Piezo-phototronic Effect Enhanced UV/Visible Photodetector Based on Fully Wide Band Gap Type-II ZnO/ZnS Core/Shell Nanowire Array

Satish C. Rai,† Kai Wang,† Yong Ding,‡ Jason K. Marmon,* Manish Bhatt,† Yong Zhang,¥ Weilie Zhou,*† and Zhong Lin Wang*,‡,§

†Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana 70148, United States, ‡School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, United States, *Nanoscale Science, University of North Carolina, Charlotte, North Carolina 28223, United States, §Department of Electrical and Computer Engineering/Optoelectronic Center, University of North Carolina, Charlotte, North Carolina 28223, United States, and ¥Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, 100083 Beijing, China

ABSTRACT A high-performance broad band UV/visible photodetector has been successfully fabricated on a fully wide bandgap ZnO/ZnS type-II heterojunction core/shell nanowire array. The device can detect photons with energies significantly smaller (2.2 eV) than the band gap of ZnO (3.2 eV) and ZnS (3.7 eV), which is mainly attributed to spatially indirect type-II transition facilitated by the abrupt interface between the ZnO core and ZnS shell. The performance of the device was further enhanced through the piezo-phototronic effect induced lowering of the barrier height to allow charge carrier transport across the ZnO/ZnS interface, resulting in three orders of relative responsivity change measured at three different excitation wavelengths (385, 465, and 520 nm). This work demonstrates a prototype UV/visible photodetector based on the truly wide band gap semiconducting 3D core/shell nanowire array with enhanced performance through the piezo-phototronic effect.

KEYWORDS: UV/visible photodetector · piezo-phototronic effect · core/shell nanowire · type-II heterojunction
could be further augumented in three-dimensional arrays where photoabsorption was enhanced by the trapping and rescattering of incident photons.\textsuperscript{13} Additionally, in nanowire arrays, simultaneous multi-channel charge transport facilitates efficient collection of photo generated electron–hole pairs, thereby leading to improved quantum efficiency,\textsuperscript{14,15} which when combined with the piezo-phototrionic effect, opens up a new avenue for achieving significantly enhanced device performance.\textsuperscript{16} Moreover, the type-II heterostructure may extend the photoresponse spectral range to a significantly longer wavelength that is determined by the lower bandgap component.\textsuperscript{8,10,17} Herein, we report an efficient and highly sensitive broad band UV/visible photodetector based on fully wide band gap, three-dimensional (3D) ZnO/ZnS core/shell nanowire array in which the type-II transition plays a crucial role. More importantly, the device efficiency can be further improved, at least, by an order of magnitude rendering three orders of increase in relative responsivity by piezo-phototrionic effect.\textsuperscript{18}

**RESULTS AND DISCUSSION**

Figure 1 represents the structural characterization of a ZnO/ZnS core/shell nanowire array, where Figure 1a, b are top views of low magnification field emission scanning electron microscope (FESEM) images of the as-grown ZnO nanowire array and a ZnO/ZnS core/shell nanowire on indium tin oxide coated (ITO) glass substrate.\textsuperscript{9} Rational density and smooth surface ZnO nanowires, with lengths and diameters in the range of 5–6 μm and 150–200 nm, respectively, can be seen in Figure 1a, whereas a slightly rough surface and increased diameter, with few ZnS particulates deposited on the tips, is observed in Figure 1b for the core/shell nanowires.

A high resolution transmission electron microscope (HRTEM) image of a typical single ZnO/ZnS core/shell nanowire is displayed in Figure 1c, where two different lattice fringes corresponding to the zinc-blend ZnS shell and wurtzite ZnO core separated by an abrupt interface can be seen, which is similar to the previously reported work.\textsuperscript{19} Furthermore, Figure 1d illustrates an energy dispersive (EDS) line scan collected along the lateral direction of a core/shell nanowire, which shows the characteristic core/shell elemental distribution, further confirming the successful synthesis of ZnO/ZnS core/shell nanowires.\textsuperscript{20,21}

A 3D photodetector was integrated on ZnO/ZnS core/shell nanowire array by positioning the Ag/polyester zigzag electrode on top of the nanowire array for the contact formation at the nanowire tips only and to ensure optimal compression under applied load (inset in Figure 2d).\textsuperscript{22} Complete fabrication and device integration details can be found in the Experimental Section.

