Particle Systems Characterization www.particle-journal.com

TiO₂ Nanotube Array/Monolayer Graphene Film Schottky Junction Ultraviolet Light Photodetectors

Ming-Zheng Wang, Feng-Xia Liang,* Biao Nie, Long-Hui Zeng, Ling-Xia Zheng, Peng Lv, Yong-Qiang Yu, Chao Xie, Yang Yang Li,* and Lin-Bao Luo*

Schottky junctions made from a titanium dioxide nanotube (TiO₂NT) array in contact with a monolayer graphene (MLG) film are fabricated and utilized for UV light detection. The TiO₂NT array is synthesized by the anodization and the MLG through a simple chemical vapor deposition process. Photoconductive analysis shows that the fabricated Schottky junction photodetector (PD) is sensitive to UV light illumination with good stability and reproducibility. The corresponding responsivity (R), photoconductive gain (G), and detectivity (D[±]) are calculated to be 15 A W⁻¹, 51, and 1.5×10^{12} cm Hz^{1/2} W⁻¹, respectively. It is observed that the fabricated PD exhibits spectral sensitivity and a simple power-law dependence on light intensity. Moreover, the height of the Schottky junction diode is derived to be 0.59 V by using a low temperature I–V measurement. Finally, the working mechanism of the TiO₂NT array/MLG film Schottky junction PD is elucidated.

1. Introduction

Titanium dioxide (TiO₂) is a material of wide applications ranging from white pigments to photocatalysts. Owing to the large surface to volume ratio, the prominently different bonding characteristics and environment for the surface and bulk, nanostructured TiO₂ have distinctly different properties from their thin film or bulk counterparts.^[1,2] A number of synthetic methods, such as the sol–gel process,^[3] hydrothermal

M.-Z. Wang, B. Nie, L.-H. Zeng, P. Lv, Y.-Q. Yu, C. Xie, Prof. L.-B. Luo School of Electronic Science and Applied Physics and Anhui Provincial Key Laboratory of Advanced Functional Materials and Devices Hefei University of Technology Hefei Anhui, 230009, P. R. China E-mail: luolb@hfut.edu.cn M.-Z. Wang, L.-X. Zheng, Prof. Y. Y. Li Department of Physics and Materials Science City University of Hong Kong Kowloon, Hong Kong SAR, P. R. China E-mail: yangli@cityu.edu.hk Dr. F.-X. Liang School of Materials Science and Engineering Hefei University of Technology Hefei Anhui, 230009, P. R. China E-mail: fxliang@hfut.edu.cn



synthesis,^[4] and chemical vapor deposition (CVD),^[5] have been developed recently to produce various one-dimensional TiO₂ nanostructures (e.g., nanowires, nanorods, or nanotubes)^[6] with unique properties in chemistry, optics, electronics, and photocatalysis.^[7-9] Among these nanostructures, TiO₂ nanotubes (TiO₂NTs), particularly the highly ordered TiO₂NTs arrays standing vertically on the substrates that are fabricated through anodization of Ti, have attracted increasing research interest in the past decade for the ease of fabrication and good control over the morphologies (e.g., tube length, spacing between neighboring tubes, and inner and outer tube diameters).^[10]

www.MaterialsView

To date, anodic TiO_2NT films have found wide applications in various fields.

For example, TiO₂NTs can act as the recipient of the electrons from the photoexcited dye and as the electron-transfer pathway from the dye to the back contact of the sensitized electrode,^[11,12] rendering TiO₂NTs an attractive material for fabricating high-performance photovoltaic devices.^[13] What is more, TiO₂NTs with large surface areas can act as efficient sensors for hydrogen,^[14] oxygen,^[15] humidity,^[16,17] and glucose.^[18] It is found that these TiO₂NT-based sensors usually exhibit high performance with low detection limit, high stability, good reproducibility, and fast response.^[19]

