Broadband (UV to NIR) Photodetector Fabricated in n-ZnO/p-Si NWs Core-Shell Arrays with Ligand-Free Plasmonic Au Nanoparticles

Chandan Samanta¹, Sekhar Bhattacharya², A. K. Raychaudhuri³, and Barnali Ghosh^{1*}

¹*Department of Condensed Matter Physics and Material Sciences, S. N. Bose National Centre for Basic Sciences, Salt Lake, Block-JD, Sector-III, Kolkata 700106, India*

²*Core Laboratories, King Abadullah University of Science and Technology, Saudi Arabia*

³*CSIR- Central Glass and Ceramic Research Institute, Raja S C Mullick Road, Kolkata 700 032*

*Corresponding author's email: barnali@bose.res.in

ABSTRACT

We report a high response optical detector based on n-ZnO/p-Si NWs core-shell arrays decorated with plasmonic Au nanoparticles (NPs), that works in the broad frequency range from UV (300 nm) to NIR (1100 nm) and consumes low power (few μW). The optical detector combines the visible and NIR detectability of Si NWs with the UV detectivity of ZnO through the core-shell structure and broad band detectivity in the visible range has been achieved by decorating core-shell arrays with ligand-free Au NPs synthesized by using pulsed laser ablation in liquid. The photo-detector uses n-ZnO as the active photoconductive channel that is sensitive in UV region. However, using photo-gating as well as favourable band alignments the carriers generated at longer wavelengths in visible and NIR in Au NPs and Si NWs arrays were introduced into the conduction band of ZnO leading to its broad band performance. We observed significant enhancement of responsivity R not only in visible range but also in UV and NIR region with a high detectivity of 10^{11} ($\text{cmHz}^{1/2}\text{W}^{-1}$). The responsivity of the detector ~ 1 A/W from 700nm to longer wavelength (at bias of 1V) and in the visible region the responsivity of the photo detector with Au NPs is > 0.5 A/W and increases to > 1 A/W at UV region.

INTRODUCTION

Development of broadband optical detectors with low power consumption is a topic of considerable current interest due to its wide impact on various application needs like sensing of low level optical radiation, secure communication, portable electronic equipment, and many other fields.^{1,2} In addition to low power consumption, the focus on development of an optical -detector sensor working in a broad spectral range is attractive proposition as that would avoid use of multiple detectors to cover the same range. Most of the conventional photodetectors that are widely used are based on p-n junctions using elemental (Si and Ge) or binary (GaAs) and ternary (InGaAs) semiconductors. Each of these detectors have a spectral range depending on fundamental band gap of the semiconductor being used which for most of lie in NIR region. They show peak responsivity at wavelengths shorter than but close to their band edge and the responsivity is < 0.7 A/W, barring InGaAs where higher responsivity has been reported.³ In these semiconductors where the band edge is in NIR, the responsivity of device falls precipitously in UV/Visible region due to various optical losses such as reflection, thermal effects, incomplete absorption and recombination of photo induced carriers.

Among the photoconductivity based detectors, ZnO is useful in UV range while CdSe and PbS can be used in visible and NIR range.⁴⁻⁶ Most of ZnO based optoelectronic devices are either photoconductive detectors in thin film transistor (TFT) configuration or they are heterojunction between n-type ZnO and p-type semiconductor materials. The most common choice is p-type silicon due to its distinct advantages, such as abundance, stability, and ease of processing. Recently nanostructured materials such as heterostructure and core-shell structure based devices have shown greater advantages for improving the photon capture and collection of photo generated charge carriers. There is report of n-ZnO/p-Si NWs core shell heterostructure type photodetector working in UV to visible region with a maximum responsivity of 0.98 A/W at a bias voltage of 5 V.⁷ A core - shell heterostructure n-ZnO/n⁺-Si NWs has been reported for NIR region with a maximum zero biased responsivity of 0.54 A/W.⁸ These photo-detectors though easy to fabricate has the main drawback that they show response in specific wavelength region either in ultraviolet (UV) /visible (Vis) or NIR region.