A typical $I-V$ measurement of the photodetector integrated on 3D ZnO/ZnS core/shell nanowire array under a UV (385 nm) excitation source is displayed in Figure 3. It can be seen that the photocurrent increases with an increase in the UV illumination density resulting from the higher intensity influenced increment in the generation rate ($G$) of electron–hole pairs, within the limit of $h\nu > E_g$ and defined by $G = \alpha F (1 - R)e^{-\alpha x}$ where, $\alpha$ is the absorption coefficient, $R$ is the surface reflectivity, and $F$ is the incident photon flux.\textsuperscript{23}

![Figure 1](image-url)  
*Figure 1. Structural characterization of a ZnO/ZnS core/shell nanowire showing low magnification top view, FESEM images of (a) an as-grown, ZnO nanowire array and (b) a ZnO/ZnS core/shell nanowire array, (c) an HRTEM image of a single ZnO/ZnS core/shell nanowire, and (d) the corresponding energy dispersive spectroscopy (EDS) lateral line scan depicting elemental peaks characteristic to core/shell nanowire structure.*
Under steady state illumination at a fixed wavelength, the generation rate is solely determined by incident photon flux density ($F$), where an increase in $F$ will improve the electron–hole pair generation rate. Because $E_{g,ZnS} (3.7 \text{ eV}) > E_{g,ZnO} (3.2 \text{ eV}) \approx E_{g,385 \text{nm}} (3.22 \text{ eV})$, the excitation wavelength used only matches ZnO optical band gap, and it is reasonable to assume that the photocurrent contribution from the electron–hole pairs predominantly arise from photoabsorption taking place in the ZnO core in a core/shell nanowire. In addition to band-to-band absorption in ZnO, the contribution from simultaneous indirect type-II transitions occurring between the valence band maxima of the ZnS VBM to the conduction band minima of the ZnO CBM has to be considered, and its effect on device performance will be discussed in details to follow. Variation in photocurrent with illumination intensity is plotted in Figure 3b, where an increase of 325% in photocurrent ($\sim 51 \mu A$) at an intensity of 1.32 mW/cm$^2$ can be seen as compared to the ($\sim 12 \mu A$) dark current. Time-dependent photocurrent measurement at a power density of 1.32 mW/cm$^2$ and bias of 1.5 V is shown in Figure 3c, which suggests stable device switching behavior. The performance of a practical photodetector is also characterized by its responsivity ($R_{\lambda}$) at a particular wavelength, which is an important parameter that is defined as

$$R_{\lambda} = \frac{I_{\text{light}} - I_{\text{dark}}}{P_{\text{ill}}}$$

$$P_{\text{ill}} = I_{\text{ill}} \cdot A$$

where $I_{\text{light}}$ and $I_{\text{dark}}$ are currents when the photodetector is under illumination and in the dark, respectively. $P_{\text{ill}}$, $I_{\text{ill}}$, and $A$ are the excitation power, illumination density, and the active/illuminated device area, respectively.
The responsivity for UV (385 nm) excitation source, denoted as $R_{S_{385 nm}}$ with a 0.04 mW/cm$^2$ illumination density, was found to be 0.2 A/W, which is similar to a single crystal ZnS nanobelt UV sensor$^{24}$ and is orders of magnitude higher than similar photodetectors fabricated with a 3D array of nanowires.$^{25-30}$ This responsivity value corresponds to an external quantum efficiency (EQE) of about 65% if the internal photoconductive gain is assumed to be one.$^{31}$ The high responsivity achieved in the ZnO/ZnS core/shell nanowire array device can mainly be attributed to the abrupt nature of the interface between ZnO and ZnS, which effectively inhibits carrier recombination and facilitates an efficient carrier separation.

The performance of the ZnO/ZnS core/shell nanowire array photodetector was also investigated under blue (465 nm) and green (520 nm) excitation source, and the results are summarized in Figures S2 and S3 (Supporting Information), respectively. It should be noted that the photon energy corresponding to blue (2.66 eV) and green (2.38 eV) wavelengths are significantly lower than those needed to promote direct band-to-band absorption in ZnO ($E_g \sim 3.2$ eV)$^{32}$ and ZnS ($E_g \sim 3.7$ eV), which leads us to believe that the photocurrent response must be arising from an indirect type-II transition of electrons between the ZnS$_{VBM}$ (shell) and ZnO$_{CBM}$ (core). Remarkably, the photodetector response exhibits a similar behavior, as observed for UV (385 nm) excitation source (Figure 3). The peak photocurrents under blue and green excitations reached $\sim 44$ $\mu$A (3 mW/cm$^2$, Figure S2a (Supporting Information) and $\sim 18$ $\mu$A (3.2 mW/cm$^2$, Figure S3a (Supporting Information)), respectively, which correspond to an increase of 267% for blue and 50% for green wavelength as compared to the $\sim 12$ $\mu$A dark current. The photocurrent variation plot, with illumination intensities (Figures S2–S3b (Supporting Information)) and time dependence (Figures S2–S3c (Supporting Information)), shows electron–hole pair generation rate dependent linear increase of photocurrents in addition to fast and stable response as seen from the switching behavior of the device. It has been reported previously that strain at the heterostructure interface could reduce the natural band gap$^{33-36}$ slightly, whereas only a staggered type-II band alignment could give rise to a much smaller band gap than either of the individual core or shell material.$^{8}$