Another important application of TiO2NTs is for efficient UV photodetection, which is vital for space communication, flame sensing, ozone-layer monitoring, and so on.^[20,21] Due to the appropriate bandgap heights (3.2 eV for anatase and 3.0 eV for rutile) and distinctive absorption characteristics, TiO₂ nanostructures are particularly suitable for UV detection against a background with infrared and visible light. To date, while several ultraviolet photodetectors (UVPDs) based on TiO₂ nanowires and nanocrystalline films have been reported,^[22-24] relatively little attention has been paid to UVPDs made from TiO₂NTs.^[25] Herein, we report the fabrication of the Schottky junction devices from TiO2NTs coated with a monolayer graphene (MLG) film and their application as UVPDs. It was observed that this novel type of UVPD is highly sensitive to 365 nm UV irradiation with good reproducibility, stability, and selectivity. Furthermore, the relationship between the photocurrent and UV intensity can be fitted by a power law. The working mechanism of the novel UVPDs was elucidated at last.

DOI: 10.1002/ppsc.201300040



www.MaterialsViews.com

2. Experimental Section

2.1. Device Construction

The TiO₂NTs were synthesized by an anodization method following previous studies.^[26] Briefly, Ti foils (Sigma-Aldrich) were first cleaned by ultrasonification in acetone, deionized water, and ethanol sequentially and then dried in a nitrogen stream. The anodization was carried out in a two-electrode cell, where the cleaned Ti foil was pressed against an O-ring and used as the anode while a platinum ring was used as the counter electrode. The electrolyte used in this study is an ethylene glycol solution containing 0.27 wt% NH₄F and 2.0 vol% H₂O. The Ti foil was anodized at a constant voltage of 60 V for 3 h with a Keithley 2400 Sourcemeter. The MLG was synthesized at 1000 °C by using a mixed gas of CH₄ (40 SCCM) and H₂ (20 SCCM) via a CVD process, during which, a 25- µm-thick Cu foil was employed as the catalytic substrate. After growth, the MLGs were spin-coated with 5 wt% polymethyl methacrylate (PMMA) in chlorobenzene, and the underlying Cu foils were removed in Marble's reagent solution (CuSO₄:HCl:H₂O= 10 g:50 mL:50 mL).

2.2. Structural Analysis and Device Characterization

The morphology and phase studies were, respectively, carried out using field emission scanning electron microscopy (Philips XL 30 GEG) and X-ray diffraction (XRD) (D/max- γ B). The chemical composition analysis was performed with an energy dispersive X-ray (EDX) detector, attached to the scanning electron microscopy (SEM) chamber. The Raman scattering analysis was performed on a Renishaw 2000 spectrometer with the incident wavelength at 633 nm. The optoelectronic properties of the PD were evaluated by a semiconductor *I–V* system (Keithley

4200-SCS). The low-temperature *I–V* measurements were performed in the range of 80 to 300 K using an automatic cooling system (CCS-350S cryogenic cycle refrigeration).

3. Results and Discussion

The construction of the TiO₂NT array/MLG film device begins with the fabrication of TiO₂NT arrays. Firstly, TiO₂NT arrays were synthesized by directly anodizing Ti foils. The as-anodized sample was then thermally oxidized in air at 450 °C for 2 h. For insulating purpose, sellotape was attached at the four edges of the TiO₂NT array. The exposed area was then covered by a layer of a PMMA-supported MLG film. Finally, at the corners of the graphene films, Ag paste was deposited, which together with the backside of the Ti substrate serve as the top and back electrodes. The step-wise device construction process was illustrated in **Figure 1**.

Figure 2a–c shows the representative SEM images of the as-anodized TiO_2NT array



Figure 1. Flow chart for the fabrication of TiO_2NTs arrays/MLG film Schottky junction.

before thermal treatment. The clean and smooth top surface of the sample with tube opening can be easily visualized. The average length and diameter of the TiO₂NTs were measured to be ~9 μ m and 150 nm, respectively. The EDX analysis of these TiO₂NTs revealed an atomic ratio of 1/1.91 (Ti/O). It is well that the TiO₂NT arrays fabricated under the specific anodization conditions in this study are amorphous, and thus not suitable for device applications. In light of this, the as-prepared TiO₂-NTs arrays were intentionally oxidized to improve the crystallinity.^[27] Figure 3a,b shows the typical SEM images of the TiO₂NTs after annealing at 450 °C for 2 h. Apparently, the tubular morphology was retained, although the film top surface became