The photoconductive detectors like TFT are mostly based on planar metal-semiconductor-metal (MSM) configuration. In this configuration, the active material surface being exposed, it allows innovative ways to induct carriers in the active channel in addition to those created by photo-excitation on illumination. A report of ZnO based photodetector shows a large enhancement of responsivity in UV region by synergy of illumination and gate voltage,⁹ where the charge has been induced through an electric double layer gate dielectric. In this case the detector has enhanced sensitivity but the spectral range of response has not been widened.

An example of utilizing the surface oxide and band bending as an active agent of inhibiting carrier recombination has been done for single Ge NW based broad band (300-1100 nm) photodetector where a peak responsivity of 10^7 A/W at a low power consumption has been achieved.^{10,11} Broad band high responsivity in single Si NW and Si NWs array based detectors have been achieved using similar concepts.^{12,13} These single NW detectors can function as self-biased (zero applied bias) detectors with high responsivity of the order of 10^4 A/W with Si NW¹² and 10^5 A/W with Ge NW.¹⁴ In spite of ultra-high responsivity over a broad spectral range and extremely low power dissipation, these detectors suffer from the disadvantage that the fabrication process is lithography intensive and needs availability of nano-lithography facilities.

Example of photo-gating to circumvent the limitation of spectral range of response arising from the band-gap of the channel material has been demonstrated through use of plasmonic metal nanoparticles (NPs). In this case the photoconductive channel is not the only place where carrier generation occurs by illumination. Use of plasmonic metal NPs of aluminium (Al), silver (Ag), nickel (Ni), platinum (Pt) and gold (Au) etc can enhance response in visible region by plasmonic excitation and charge transfer to the active photoconductive channel.¹⁵⁻²⁰ Localized surface plasmon resonance (SPR) mediated by Al NPs has been employed to enhance the UV response of the ZnO nanorod arrays with a maximum responsivity of 1.59 A/W at a bias of 5 V.¹⁵ Another observation shows the improvement of UV response of ZnO nanotubes by resonant coupling of anchored plasmonic Ag NPs.¹⁶ One report shows the raising of UV photoresponse of plasmonic Ni NPs decorated ZnO nanorod arrays with a maximum responsivity of 0.124 A/W at a bias of 1 V.¹⁷ Pt NPs Surface plasmon enhanced responsivity of ZnO based sandwich structure in UV region has also been reported.¹⁸ There is a report of ligand-free surface plasmon resonance of Au NPs implemented to improve the visible response of ZnO nanowires arrays with a maximum responsivity of 0.4 A/W in UV region at a bias of 1 V.¹⁹ The decoration of Au NPs on ZnO NWs arrays with a maximum responsivity of 1.9 A/W in UV region at bias of 5 V has also been reported but seen decrease in responsivity due to Au NPs from bare ZnO NWs arrays.²⁰ These reports have been summarized for comparison in Table II later in the paper.

In this paper we develop further the concept of using photo-gating to circumvent the band width limitation by using photo generated carrier infusion in the conduction band of the photoconductive channel n-ZnO using a tandem effect where Visible-NIR range the carriers are generated in Si NWs and in Visible as well as in UV carriers are generated in Au NPs. Favorable band alignments enable both the materials to transfer there photogenerated carriers (electrons) to the conduction band of n-ZnO. This leads to a substantially flat photo-response of 1 A/W in the wavelength range 650nm to 1100nm and somewhat reduced response in the range down to 375 nm (but the responsivity minima > 0.5 A/W) and enhanced response reaching 2 A/W in the UV. The high responsivity is reached at a low applied bias of 1V with total power consumption ≤ 3 μ W, thus making them operable with batteries for very long periods (e.g, Li batteries with 3200 mAh rating). The schematic of the device photo-response and

the response of the underlying component parts are shown in Figure 1 which in a nutshell explains the ideas utilized in this paper.

Figure 1. Schematic of Variation of spectral responsivities of individual components (ZnO, Si NWs and Au NPs) and that of the Au NPs decorated core-shell arrays.