The strain and quantum confinement effect are the two reasons which may affect the natural type-II band gap ($\sim 1.93$ eV) of ZnO/ZnS core/shell nanowire, and these two effects were considered to predict an effective energy gap at the ZnO/ZnS interface near 2 eV for very small core/shell nanowires.$^{37}$ In regard to the ZnO/ZnS core/shell nanowire diameter (150–200 nm), no quantum confinement effect can play a role in modifying the band gap although a weak effect of strain on type-II energy gap may exist. Figure 4 contains room temperature photoluminescence (PL) spectra measured with three excitation wavelengths: 325, 442, and 532 nm, where 325 nm excitation revealed ZnO band edge emission at 3.26 eV, but the ZnS band edge emission (3.7 eV) was not present, presumably due to the fact that ZnS shell is relatively thin.$^{38}$ Both blue (442 nm) and green (532 nm) excitations yield a broadband emission with its peak at around 2 eV, in general agreement with the predicted value for type-II transition.$^{39}$ Within this range, ZnO has defect-related peaks at 2.33 and 2.53 eV, respectively, while 2.64 eV (ZnS) and 2.25 eV (ZnO/ZnS) were previously reported with above bandgap excitation.$^{39,40}$ These emissions are expected to be very weak under either 442 or 532 nm excitation. Both green emission quenching$^{41}$ and weak ZnS emission$^{38}$ would result in some contributions that could lead to the broad emission band, which can be understood as resulting from structural fluctuations in nanowire core size and/or shell thickness and perhaps also some defect related transitions, as observed similarly in the type-II ZnO/ZnSe core/shell nanowire array.$^{42}$ The dominant effect of the type-II transition$^{43}$ observed in photodetection measurements under blue and green excitation sources is mainly attributed to the abrupt interface between the ZnO core and ZnS shell.

Figures S2d–S3d (Supporting Information) contain responsivity vs intensity plots of the photodetector under blue and green illumination, respectively. Apparently, the responsivity values under blue and green excitation are smaller than under UV, mainly due to the absence of the direct band-to-band absorption in ZnO and weaker absorption at longer wavelengths. To confirm that piezoelectric property of wurtzite, ZnO is unaffected by zinc blend ZnS shell layer deposition, a current versus time ($I–t$) measurement of the ZnO/ZnS core/shell nanowire array under cyclic strain
both in dark and in the absence of any external bias was performed. Figure S1 (Supporting Information) represents the result of a typical $I/C_0$ measurement where peak piezo-current exhibits an increase as the load increases, which is in accordance with earlier report. Furthermore, to investigate the effect of the built-in piezopotential on photodetector performance, ZnO/ZnS core/shell nanowire array devices were subjected to compressive loads under UV, blue, and green excitation sources. Figure 5a is a typical $I/C_0$ measurement of the device at peak illumination densities under UV, blue, and green excitation. In the absence of a compressive load, the peak photocurrent increases with the photon energy. Figure 5b displays the result of $I/C_0$ measurements under a compressive load varying from 0.05 kgf to 0.4 kgf at a UV illumination density of 1.32 mW/cm² (UV), 3.0 mW/cm² (blue) and 3.2 mW/cm² (green), respectively, with variable compressive loads. (e) Photocurrent response with respect to compressive loads and (f) the (%) change in responsivity with compressive loads.

Figure 5. Electrical characterization of ZnO/ZnS core/shell nanowire array devices showing (a) the photocurrent response under dark, green, blue, and UV excitation, (b–d) photocurrent response at a fixed illumination densities of 1.32 mW/cm² (UV), 3.0 mW/cm² (blue) and 3.2 mW/cm² (green), respectively, with variable compressive loads. (e) Photocurrent response with respect to compressive loads and (f) the (%) change in responsivity with compressive loads.