Figure 2. a–c) Cross-sectional and d) top-view SEM images of the as-anodized $\rm TiO_2NT$ arrays without thermal treatment.

www.particle-journal.com



www.MaterialsViews.com



Figure 3. Cross-sectional (a) and top-view (b) SEM images of the TiO_2NT arrays after thermally treated at 450 °C for 2 h. c) XRD pattern of the thermally oxidized TiO_2NT arrays. d) Cross-sectional SEM image of a TiO_2NT array with a PMMA-supported MLG film on the surface. e) Raman spectrum of the graphene film. The inset shows the corresponding SEM image of the graphene film on Si/SiO₂ substrate.

slightly rougher. Further XRD study confirmed that the TiO₂NT array changed from amorphous to coexisting anatase and rutile phases after thermal treatment. Figure 3d shows the cross-sectional SEM image of the TiO₂NT array coated with a PMMA-supported graphene film. The Raman spectrum (Figure 3e) is found to contain two sharp peaks, i.e., a 2D-band peak at ≈2649 cm⁻¹ and a G-band peak at ≈1590 cm⁻¹. The intensity ratio of I_{2D} : I_G , which equals 2.49, along with the weak D-band scattering at ≈1327 cm⁻¹, confirms the high crystal quality of the MLG film.

The TiO₂NT array/MLG film Schottky junction shows high sensitivity to UV light illumination. **Figure 4**a compares the I-V characteristics of the device with and without UV light irradiation. Clearly, one can see that at both forward and reverse biases, the current in dark is less than that under UV light irradiation. Further, time response of the nanodevice suggests the excellent stability and repeatability of the device. As observed from Figure 4b, when the light was repeatedly turned

on and off, the nanodevice can be reversibly switched between low and high conductance. Spectral photoresponse study reveals that the photocurrent is highly dependent on the wavelength of the incident light. Figure 4c depicts the I-V curves measured under light illumination with different wavelengths. To make the data obtained more consistent, the light intensity was kept the same during the spectra response analysis. It can be seen that the photocurrent of the PD is relatively low for wavelengths over 400 nm. When the wavelength is less than 400 nm, the sensitivity increases steeply and reaches a maximum at 365 nm. This photosensitive selectivity is actually associated with the working mechanism of the device.^[28,29] When the TiO₂NTs photodetector (PD) is irradiated with UV light, photons with wavelength of 365 nm are sufficient to directly lift electrons in the TiO₂NTs from the valence band to the conduction band. As a result, photocurrent is formed in the circuit. In contrast, the photons with less energy, cannot excite





Figure 4. a) The *I*–*V* curve of the TiO_2NT array/MLG film PD with and without UV light illumination at 365 nm. The inset shows the schematic setup for the *I*–*V* measurements under UV light illumination. b) Photoconductive characteristics of the PD repeatedly exposed to UV light at 365 nm. c) Spectral response of the TiO_2NTs arrays/MLG film PD.

electrons from the valence band to the conduction and thus do not contribute to photocurrent.

In addition to wavelength, the photocurrent is found to depend on light intensity as well.^[30,31] **Figure 5**a plots the *I*–*V* curves of device irradiated by UV light (365 nm) with varied light intensity. It is apparent that the photocurrent increases drastically with increasing light intensity. The dependence of photocurrent on the light intensity, *I*, can be expressed by a power law: $I = AP^{\theta}$, where *A* is a constant for a certain wavelength, *P* the light intensity, and θ the exponent (0.5 < θ < 1), determining the response of the photocurrent to light intensity. By fitting the curve in Figure 5b with this equation, $\theta = 0.77$ is obtained. This fractional power dependence is likely to be related to the carrier traps in the TiO₂NTs.



Figure 5. a) Photocurrent of the TiO_2NT array/MLG film PDs with different UV light intensities. b) the Fitting of the relationship between the photocurrent and light intensity, the light wavelength was 365 nm.