The transfer of photo generated carriers from p-Si NWs array into n-ZnO were done using a core-shell structure where the n-ZnO shell that makes the photoconductive channel and surrounds the shell of p type Si NWs arrays. This core-shell structure then is decorated by ligand-free Au NPs made using pulsed laser ablation in liquid (PLAL) method in aqueous medium. This structure may be contrasted with n-ZnO/p-Si NWs heterostructure p-n junctions used before.^{7,8}

In addition to good responsivity over an extended wavelength range and no sizeable droop in sensitivity at wavelengths in visible range and shorter wavelength (unlike Si and Ge detectors), extremely low power consumption, the detector has the added advantage of ease of fabrication that is compatible with standard semiconductor and TFT processing routes.

EXPERIMENTAL METHODS

Fabrication of the Optical device

The device has been fabricated around a base of vertically aligned Si nanowires (Si NWs) on a p-type silicon wafer. The vertically aligned silicon nanowires (Si NWs) were synthesised by using metal assisted chemical etching process reported previously.²¹ A schematic diagram of overall fabrication processes of Au NPs-ZnO/p-Si NWs core shell structure is shown in Figure 2. A thin layer of Zinc oxide (ZnO) of thickness ~ 50 nm is deposited on the prefabricated p-Si NWs arrays by thermal atomic layer deposition (ALD) at a temperature of 200 °C by using Diethyl zinc (DEZ) and H₂O as precursors. Four steps of an ALD cycle were: DEZ pulse of 50 milliseconds, purge with Ar for 5 sec, H₂O pulse of 1 sec and purge with Ar 8 sec. The deposition rate was about 1.6 Å /cycle. The ALD deposition is

done in a way that there is a core-shell structure with p-Si NW as core and ZnO as shell with a top layer of ZnO that forms the channel in the device. After that plasmonic gold nanoparticles (Au NPs) prepared by pulsed laser ablation in liquid (PLAL) method were deposited on the core-shell structure. For PLAL, a KrF excimer laser of wavelength (λ) 248 nm was focused on a pure Au metal target immersed in DI water at room temperature and was pulsed with repetition rate of 5 Hz with an energy fluence $\sim 2 \text{ J/cm}^2$. The PLAL process is distinctly different from chemical attachments through ligands; it gives a ligand-free growth of Au NPs. The presence of ligands between ZnO and Au NPs inhibits charge transfer. Since the photoresponse of the device as discussed later on depends on the efficiency of the charge transfer, a ligand-free attachment is preferred.¹⁹ The overall synthesis processes of different growth method are depicted schematically in Figure 2. Details of PLAL are given in reference.¹⁹

Figure 2. A schematic diagram of fabrication process of Au NPs-ZnO/p-Si NWs core shell heterostructure arrays. The process starts from a p-type wafer thickness 0.45 mm.

Characterizations

The Au NPs-ZnO/p-Si NWs core shell array was characterised by X-ray diffraction (XRD). Morphology and chemical composition were characterised by field emission scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). The nanostructured complete device has been also characterised by high resolution transmission electron microscopy (HRTEM) as well as energy dispersive X-ray spectroscopy (TEM-EDS). Cross-sectional TEM (XTEM) sample was prepared by conventional method using Gatan PIPS precision ion-polishing system to obtain electron transparency in the sample. The XTEM studies, as explained later on (see supporting information), show the physical structure of the device.

Opto-electronics measurements

The absorption spectra of Au NPs-ZnO/p-Si NWs was recorded with an integrating sphere at diffuse reflection mode for solid sample in an UV-Visible spectrophotometer in the wavelength range of 300-900 nm.

For photo conductivity measurement two Cr/Au contact-pads were deposited by thermal evaporation on the n-ZnO top layer of the Au NPs-ZnO/p-Si NWs core shell heterostructure through a hard mask, The resulting detector (in MSM configuration) has a channel length of 1.5mm and width of 1mm.

