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Au/TiO_2 nanorod-based Schottky-type UV photodetectors

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TiO_2 nanorods (NRs) were synthesized on fluorine-doped tin oxide (FTO) pre-coated glass substrates using hydrothermal growth technique. Scanning electron microscopy studies have revealed the formation of vertically-aligned TiO_2 NRs with length of ~2 μm and diameter of 110–128 nm, homogenously distributed over the substrate surface. 130 nm thick Au contacts using thermal evaporation were deposited on the n-type TiO_2 NRs at room temperature for the fabrication of NR-based Schottky-type UV photodetectors. The fabricated Schottky devices functioned as highly sensitive UV photodetectors with a peak responsivity of 134.8 A/W (λ = 350 nm) measured under 3 V reverse bias.

Today, ultraviolet (UV) photodetection is drawing a significant attention due to its importance in many applications including space communication, environmental monitoring, military and civil applications [1, 2]. Silicon is one of the most widely used materials in UV photodetectors due to its low noise and quick response in the UV region [1, 3]. In spite of these benefits, Si-based UV photodetectors exhibit low efficiency and need costly specific filters to block photons having low energies due to the relatively low band gap. The problems associated with Si-based UV photodetectors can be avoided by the fabrication of UV photodetectors based on wide-bandgap semiconductor materials such as SiC, III-nitrides and most of the II–VI compounds [1, 4].

Among the wide-bandgap semiconductors, TiO_2 can be regarded as the strongest candidate for realization of highly sensitive UV photodetectors due to its outstanding chemical, physical and optical properties [5]. Especially, one-dimensional (1D) TiO_2 structures (nanowires and nanorods) offer great advantages for the realization of highly sensitive UV photodetectors. The incorporation of TiO_2 nanorods (NRs) in a conventional UV photodetector device structure is expected to reduce the recombination probability of electron–hole pairs generated under illumination due to the presence of surface trap states associated with adsorbed O_2 molecules on the surface of TiO_2 NRs. Although there are many studies reporting the synthesis and characterization of 1D structures of TiO_2, there is very limited effort to fabricate UV photodetectors based on these structures with Schottky-type device configuration, which is expected to provide higher performance over the conventional p–n junction based devices [6].

In this investigation, TiO_2 NRs were successfully synthesized by using hydrothermal technique and subsequently employed for the fabrication of highly sensitive UV photodetectors as a device application. The synthesized TiO_2 NRs and the fabricated photodetectors were subsequently characterized in detail by performing several types of characterization measurements.

TiO_2 NRs were grown on pre-cleaned FTO glass substrates by using hydrothermal technique [7]. Following the growth of TiO_2 NRs, to fabricate NR-based Schottky-type UV photodetectors, gold (Au) metallic top contacts were deposited by thermal evaporation using dot (1 mm diameter) patterned 2 × 2 cm^2 copper shadow masks.

Figure 1(a), (b) shows the scanning electron microscopy (SEM) images of TiO_2 NRs grown on FTO glass substrate. It is clear from the images that the diameter and

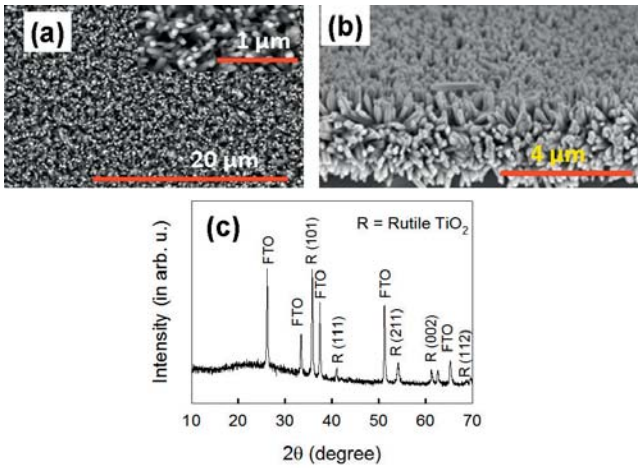

Figure 1 (online colour at: www.pss-rapid.com) (a), (b) SEM images of TiO_2 NRs grown on FTO pre-coated glass substrate recorded at different magnifications. (c) XRD pattern obtained for TiO_2 NRs grown on FTO pre-coated glass substrate, showing significant rutile TiO_2 peak with (101) direction.