In order to quantify the performance of such a diode-based PD, responsivity (R) and photoconductive gain (G), the two key parameters that reflect the sensitivity of a PD to the incident light,^[32] were calculated by using the following equations:

$$\begin{split} R(A/W) &= \frac{I_{\rm p}}{P_{\rm opt}} = \eta \left(\frac{q \lambda_{\rm hc}}{\rho} \right) G \\ G &= \frac{N_{\rm el}}{N_{\rm ph}} = \frac{\tau}{\tau_{\rm tr}} \end{split}$$

where I_P is the photocurrent, P_{opt} is the incident light power, η is the quantum efficiency, *h* is Planck's constant, *c* is the speed of light, λ is the incident light wavelength, *q* is the unit of elementary charge, and *G* is the photoconductive gain, which is equal to the ratio of the number of electrons collected per unit time $(N_{\rm el})$ to the number of photons absorbed per unit time $(N_{\rm ph})$ or the ratio of carrier lifetime (τ) to carrier transit time $(\tau_{\rm tr})$. On the basis of these values and formulas, *R* is estimated to be 15 AW⁻¹ at a bias of -5 V, assuming $\eta = 1$ for simplification. Meanwhile, G is calculated to be 51. It is noted that these calculated R and G are higher than previous investigations on the UVPDs merely based on TiO₂NTs array.^[33] The large photoconductive gain (>1) of this device could be attributed to the following three factors: i) The reduction of the Schottky barrier at TiO2NTs/MLG film junction under UV light irradiation, due to the oxygen adsorption and desorption.[34] The reduced Schottky barrier would facilitate electrons to pass through the barrier, thereby, can lead to large photocurrent. This mechanism is

www.particle-journal.com

Particle Systems Characterization www.particle-journal.com

consistent with the observed super-linear intensity dependence of the photocurrent (see Figure 5b). ii) The presence of huge amount of O vacancy within the TiO2NT arrays. The huge amount of O can function as efficient trapping centers for carriers, and thus will greatly extend the carrier lifetime (τ) . iii) Trapping of free electrons from its conduction band, as a result of oxygen molecules adsorption onto the surfaces of ntype TiO₂NT array $(O_2(g) + e^- \rightarrow O_2^-(ad))$. This trapping effect can cause the formation of a low-conductivity depletion region, which is significant to the efficient separation of the electrons and holes, reduced electron-hole recombination and extended carrier lifetime.^[35,36] Furthermore, another important parameter used to quantitatively evaluate the performance of a PD is detectivity (D*). Physically, it denotes the normalized radiation power required to give a signal from a photoconductor that is equal to noise. Generally, this parameter can be calculated by using the following formula:[37]

$$D^* = rac{(AB)^{1/2}}{NEP} pprox rac{A^{1/2}R}{(2e\,I_{
m d})^{1/2}}$$

where *A* is the PD area, I_d is the dark current, *R* is the responsivity, *e* is the electron charge. Based on these values, D^* is estimated to be 1.5×10^{12} cm Hz^{1/2} W⁻¹, comparable with that ofa ZnTe:Sb nanoribbons-based PD.^[38]

To evaluate the barrier height of the TiO₂NTs array/MLG film Schottky diode, the *I*–*V* characteristics of Schottky junction in various temperatures ranging from 80 to 300 K were studied. As shown in **Figure 6**a, the current of Schottky junction consistently decreases with the decrease of temperature, as a consequence of series resistance and the interfacial layer effect.^[39,40] It has been previously established that, at higher temperature, when the current carriers are thermally generated, the large current will tend to flow through the Schottky diode.^[41,42] The barrier height (Φ_{bo}) of such a diode can be calculated given that it is strongly forward biased. According to the thermionic emission theory, the current across an ideal Schottky barrier at forward bias voltage $V(V \ge 3kT/q)$, neglecting series and shunt resistance, is described by the relation^[43,44]

$$I = I_0 \exp\left(\frac{q V}{nkT}\right) \left[1 - \exp\left(-\frac{q V}{kT}\right)\right]$$

where I_0 is the reverse saturation current derived from the straight line intercept of $\ln I - V$ plot at zero bias and can be estimated by:



Figure 6. a) I-V curves of Schottky junction in the temperature ranging from 80 to 300 K. b) Richardson and fitting curves of the UVPDs as a function of the reciprocal of *T*, the Richardson curve was measured at 1 V.



www.MaterialsViews.com

$$I_0 = AA^* T^2 \exp\left(-\frac{q \Phi_{\rm bo}}{kT}\right)$$

where Φ_{b0} , *A*, *A**,*n*, *q*, *k*, and *T* are the barrier height at zero bias, the rectifier contact area, the effective Richardson constant, the ideality factor, the electron charge, the Boltzmann constant, and the temperature in kelvin, respectively. Taking natural logarithm of the above formula yields

$$ln\left(\frac{I_0}{T^2}\right) = ln(AA^*) - \frac{q(\Phi_{\rm bo})}{kT}$$

When a forward turn-on voltage (V_F) was applied to the device, a saturation current I_F can be obtained, thus the formula above can transform to

$$ln\left(\frac{I_F}{T^2}\right) = ln(AA^*) - \frac{q(\Phi_b - V_F)}{kT}$$

In this equation, the actual barrier height Φ_b is less than Φ_{b0} due to image force barrier lowering and other factors, and the term $q(\Phi_b - V_F)$ is called activation energy.^[45,46] At room temperature, both A^* and Φ_b are independent of temperature. Thereby, the value of the barrier height can be extracted by the slope of the $\ln(I_F/T^2)$ versus 1000/T. Figure 6b shows the Richardson plot of the $\ln(I_F/T^2)$ versus 1000/T for the TiO₂NT array/MLG film structure, the fitting curve of the linear plot of the $\ln(I_F/T^2)$ versus 1000/T was found to be linear in the measured temperature range and Φ_b was estimated to be 0.59 eV from the slope of this straight line.

The photoresponse characteristics of the TiO₂NT array/MLG film Schottky junction UVPDs can be explained by examining the energy band diagrams. As shown in Figure 7a,b, at a forward bias, the upward movement of Fermi level of TiO2NT array allows the electrons within the nanostructures to pass through the Schottky barrier and reach graphene, leading to an "on" state of the diode. Upon UV light irradiation, the photogenerated electron-hole pairs were separated by the electric field between the TiO₂NTs and graphene film, giving rise to a photocurrent in the external circuit. In this case, the Schottky barrier disappears. By contrast, when the PDs were reversely biased, the energy band of TiO2NT array will bend downwards and a larger space charge region is formed. The electric field in the space charge region has a direction from the conductor (MLG) to the semiconductor (TiO₂NTs). Due to the large Schottky barrier at the interface, electrons can hardly drift from the graphene electrode into the nanotubes, resulting in a low dark current. Once the diode is irradiated with UV light, electron-hole pairs generated by the absorbed photons in the space charge region were separated by the built-in electric field in opposite directions, leading to the photocurrent in the external circuit. The photogenerated holes were injected into the graphene and the photogenerated electrons are diffused into the inside part of the semiconductor.

4. Conclusions

In summary, Schottky junction devices were fabricated by integrating TiO_2NT arrays and MLG films. The as-assembled