The optical response was measured with a Xenon lamp and a monochromator working in the wavelength (λ) range 300nm to 1100nm. A schematic of the experimental set-up is given in Figure 3. The power density of the incident light was calibrated in the wavelength range up to 1100 nm using a Si detector with calibration traceable to National Institute of Standards and Technology (NIST). The optical responses, such as device current vs. wavelength ($I - \lambda$) and the current-voltage ($I - V$) characteristics in dark as well as under illumination of different power intensity at different fixed wavelengths, were measured using a Source meter with a current resolution of 10 pA. From the observed data following opto-electronic parameters have been obtained: (a) The photocurrent (PC) defined as $I_{PC} \equiv I - I_d$, where I is the total device current under illumination and I_d is the dark current. I_{PC} and I_d depend on the bias V where as I_{PC} also depend on the illumination power P (Watt) falling on illumination area A of the device and its wavelength (λ). P is obtained from the illumination intensity $\mathfrak{S}$ (in Watt/cm²) measured with the Si standard photo diode, so that $P = \mathfrak{S} \times A$, (b) The current gain $G \equiv \left(\frac{I_{PC}}{e}\right) \left(\frac{h\nu}{P}\right)$, the first term in bracket is the charge generated per unit time and $\left(\frac{P}{h\nu}\right)$ being the number of photons of wavelength λ absorbed by the device per unit time. The absorbed power is less than the power falling on the device, P is an upper limit of light absorbed and thus G is a lower limit of the value, (c) The responsivity $R \equiv \frac{I_{PC}}{P}$ in units of A/Watt, and (d) the specific detectivity (D^*) arising from shot noise is defined as $D^* = \frac{R}{(2eJ_d)^{1/2}}$ where J_d is dark current density, and D^* has a unit of cm.Hz^{1/2}W⁻¹.

Figure 3. A schematic of photoresponse measurement set up.

RESULTS AND DISCUSSION

Electron Microscopy of the Physical Structure of the Device:

The cross-sectional view of the device in Figure 4(a) and (b) shows the scanning transmission electron microscopy high angle annular dark field (STEM-HAADF) image in different magnifications. A cross sectional SEM image of Au NPs decorated ZnO/p-Si NWs core shell arrays is shown in Figure 4(c) that shows the top ZnO layer and the core-shell structure of the vertically aligned ZnO/p-Si NWs arrays. The figure also shows the ligand-free Au nanoparticles (Au NPs) that decorate the ZnO. The high resolution TEM (HRTEM) image in Figure 4(d) shows the presence of Au NPs on the ZnO of the ZnO/p-Si NWs array. The average diameters of the Au NPs are ~ 10 nm. The lattice spacing of Au NP is ~ 0.24 nm for (111) planes and there is cross-linked fringes of ZnO/p-Si NWs with Au NPs interface. Inset of Figure 4(d) shows the selected area electron diffraction (SAED) pattern of nano crystalline ZnO/p-Si NWs heterostructure arrays decorated with Au NPs.

Figure 4. (a) and (b) STEM-HAADF image of Au NPs decorated on ZnO/p-Si NWs arrays in different magnifications (c) Cross sectional SEM image of Au NPs decorated ZnO/p-Si NWs core shell arrays (d) HRTEM image ZnO/p-Si NWs decorated with Au NPs. Inset (upper left) is the SAED pattern and lower right is HRTEM image of Au NPs.

The crystalline structure as well as phase formation and phase purity of the sample is identified through X-ray diffraction (XRD) (given in supporting information of Figure S1). The physical structure of photo detector is characterised by the cross sectional TEM (XTEM) along with elemental analysis (EDS) (given in supporting information of Figure S2 and S3). The STEM-EDS mapping for the Au M shell, Zn L shell, O K shell and Si K shell are given in supporting information of Figure S3 (a) - (d) respectively. STEM-EDS mapping on a portion of Au NPs decorated ZnO/p-Si NWs arrays (marked by orange box in figure S2 (a)) shows a conformal layer of ZnO through the Si NWs arrays and Au M shell mapping shows that concentrations of Au NPs are fairly uniform and homogeneous throughout the surface of the ZnO/p-Si NWs arrays.

