Monolayer Graphene Film on ZnO Nanorod Array for High-Performance Schottky Junction Ultraviolet **Photodetectors**

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A new Schottky junction ultraviolet photodetector (UVPD) is fabricated by coating a free-standing ZnO nanorod (ZnONR) array with a layer of transparent monolayer graphene (MLG) film. The single-crystalline [0001]-oriented ZnONR array has a length of about 8–11 µm, and a diameter of 100~600 nm. Finite element method (FEM) simulation results show that this novel nanostructure array/MLG heterojunction can trap UV photons effectively within the ZnONRs. By studying the I-V characteristics in the temperature range of 80–300 K, the barrier heights of the MLG film/ZnONR array Schottky barrier are estimated at different temperatures. Interestingly, the heterojunction diode with typical rectifying characteristics exhibits a high sensitivity to UV light illumination and a quick response of millisecond rise time/fall times with excellent reproducibility, whereas it is weakly sensitive to visible light irradiation. It is also observed that this UV photodetector (PD) is capable of monitoring a fast switching light with a frequency as high as 2250 Hz. The generality of the above results suggest that this MLG film/ZnONR array Schottky junction UVPD will have potential application in future optoelectronic devices.



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1. Introduction

Zinc oxide (ZnO), with a direct wide-bandgap (\sim 3.4 eV) and a large exciton binding energy (60 meV), is one of the most studied II-VI group semiconductors. Due to quantum confinement effects, as well as small size effects, ZnO nanomaterials exhibit novel properties in optics,^[1] electrical transport,^[2] photoconductivity,^[3] and piezotronics,^[4] relative to their thin film and bulk counterparts.^[5] For this reason, ZnO nanostructures have found wide application in various fields. Take 1D ZnO nanostructures (e.g., nanorods, nanowires, nanotubes, and nanoribbons) for example: by using micro/ nano fabrication techniques, a number of optoelectronic devices with good performance have been demonstrated, include light-emitting diodes,^[6,7] UV nanolasers,^[8] photodetectors (PDs),^[9] field-effect transistors (FET),^[10] photovoltaic devices.^[11] Among these nano-devices, PDs assembled from 1D ZnO nanostructures have received special research interest.^[12,13] By virtue of the appropriate bandgap and enhanced optical properties, 1D ZnO nanostructure-based PDs are able to probe UV light illumination with high

sensitivity and fast response times,^[14] which are central to a wide range of applications including emitter calibration, flame sensors, and space communications.^[15,16]

Graphene, a single layer of carbon atoms in a closely packed 2D honeycomb lattice is one of the most hotly pursued materials. Owing to its fascinating physical properties including high electrical conductivity, ultrahigh mobility, and high transparency, graphene has been successfully modified on various ZnO nanostructures for high-efficiency photovoltaic devices,^[17] highly sensitive flexible gas sensors,^[18] transparent and flexible field emitters,^[19] and supercapacitors.^[20] In spite of this progress, graphene-modified ZnO nanostructures for UV light detection have rarely been explored. Research on this topic is highly desired in that the incorporation of transparent and conductive graphene into ZnO nanostructures will possibly provide synergistic effects in light absorption and electron transport, and therefore will bring about improved device performance.

Herein, we report a new kind of photodetector for UV light sensing. The UVPD was fabricated by covering a freestanding single-crystalline ZnO nanorod (ZnONR) arrays with a layer of highly transparent monolayer graphene (MLG). The barrier height of the ZnONR array/MLG Schottky junction was estimated by low temperature I-V measurement. Theoretical simulation reveals that the as-fabricated ZnONR array/MLG heterojunction is capable of trapping most of the incident UV light within the nanostructures. Thanks to this light trapping effect and the Schottky junction, the MLG film/ZnONR array UVPD exhibits high sensitivity to UV light illumination, with good reproducibility and fast response speed.