FULL PAPER



www.particle-journal.com

- [1] C. Richter, C. A. Schmuttenmaer, Nat. Nanotechnol. 2010, 5, 769.
- [2] F. X. Liang, T. L. Kelly, L. B. Luo, H. Li, M. J. Sailor, Y. Y. Li, ACS Appl. Mater. Interfaces 2012, 4, 4177.
- [3] Z. Miao, D. S. Xu, J. H. Ouyang, G. L. Guo, X. S. Zhao, Y. Q. Tang, Nano Lett. 2002, 2, 717.
- [4] Y. H. Lee, J. M. Yoo, D. H. Park, D. H. Kim, B. K. Ju, Appl. Phys. Lett. 2005, 86, 033110.
- [5] J. M. Baik, M. H. Kim, C. Larson, X. H. Chen, S. J. Guo, A. M. Wodtke, M. Moskovits, *Appl. Phys. Lett.* **2008**, *92*, 242111.
- [6] Y. S. Wang, R. Wang, C. F. Guo, J. J. Miao, Y. Tian, T. L. Ren, Q. Liu, Nanoscale 2012, 4, 1545.
- [7] K. Shankar, J. I. Basham, N. K. Allam, O. K. Varghese, G. K. Mor, X. J. Feng, M. Paulose, J. A. Seabold, K. S. Choi, C. A. Grimes, *J. Phys. Chem. C* 2009, *113*, 6327.
- [8] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, C. A. Grimes, *Nano Lett.* 2005, 5, 191.
- [9] H. S. Qian, J. L. Hu, J. J. Li, Y. Hu, Z. Q. Li, S. H. Yu, Part. Part. Syst. Charact. 2013, DOI:10.1002/ppsc.201200110.
- [10] M. Paulose, K. Shankar, S. Yoriya, J. Phys. Chem. B 2006, 515, 1802.
- [11] O. K. Varghese, M. Paulose, C. A. Grimes, Nat. Nanotechnol. 2009, 4, 592.
- [12] J. Q. Luo, L. Gao, J. Sun, Y. Q. Liu, RSC Adv. 2012, 2, 1884.
- [13] M. D. Ye, X. K. Xin, C. J. Lin, Z. Q. Lin, Nano Lett. 2011, 11, 3214.
- [14] M. Paulose, O. K. Varghese, G. K. Mor, C. A. Grimes, K. G. Ong, *Nanotechnology* **2006**, *17*, 398.
- [15] Q. Zheng, B. X. Zhou, L. H. Li, Z. J. Jin, J. L. Zhang, J. H. Li, Y. B. Liu, W. M. Cai, X. Y. Zhu, *Adv. Mater.* **2008**, *20*, 1044.
- [16] F. X. Liang, L. B. Luo, C. K. Tsang, L. X. Zheng, H. Cheng, Y. Y. Li, Mater. Res. Bull. 2012, 47, 54.
- [17] Y. Y. Zhang, W. Y. Fu, H. B. Yang, Q. Qi, Y. Zeng, T. Zhang, R. X. Ge, G. T. Zou, *Appl. Surf. Sci.* **2008**, *254*, 5545.
- [18] S. Peng, S. J. Ding, J. Yuan, X. W. Lou, D. H. Kim, ACS Nano 2011, 5, 7617.
- [19] C. A. Grimes, J. Phys. Chem. C 2007, 17, 1451.
- [20] E. Monroy, F. Omnes, F. Calle, Semicond. Sci. Technol. 2003, 18, 33.
- [21] H. B. Yao, Y. Guan, J. Zheng, G. Huang, J. Xu, J. W. Liu, S. H. Yu, Part. Part. Syst. Charact. 2013, 30, 97.
- [22] Z. R. Wang, H. Wang, B. Liu, W. Z. Qiu, J. Zhang, S. H. Ran, H. T. Huang, J. Xu, H. W. Han, D. Chen, G. Z. Shen, ACS Nano 2011, 5, 8412.
- [23] Y. G. Han, C. C. Fan, G. Wu, H. Z. Chen, M. Wang, J. Phys. Chem. C 2011, 115, 13438.
- [24] T. Y. Tsai, S. J. Chang, W. Y. Weng, C. L. Hsu, S. H. Wang, C. J. Chiu, T. J. Hsueh, S. P. Chang, J. Electrochem. Soc. 2012, 159, 132.
- [25] H. F. Zhang, S. P. Ruan, H. L. Li, M. Zhang, K. B. Lv, C. H. Feng, W. Y. Chen, *IEEE Electron Device Lett.* **2012**, *33*, 83.
- [26] F. X. Liang, J. W. Cheng, C. K. Tsang, H. Cheng, Y. Y. Li, J. Nanosci. Nanotechnol. 2011, 11, 11059.
- [27] G. K. Mor, O. K. Varghese, M. Paulose, K. Shankar, C. A. Grimes, Sol. Energy Mater. Sol. Cells 2006, 90, 2011.
- [28] L. B. Luo, F. X. Liang, J. S. Jie, Nanotechnology 2012, 22, 485701.
- [29] L. B. Luo, X. B. Yang, F. X. Liang, J. S. Jie, Q. Li, Z. F. Zhu, C. Y. Wu, Y. Q. Yu, L. Wang, CrystEngComm 2012, 14, 1942.
- [30] Y. L. Cao, Z. T. Liu, L. M. Chen, Y. B. Tang, L. B. Luo, J. S. Jie, W. J. Zhang, S. T. Lee, C. S. Lee, *Opt. Express* **2011**, *19*, 6100.
- [31] Z. Li, J. Salfi, C. De Souza, P. Sun, S. V. Nair, H. E. Ruda, Appl. Phys. Lett. 2010, 97, 063510.
- [32] Y. Q. Yu, L. B. Luo, Z. F. Zhu, B. Nie, Y. G. Zhang, L. H. Zeng, Y. Zhang, C. Y. Wu, L. Wang, Y. Jiang, CrystEngComm 2013, 15, 1635.
- [33] J. P. Zou, Q. Zhang, K. Huang, N. Marzari, J. Phys. Chem. C 2010, 114, 10725.
- [34] Y. Z. Jin, J. P. Wang, B. Q. Sun, J. C. Blakesley, N. C. Greenham, *Nano Lett.* 2008, 8, 1649.