The change in peak photocurrent at compressive loads varying from 0.05 to 0.4 kgf for UV (1.32 mW/cm²), blue (3.0 mW/cm²), and green (3.2 mW/cm²) illumination at a bias of 1.5 V is summarized in Figure 5e, where the increasing photocurrent with compressive load is a trend. Additionally, the increment in peak photocurrent...
is found to be higher for UV illumination followed by blue and green illumination, which can be attributed to the combined effect of direct band-to-band UV absorption in ZnO and the type-II transition occurring from the ZnS VBM to the ZnO CBM. This band-to-band absorption for blue and green wavelengths, however, will not happen in either the ZnO core or the ZnS shell because of the very high/wide bandgap energies. This leads to photoabsorption only via an indirect type-II transition below individual core and shell bandgap energies.

Absolute responsivities calculated for a 0.4 kgf compressive load under UV (1.32 mW/cm²), blue (3 mW/cm²), and green (3.2 mW/cm²) illumination at 1.5 V bias are 2.5, 0.54, and 0.13 A/W, respectively, which are at least an order of magnitude higher for all the illumination sources compared to no load conditions. A comparative change in responsivity, conventionally calculated as $R_\text{Load} / R_\text{0}$, where $R_\text{Load}$ and $R_\text{0}$ are defined as responsivities with and without load, is displayed in Figure 5f. The (%) change in responsivity under compressive load observed in the ZnO/ZnS core/shell nanowire array photodetector is 3 orders of magnitude higher than the responsivity without a load.

The piezo-phototronic effect enhanced performance of ZnO/ZnS core/shell nanowire array photodetector under compressive load can be qualitatively explained through band diagram and realignment of band positions under the influence of the inner piezopotential. Figure 6 displays the relative band positions of a ZnO/ZnS core/shell nanowire in different configurations. As shown in Figure 6a, in the absence of silver (Ag) metal contact to ZnS, there is no net charge transport across the junction because of staggered type-II band alignment where the Fermi level of ZnO is higher than that of ZnS, whereas the ZnS CBM is higher than that for ZnO CBM. Once silver contact to ZnS was made, the net electron transfer from silver to ZnS compensates the Fermi level imbalance, causing a downward bending of ZnS conduction and valence bands and also compensates ZnO Fermi level imbalance with minor downward band bending as shown in Figure 6b. Under UV illumination, as shown in Figure 6c, a direct band-to-band transition takes place only in ZnO, and a weak type-II transition occurs between the ZnS VBM and ZnO CBM. The type-II transition is a preferred absorption mode under both blue and green illumination. No significant Fermi level shift exists in ZnO and ZnS because of weak absorption under low illumination densities, whereas the net charge transfer between ZnO and ZnS is suppressed due to the barrier created for hole injection from ZnO to ZnS, and interface trap states for electron transport generated from downward bending of ZnO. The appearance of hole and electron trap state barriers ($\Delta\Phi_1$ and $\Delta\Phi_2$) are unfavorable for photosensing devices and can be tuned through the inner piezopotential to improve charge transport.

When nanowires are compressed under zigzag top electrode, each individual nanowire may undergo one of the three possible (Figure S4 (Supporting Information)) elastic deformation modes, resulting in a piezopotential distribution in ZnO core of ZnO/ZnS core/shell nanowire array. In view of slight off the vertical axis oriented growth of ZnO nanowires on ITO and high length/diameter (aspect) ratio (Figure 1a),
it is reasonable to believe that under externally applied load majority of the nanowires experienced shear deformation, as shown in Figure S4a (Supporting Information) for a single nanowire, that dominates the electrical transport properties of the device. However, the existence of either uniaxial compression (Figure S4b (Supporting Information)) or bending only (Figure S4c (Supporting Information)) mode of elastic deformation in few nanowires cannot be completely ruled out. In the absence of piezoelectric effect in zinc blend structured ZnS, the localized negative polarization charges appearing in ZnO at the ZnO–ZnS interface bends the edges of valence (VB) and conduction bands (CB) of ZnO to higher energy (Figure 6d). It should be noted that in each outlined deformation mode (Figure S4a–c (Supporting Information)), the band position at ZnO–ZnS interface changes in similar manner provided we consider the negative polarization charges at the interface. This upward bending of bands of ZnO due to the presence of negative piezoelectric charges eliminates the pre-existing barrier ΔΨp that is not favorable for the separation of electrons resulting in a quick separation of holes and electrons in ZnS and ZnO, respectively (Figure 6d), in addition to una...
device as a photodetector under (2) blue and (3) green illumination source, respectively. (4) Simulated cross-sectional piezopotential distribution under three different strain modes in an individual core/shell nanowire. (5) Photograph of a ZnO/ ZnS core/shell nanowire array device. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b02081.

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REFERENCES AND NOTES


