ULVAC–PHI, Japan) for analysis of oxygen vacancies and chemical nature of the films. For further microstructural analysis of TiO_2 films, cross-sectional transmission electron microscopy (XTEM) measurements were carried out on selective samples using a high-resolution transmission electron microscope (HRTEM) (FEI, Tecnai G2 F30, S-Twin microscope, operating at 300 kV and equipped with a GATAN Orius CCD camera). High-angle annular dark field scanning transmission electron microscopy (STEM-HAADF) was employed using the same microscope which is equipped with a scanning unit and a HAADF detector (Fischione, model 3000). The compositional analysis was also performed by energy dispersive x-ray spectroscopy (EDS, EDAX Inc.) attachment on the Tecnai G2 F30. For electrical measurements, silver paste was used to make electrical contacts on the top of TiO_2 films and the back side of the substrate. The performance of the Ag/TiO_2/Si/Ag heterostructure diodes in terms of transient photocurrent was evaluated using a spectral response setup (Sciencetech, Canada) equipped with a source meter (Keithley, 2410) under both dark and white light illumination. The specular reflectance and transmittance data were recorded by ultraviolet (UV)–visible (vis)-near infrared (NIR) spectrophotometer (Shimadzu-3101PC, Japan), using an unpolarized light.

3. Results and discussion

Fig. 1(a) depicts the SEM image of a *pristine*-Si sample, whereas Figs. 1(b) and (c) show plan-view FESEM images of S1 and S2, respectively. From the last two SEM images, granular nature of TiO_2 thin films is confirmed, albeit uniformly distributed grains show an enhancement in size as the film thickness increases to 20 nm. On the other hand, Fig. 1(d) shows the SEM image of an as-prepared *txt*-Si substrate, whereas Figs. 1(e) and (f) depict plan-view FEGSEM images of TiO_2 films of thickness 5 and 20 nm, respectively grown on *txt*-Si substrates which clearly depict the signature of conformal film growth (having randomly distributed pyramids) and a very high root mean square roughness of 225 nm, as is extracted from the corresponding AFM image (not shown). For a better clarity, the insets in Figs. 1(e) and (f) show the high-resolution plan-view SEM images for the respective TiO_2-