2. Results and Discussion

The scheme in Figure 1a illustrates the procedures to fabricate the MLG film/ZnONR array UVPD. Briefly, it began with synthesis of the ZnONR array on the Si wafer. For insulation, sellotape was then stuck at the periphery of the ZnONRs. Afterwards, poly(methyl methacrylate) (PMMA)supported MLG film was transferred onto the surface of the ZnONR array. Finally, Ag paste was placed at the corners of the MLG films where the PMMA was removed by acetone solution. The as-prepared ZnONRs and graphene were structurally analyzed to check their crystallinity, morphology, and chemical composition. The X-ray diffraction (XRD) pattern of ZnONRs reveals that all diffraction peaks can be readily indexed to wurtzite structure of ZnO (JCPDS: 89-0511),^[21] and no obvious peaks ascribable to impurity and contaminants were detected (Supporting Information, Figure S1). Figure 1b shows a typical cross-sectional scanning electron microscopy (SEM) image of the product, from which wellaligned ZnONRs with a length of about 8-11 µm were observed. The high density and the uniformity suggest the excellent quality of the ZnONRs. Further energy dispersive spectrometer (EDS) analysis confirmed the ZnONRs consist of Zn and O in a roughly 1:1 ratio (inset in Figure 1b). Figure 1c depicts a typical smooth and straight ZnONR with a diameter of ~200 nm. The corresponding selected area electron diffraction (SAED) pattern taken on the single NR shows its single crystallinity. HRTEM analysis and the insitu fast Fourier transform (FFT) pattern confirmed that the ZnONR grew preferentially along the [0001] direction (inset of Figure 1d), which is consistent with the unusual strong



Figure 1. (a) Schematic illustration of step-wise process for the fabrication of MLG film/ZnONR array Schottky junction UVPD. (b) Cross-sectional SEM image of the ZnONR array, the inset shows the corresponding EDS spectrum. (c) TEM image of a typical ZnONR with a diameter of ~180 nm, inset is the corresponding SAED pattern. (d) High-resolution transmission electron microcopy (HRTEM) image of the ZnONRs, the inset shows the corresponding FFT. (e) Raman spectrum of the MLG film, the inset shows an SEM image of the isolated MLG film on a SiO₂/Si substrate.

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Figure 2. (a) Simulated electric field energy density distribution of the PMMA-supported MLG film/ZnONR array at 365 nm light illumination. (b) Magnified simulated electric field energy density distribution. (c) Simulated electric field energy density distribution of the PMMA/ZnONR array at 365 nm light illumination. (d) Magnified simulated electric field energy density distribution.

(002) reflection peak observed in XRD patterns. Raman spectrum of the graphene film reveals two major scattering peaks: 2D-band peak at ~2653 cm⁻¹ and G-band peak at ~1590 cm⁻¹. The intensity ratio of I_{2D} : $I_G \approx 2.53$, combined with the weak D-band scattering peak at ~1327 cm⁻¹ suggests the high-quality monolayer graphene (Figure 1(e)).

This special device configuration can offer two obvious advantages: firstly, like traditional metal grating structures, the ZnONR/MLG device is capable of trapping UV light in an efficient way. Figure 2(a) and (b) show the electric field energy density distribution of the nanostructure which was obtained by the finite element method (FEM). One can clearly see that the incident energy can be confined in the shallow region, ~0.5 µm away from the Schottky contact (actually the hot spot with highest field intensity is located about 0.2 µm below the top end), leading to very high energy utilization efficiency (see top view of the energy distribution in the x-y plane shown in Figure 2(b)). Without question, this light trapping effect will be highly beneficial to the UV light photodetection. Note that in the simulation, the permittivity for the MLG is calculated to be 0.9402 + 0.00002i (c.f. Experimental Section), the negligible imaginary part signifies that the MLG film is virtually transparent to UV light. Figure 2(c) and (d) show the electric field distribution of ZnONRs without MLG coverage which are almost identical to that of ZnONRs with MLG coverage. Secondly, due to the near-zero bandgap and high conductivity behavior of MLG,^[22] the ZnONR array/graphene can be regarded as a semiconductor/metal Schottky junction. According to our previous study, the resultant built-in electric field would facilitate the separation of the photogenerated electron–hole pairs and formation of photocurrent in external circuits.^[23]

The highest curve in **Figure 3**(a) plots the typical I-Vcharacteristics of the heterojunction at room temperature. Obviously, one can see that the as-fabricated MLG film/ ZnONRs array heterojunction displays distinctive rectifying behavior, namely, it can allow the current to flow in one way only. The turn-on voltage and rectifying ratio are around 1.0 V and 10^2 , respectively. This rectifying behavior, often observed in metal/semiconductor Schottky junction, shall not arise from Ag/MLG film contact considering the fact that silver paste can form good contact with MLG film without obvious Schottky barrier.^[24] Furthermore, the contribution of Ag/MLG film contact to this rectifying effect can be also neglected because obvious linear I-V curves were observed on five representative ZnONR/Si device (Supporting Information, Figure S2). To determine the barrier height of this Schottky junction, the current-voltage curves of the MLG film/ZnO NRs array Schottky junction in the temperature range of 80-300 K were analysized. As shown in Figure 3(a), all curves exhibits similar rectifying behavior at all temperatures with turn-on voltages of ~0.5-1 V, and breakdown voltages of up to -4 V. For an idea diode, the ideality factor (*n*) should be equal to unity at all temperatures. Nonetheless, in reality, this value is highly temperature dependent, as a result of combined effects of leakage current and series resistance.