www.MaterialsViews.com





Figure 7. Energy band diagrams of the TiO₂NT array/MLG Schottky junction without a) and with b) UV light illumination. Φ_G/Φ_{TiO2} and E_F represent the work functions and Fermi energy level of TiO₂NTs/MLG film, respectively, χ_{TiO2} is the electron affinity of TiO₂, E_C and E_V are the conduction band and valence band of TiO₂ NTs, respectively.

 TiO_2NT array/MLG film Schottky junction is sensitive to UV light illumination with good stability, reproducibility, and spectral selectivity. Detailed reasons for the spectral selectivity are proposed. The relationship between the photocurrent and light intensity can be fitted by a simple power law. To explain the working mechanism of the TiO_2NT array/MLG film PDs, energy band diagrams of the formed Schottky junction is plotted. It is expected that this Schottky junction-based PDs will have potential applications in the future nano-optoelectronic devices.

Acknowledgements

This work was supported by the City University of Hong Kong (PJ 9667056), the Fundamental Research Funds for the Central Universities (2012HGCX0003), and the National Natural Science Foundation of China (NSFC, Nos. 21101051).

Received: February 2, 2013 Revised: March 9, 2013

Particle Particle Systems Characterization

www.particle-journal.com



www.MaterialsViews.com

- [35] H. Kind, H. Q. Yan, B. Messer, M. Law, P. D. Yang, Adv. Mater. 2002, 14, 158.
- [36] C. S. Lao, M. C. Park, Q. Kuang, Y. L. Deng, A. K. Sood, D. L. Polla, Z. L. Wang, J. Am. Chem. Soc. 2007, 129, 12096.
- [37] J. M. Liu, *Photonic Devices*, Cambridge University Press, New York **2005**.
- [38] D. Wu, Y. Jiang, Y. G. Zhang, J. W. Li, Y. Q. Yu, Y. P. Zhang, Z. F. Zhu, L. Wang, C. Y. Wu, L. B. Luo, J. S. Jie, J. Mater. Chem. 2012, 22, 6206.
- [39] O. Pakma, N. Serin, T. Serin, S. Altindal, *Semicond. Sci. Technol.* **2008**, *23*, 105014.
- [40] S. Chand, J. Kumar, Semicond. Sci. Technol. 1995, 10, 1680.
- [41] J. Osvald, Solid State Commun. 2006, 138, 39.
- [42] S. Chand, S. Bala, Appl. Surf. Sci. 2005, 252, 358.
- [43] S. M. Sze, K. Ng Kwok, Phys. Semicond. Devices, John Wiley and Sons, Hoboken 2007.
- [44] E. H. Rhoderick, R. H. Williams, Metal-Semiconductor Contacts, Clarendon Press, New York 1978
- [45] G. P. Ru, R. L. V. Meirhaeghe, Solid-State Electron 2005, 49, 606
- [46] M. M. Abdul-Gader Jafar, Semicond. Sci. Technol. 2003, 18, 7