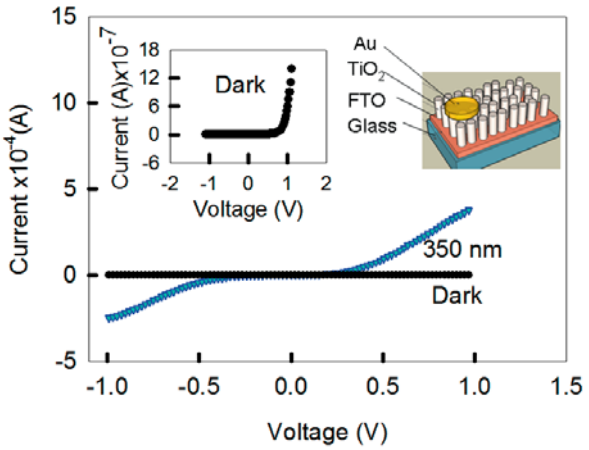

Figure 3 (online colour at: www.pss-rapid.com) Current–voltage (I–V) characteristics of the fabricated Au/TiO_2(NRs)/FTO Schottky diodes in dark and under light illumination at 350 nm. The inset figures show the dark I–V characteristic and a schematics of the device cross section.

length of NRs range in between 110–130 nm and 2.0–2.1 µm, respectively. Figure 1(c) presents the X-ray diffraction (XRD) pattern of TiO_2 grown on FTO glass substrate. As can be seen from the diffraction pattern, all peaks are associated with FTO glass substrate and grown TiO_2 NRs [8]. The pattern reveals that the peaks are indexed as (101), (111), (211), (002) and (112) corresponding to the rutile structure of TiO_2, which is attributed to the growth in strongly acidic solution [8]. From the XRD pattern, it is also observed that R(101) is the most intense peak with respect to the rest of the reflecting planes of the rutile structure, indicating that the TiO_2 NRs are dominantly oriented in this plane direction.

Detailed structural characterizations of TiO_2 NRs were carried out by performing transmission electron microscopy (TEM) and analyzing associated selected area electron diffraction (SAED) patterns as shown in Fig. 2. The recorded TEM images have revealed that the preferred growth direction is (101) that was obtained from the XRD study as well, indicating the consistency between the results of two measurements. From the observed SAED pattern presented in the inset of Fig. 2(a), a set of diffraction spots has appeared and was identified as $(1\bar{1}0)$, (001) and $(\bar{1}1\bar{1})$ confirming the formation of rutile crystal structure of TiO_2 [7]. In addition, as presented in Fig. 2(b), the space between the adjacent planes was measured to be ~0.32 nm, which is in close agreement with the reported (110) lattice constant [7].

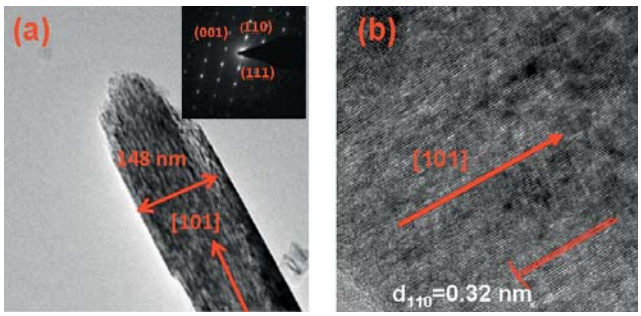

Figure 2 (online colour at: www.pss-rapid.com) (a) Low-magnification TEM image of TiO_2 NRs and SAED pattern. (b) TEM image recorded with high magnification.

Figure 3 shows the current–voltage (I–V) characteristics of the fabricated Au/TiO_2(NRs)/FTO Schottky diodes in dark and under light illumination at 350 nm. In addition, the inset figures illustrate the dark I–V characteristics and the schematic cross-section of the fabricated device. It can be seen that the device exhibits rectification under both conditions (dark and light illumination) indicating the formation of a Schottky-type diode with an Au/TiO_2(NRs)/FTO sandwich structure. The measured reverse (I_R) and forward (I_F) currents at 1 V in dark were found to be around 1.2×10^{-7} A and 1.4×10^{-6} A, respectively and the corresponding rectification ratio is $I_F/I_R \sim 12$. The observed significant increase in both reverse and forward currents upon illumination in the UV wavelength range could be attributed to the reduction in the Schottky barrier potential formed between Au and TiO_2.