Figure 3. (a) *I-V* characteristics of MLG film/ZnONR array Schottky diode at temperatures ranging from 80 to 300 K, inset shows the cross-sectional SEM image of a typical PMMA-supported MLG film/ZnONR Schottky diode. (b) Determination of I_0 by extroploting the *I-V* curves at different temperatures. (c) Variation of barrier height (Φ_B) and ideality factor (*n*) at different temperatures.

According to the thermionic emission (TE) theory, the current across the MLG film/ZnONR array Schottky junction at forward bias voltage can be described by the following equation:^[25]

$$I = AA^{*}T^{2} \exp\left(-\frac{q \Phi_{B}}{kT}\right) \exp\left[\frac{q(V - IR)}{nkT}\right]$$
$$= I_{0} \exp\left[\frac{q(V - IR)}{nkT}\right]$$
(1)

where, k is Boltzmann's constant, T the absolute temperature, R the series resistance, n the ideality factor $(n = (q/kT)(dV/d\ln I)), A$ the junction area, A^* the Richardson constant ($A^* = 4\pi qm^*k^2/h^3$), and m^* the effective mass of the charge carriers, $\Phi_{\rm B}$ the barrier height at zero bias, I_0 the reverse saturation current. For ZnO, A^* is theoretically estimated to be 32 Acm⁻²K⁻² ($m_{e}^{*} = 0.27 m_{0}$). What is more, I_{0} can be obtained by extrapolating the I-V curves at different temperatures (Figure 3(b) and Supporting Information, Table 1). Based on these values, the ideality factor (n) and the barrier height $(\Phi_{\rm B})$ for the Schottky junction are calculated and summarized in Figure 3(c). As observed from other types of Schottky junction made of elemental semiconductor and compound semiconductor and metal, the $\Phi_{\rm B}$ for the MLG film/ZnONR array Schottky junction increases with increasing temperature, while n increases with decreasing temperature in a fashion generally known as the T_0 anomaly'.^[26] This variation with the measurement temperature can be explained by the effects of image force

lowering on the conduction process, tunneling, surface defect states, barrier height inhomogeneities, and Fermi level pinning in NRs.^[27]

Interestingly, when exposed to UV light irradiation the Schottky barrier virtually disappears, which is in agreement with the result reported by Keem, who found that light illumination can greatly lower the potential barrier between metal and semiconductor nanowire.^[28] Compared with the dark current, the photocurrent at reverse bias is increased by 3 orders of magnitude (Figure 4(a)) upon light irradiation. Figure 4(b) shows the photoresponse of the device at a bias of -1 V when the 365 nm UV light was turned on and off alternatively. Clearly, the PD can be reversibly switched between low and high conduction state with good stability and reproducibility. What is more, the R and G are estimated to be 113 AW⁻¹ and 385, respectively. These two values are comparable to that of Au/SiO₂/ZnONR array Schottky junction, but much higher than that of the rest (Table 1). This excellent device performance can be probably ascribed to the strong light trapping effect which was not observed on similar MLG film/ZnO thin film device (Supporting Information, Figure S3). In addition, as a consequence of the difference morphology, the relatively longer τ and shorter τ_{tr} of the ZnO nanowire should also be responsible for the larger G and R.

The photoresponse of this MLG film/ZnONRs array UVPD to pulsed UV light irradiation was investigated as well. **Figure 5**(b,c,d) show the reversible switching between high and low conductance when the incident UV light was quickly turned on and off repeatedly. The response is very fast and can exhibits long-term repeatability in the frequency range



Figure 4. (a) *I-V* characteristics of the UVPD in the dark, and under illumination of 365 nm light. During measurement, the light intensity was kept at 100 μ W/cm². (b) Time response of the MLG film/ZnONR UVPD.

from 50 to 2250 Hz. The relative balance $(I_{\text{max}}-I_{\text{min}}/I_{\text{max}})$ is larger than 45% even when the frequency is increased to 2250 Hz. Meanwhile, the fall and rise time are derived to be 0.7 and 3.6 ms, respectively. This response speed is much quicker than that of similar UVPDs (c.f. Table 1).^[29] We believe the following 2 factors are important to the fast response speed: (1) The high crystallinity of ZnO nanostructure. The obtained ZnONRs array is of high crystallinity with a low density of trap centers on the surface. As a result, the carrier mobility is very high, leading to a low τ_{tr} . (2) Excellent optical property. As mentioned above, due to the special device configuration, the ZnONRs array can trap incident light in an efficient way. This superior optical property, together with the built-in electric field formed by the Schottky junction can enable the quick separation of huge amount of photo-generated carriers.

The spectral response of the Schottky junction diode was also studied. Figure 6(a) plots the responsivity, the absorption spectrum and Photoluminescence spectrum (PL) as a function of wavelength. It can be seen that the peak sensitivity is located at around 350 nm, while the cutoff wavelength at 370 nm. The cutoff wavelength ($E \sim 3.35 \text{ eV}$) is comparable to the band gap of ZnO. This consistence with the optical properties is believed to relate to the working mechanism: When irradiated with UV light, only light with sufficient photon energy is able to lift electrons from the valence band to conduction band in the ZnONRs, whose band gap is estimated to be around 3.37 eV. Light with longer wavelength, however, has insufficient energy to excite electrons from the valence band to the conduction band and thus contributes little to the photocurrent. In addition to the peak sensitivity, our PD also exhibits weak response to light in visible region. Figure 6(b) shows the *I-V* photoresponse under visible light irradiation, the photocurrent increases by only one time. According to the rising and falling edges shown in Figure 6(c), the rise and decay time are respectively estimated to be 0.32 and 1.5 s, far slower than that under UV light illumination (rise/fall time: 0.7/3.6 ms). This unexpected photoresponse in visible region is reasonable given that other two factors also play important roles in affecting the photosensing characteristics. (1) Deep defects energy levels in ZnONRs. As revealed by PL (Figure 6(a)) analysis, a amount of defects were inherently formed during growth.^[34,35] These defects centers including single ionized oxygen vacancy, zinc vacancy, oxygen deficiency, excess oxygen have relatively lower energy levels compared with the bandgap of ZnO. It was found that these defects with various energy levels between the conduction band and valence band can enable the absorption of light in visible range, and therefore can contribute to the formation of photocurrent when irradiated with visible light.^[36-38] (2) The absorption of MLG. Though MLG is virtually optically transparent, yet it can to some extent absorb photons in visible light region. The absorbed photons can similarly form photocurrent in external circuits.^[39]

3. Conclusion

In summary, we present a new Schottky junction ultraviolet photodetector (MLG film/ZnONR array) by coating ZnO

Table 1. Summary of device performance of similar semiconductors nanostructures based photodetectors.

Materials and structures	Device	Wavelength of UV Light [nm]	$ au_{ m r}$ [ms]	$ au_{ m f}$ [ms]	<i>R</i> [AW ⁻¹]	G	Ref.
Graphene/ZnONR array	Schottky junction	365	0.7	3.6	113	385	This work
Colloidal ZnO nanoparticles	M-S-M	370	<100	~1000	61	203	[30]
Au/SiO ₂ /ZnONR array	Schottky junction	350 ~ 400	/	/	100~1000	337	[31]
ZnO NW/Si-MgO/n-Si	n-i-n junction	365	160	350	/	/	[32]
GaN/Ag	Schottky junction	360	>10	>10	4.2	14.2	[33]
ZnONW array	p-n junction	384	/	/	4.0	13.8	[13]



Figure 5. (a) Schematical illustration of the experimental setup for studying the time response of the UVPD. Response of the Schottky junction to the pulsed UV light at a frequency of (b) 50, (c) 900, (d) 2250 Hz. (e) The relative balance vs. switching frequency of the chopper. (f) A single normalized cycle at 50 Hz to estimate both rise time (τ_r) and fall time (τ_r).



Figure 6. (a) Spectral response of the UVPD (red box) measured at a constant bias of -1 V, the normalized room-temperature absorption (blue line) and PL (green line) spectra of MLG coated ZnONR arrays are also plotted for reference. (b) Time response of the MLG film/ZnONR array Schottky junction PD under white light illumination. (c) Enlarged rise and decay edges of the device.