Figure 4 exhibits the spectral photoresponsivity of the Au/TiO_2(NRs)/FTO device measured at reverse biases of 1 V, 2 V and 3 V in the wavelength range of 300–500 nm at room temperature. The responsivity (R) is defined as $R = I_p/P_{inc}$, where I_p is photocurrent and P_{inc} is the incident illumination power (normal incident on the device), which were measured using white light source (monochromated: 1/8 m grating with 600 lines/mm, and mechanically chopped) together with a lock-in amplifier (SRS830) and a calibrated silicon photodetector, respectively. As seen from Fig. 4, the photoresponsivity is quite low above the wavelength of 410 nm presenting a cut-off wavelength for the

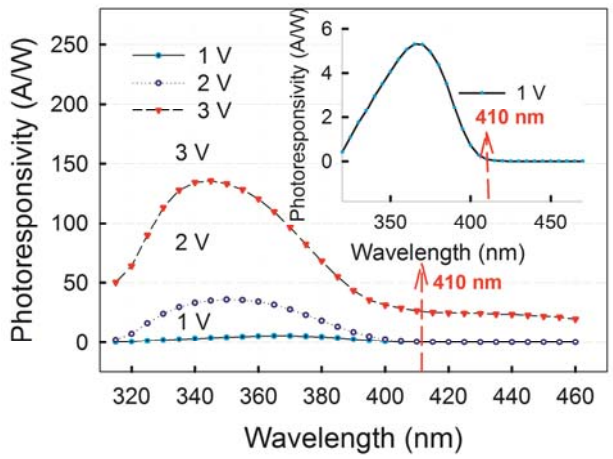

Figure 4 (online colour at: www.pss-rapid.com) Measured spectral responsivities of the Au/TiO_2(NRs)/FTO device at different applied reverse biases (1 V, 2 V, and 3 V). The inset shows explicitly the measured responsivity at 1 V reverse bias.

detector. For all measurements conducted at different biases, the photoresponsivity increases with decreasing wavelength, and reaches a peak value at 350 nm and then starts to decrease with further decrease in the wavelength. The enhancement in the responsivity below 410 nm is likely due to the generation of more electron–hole pairs upon illumination of photons with energies larger than that matching the band gap of TiO_2. Beside this, the decrease in photoresponsivity at lower wavelengths might be attributed to the shorter penetration depth of high energy photons that are absorbed near the surface of TiO_2 NRs as the device is illuminated from the glass side. Therefore, the carrier generation occurs near the TiO_2 NRs surface which subsequently triggers the recombination resulting in a decrease in the carrier lifetime [9], since the penetration depth of high energy photons is very short. The measured peak responsivities under illumination of 58 $\mu W/cm^2$ ($\lambda = 350$ nm) at reverse biases of 1 V, 2 V and 3 V were 5.3, 36.7 and 134.8 A/W, respectively. As it is expected, the photoresponsivity increases from 5.3 to 134.8 A/W as the bias voltage is increased from 1 to 3 V, indicating the generation of more carriers under Au Schottky contact which allows the effective collection of photo-generated free carriers before recombining or trapping. So far, the reported peak responsivities of fabricated UV photodetectors are in the range of 0.1–13 A/W [6, 10], which are quite lower than that obtained by us with the Au/TiO_2(NRs)/FTO device configuration. The enhanced UV photoresponsivity observed in this study could be attributed to hole-traps at the TiO_2 NRs surface incorporated through the adsorbance of O_2 molecules on n-TiO_2 NRs that have a large surface to volume ratio. In other words, adsorbed O_2 molecules capture free electrons from the conduction band of TiO_2 and induce the formation of a highly resistive depletion region near the surface which is responsible for prolonging of the photocarrier lifetime as a result of preventing charge-carrier recombination. Upon UV illumination, the generated holes are trapped by negatively charged O_2 ions that results in unpaired electrons behind, which leads to improvement in charge transportation to the electrodes [9].

In conclusion, high quality TiO_2 NRs were grown on FTO pre-coated glass substrates to fabricate Au/TiO_2(NRs)/FTO Schottky-type UV photodetectors. Measurements and analysis have shown that the devices give maximum response at 350 nm with a responsivity of 134.8 A/W at 3 V reverse bias. In addition, a significant improvement in responsivity and response time was observed over the Au/TiO_2 thin-film-based Schottky-type UV photodetector, which was attributed to the unique physical and electrical properties of the grown TiO_2 NRs.

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