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nanorod array with a transparent monolayer graphene film. The barrier height of the ZnONR array/MLG Schottky barrier has been estimated based on the I-V characteristics in the temperature ranging from 80 to 300 K. FEM simulation of this device reveals that the incident UV light can be effectively trapped and localized in the top end of ZnONR array. Further device characterization shows that this nano-UVPD exhibited highly reproducible sensitivity to UV light illumination. The responsitivity and photoconductive gain were estimated to be 113 AW⁻¹ and 385 at a bias of -1 V, respectively. Notable, due to the formation of Schottky junction, the high crystallinity of the ZnONR array, and the strong light trapping effect, the response speed of device is extremely high (rise/fall time: 0.7/3.6 ms), much quicker than that of similar UVPDs. In addition, the Schottky junction is able to monitor pulsed light with frequency as high as 2250 Hz. These results suggest that this new UVPD will open up new opportunities for future optoelectronic devices.

4. Experimental Section

Synthesis and Characterization of MLG Film and ZnONR Array: The monolayer graphene (MLG) films were synthesized via a chemical vapor deposition (CVD) method at 1000 °C using a mixed gas of CH_4 (40 SCCM) and H_2 (20 SCCM) as reaction source, and 25 µm thick Cu foils as the catalytic substrates.^[40] After deposition, the graphene films were spin-coated with polymethylmethacrylate (PMMA) solution (5 wt% in chlorobenzene) and the underlying Cu substrates were removed in Marble's reagent solution (CuSO₄:HCl:H₂O = 10 g:50 mL:50 mL). To study the structures of the as-synthesized graphene, the PMMA-supported graphene were transferred onto the SiO₂/Si substrate and dried on a hot plate at 100 °C for at least 10 min, followed by removal the PMMA by acetone. The ZnONRs array was synthesized in a horizontal tube furnace. A mixed precursor of ZnO powder (AR grade, 99.99%) and graphite powder with a molar ratio of 1:1 was placed in a quartz tube. A piece of ZnO film (200 nm)/Si (n-type (100) wafers with a resistivity of 0.0001 Ω cm) substrate was placed 13 cm away from the evaporation source in the guartz tube. The ZnO films were prepared by simple magnetron sputtering.^[41] A constant Ar (5% in O₂) gas flow of 100 SCCM (standard cubic centimeter per minute) was fed and the base pressure in the tube was kept at 200 Torr. The guartz tube was then heated up to 1050 °C and maintained at this temperature for 15-20 min. After growth, the furnace was naturally cooled down to ambient temperature and the Si substrate containing gray product was collected. The morphologies and structures of the ZnONR arrays were characterized by X-ray diffraction (XRD, D/max- γ B), field-emission scanning electron microscopy (FESEM, SIRION 200 FEG), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010, at 200 kV) and selected area electron diffraction (SAED). PL analysis was performed on a Fluorolog3-TAU-P at room temperature with an excitation wavelength of 325 nm. UV-vis spectra were recorded on UV-2501PC/2550 (Shimadzu Corporation, Japan)

Device Fabrication and Characterization: To fabricate MLG film/ZnONRs array UVPDs, the as-grown ZnONR array on ZnO film/ n^+ Si substrate were treated in an oxygen plasma (at the pressure of 100 Torr for 30 s) to make their surfaces more hydrophilic.

Then, sellotape was stuck at the four edges of ZnONR array for the sake of insulation. The as-treated specimen was soaked in deionized water, and then slowly lifted to mount the MLG film on the ZnONRs. Finally, a drop of silver paste was adhered to the graphene where PMMA film was removed by acetone. The electrical characteristics of the Schottky junction UVPDs were measured using a semiconductor characterization system (Keithley 4200-SCS). To study the optoelectronic properties, incident lights from both xenon lamp (150 μ W) and a monochromator (Omni-I300) were perpendicularly focused and guided onto the detectors. The low-temperature *I-V* measurements in the temperature range of 80 to 300 K were carried out on the semiconductor characterization system (Keithley 4200-SCS) equipped with an automatic cooling system (CCS-350 Slow temperature cycle refrigeration system).

Theoretical Simulation: The electric field energy density distribution of the MLG film/ZnONRs array was analyzed by using the finite element method (FEM). In this simulation, the incident light used has a wavelength of 365 nm. What is more, the permittivity of PMMA and ZnO are 2.3013 + 0.0014i^[42] and 6.0401 + 1.992i,^[43] respectively. What is more, The permittivity of graphene is determined to be 0.9402 + 0.00002i by the formula of $\varepsilon_g = 1 + \frac{\sigma_g \eta_0}{k_0 d}$. Clearly, the imaginary part is almost equal to zero, indicative of nominal optical loss under UV light illumination (365 nm).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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