Optical absorption α of the Au NPs decorated ZnO/p-Si NWs core-shell arrays:

The optical response of a photo-detector depends on the light being absorbed. Thus a broad band detector should have a broad band absorption. The optical absorptions (α) of the n-ZnO/p-Si NWs core-shell arrays (with and without Au NPs) are shown in Figure 5 in the wavelength range of 300nm-900 nm. Over the whole range α for the Au NPs decorated sample is much larger than that of the bare n-ZnO/p-Si NW array and the enhancement of α is largest in the visible range of the spectrum (400nm-700nm) with a prominent peak at $\lambda = 510$ nm (high lighted). This excess visible absorption of Au NPs decorated device is due to the Au NPs plasmon resonance which can be confirmed by direct comparison of the absorption of bare Au NPs in colloidal suspension (inset of Figure 5) which are also synthesised by pulse laser ablation in liquid (PLAL) method. (Note: The absorption of Au NPs extends over an extended range of measurement. In addition to the peak at 510 nm due to plasmon resonance, there is absorption in Au NPs for $\lambda \leq 650$ nm due to transition from d band to hybridized sp orbitals that extends to shorter wavelengths to UV. It can be seen from the Figure 5, that the absorption of bare n-ZnO/Si NWs (without Au NPs) has a dependence on the wavelength illumination that has characteristics of both the components namely Si NW and ZnO. In the shorter wavelength side, there is a strong absorption edge nearly at 375 nm. This can be seen for both the samples. This strong absorption edge corresponds the band gap absorption of ZnO which is established by different researchers.²² At longer wavelengths in the region 400 nm and up, the absorption is dominated by the Si NW. The Si NW like bulk Si absorbs at all wavelength $\lambda < \lambda_{edge}$, where λ_{edge} corresponds to the band edge. For Si NW arrays the absorption increases at shorter wavelength as in bulk Si due to primary absorption process leading to electron-hole creation.^{23,24} In NW array the absorption is more due to reduction in reflectivity. We also see the rise in absorption in Si NW at shorter wavelength through measurements as shown in Figure 5. There is a small broad maximum in absorption at 450 nm in NW array.²⁴ This small broad maximum exists in both bulk and film at 510 nm. The small hump seen by us in the absorption spectra of n-ZnO/Si NWs as shown in Figure 5, arises from this. It has been shown that this is due to additional

absorption process like inter-band Auger effect and emission of phonons directly connected with the generation of additional electron-hole pairs.²⁵

Figure 5. Absorption spectra of ZnO/p-Si NWs core-shell array and Au decorated core shell arrays. Inset is the absorption Au NPs alone synthesised by PLAL method.

Broadband photo-response of Au NPs decorated n-ZnO/p-Si NWs core shell arrays

In Figure 6 (a) we show a snap shot of response of the photo-detector (photocurrent I_{PC} vs. t) when it is illuminated by lights of different wavelengths for a fixed power (P) $\approx 1.5 \mu W$. The data have been taken at a bias of 1V. The data were taken with illumination ON and OFF. From the figure it is shown that with decoration of Au NPs, I_{PC} of n-ZnO/p-Si NWs core -shell device is enhanced considerably over the whole spectral range. The dark current being low ($\sim 10^{-6}$ A) the power dissipation even at 1V is $< 2 \mu W$. In Figure 6(b) shows the photo-current I_{PC} at selected wavelengths for the bare device and that with Au NPs. In the right hand scale in the same graph show the gain (G) as obtained from the data. The enhancement of G on addition of the Au NPs (marked as ΔG) for all wavelength region can be observed. However, the photo current gain (G) is comparatively higher in visible region than that in NIR region of the Au NPs decorated photo-detector. This data establishes the broad claim of the paper that Au NPs decoration of the n-ZnO/p-Si core-shell array leads to significant enhancement of the photo-response.

Figure 6. (a) Photo-current (I_{PC}) under different illumination of light of wavelength ranging from 400-1100 nm at a fixed power of $1.5 \mu W$. The illumination was turned ON and OFF. (b) Plot of I_{PC} at different wavelengths for the n-ZnO/p-Si core-shell array with and without Au NPs. The right hand scale shows the change in gain (ΔG) on decoration by ligand-free Au NPs.

Figure 7 (a) shows the spectral responsivity R of n-ZnO/p-Si NWs core shell array with and without Au NPs at a bias voltage of 1 V measured at illumination power $P = 1.5 \mu W$. Compared with bare n-ZnO/p-Si NWs core-shell array the responsivity of Au decorated core-shell array is enhanced significantly not only in visible range but also in UV and NIR regions. Presence of the Au NPs thus makes the detector broad band with substantial R over the whole frequency range. Data in Figure 7 (a) shows that at bias 1V the average value of $R \sim 1 A/W$ for the wavelength range 700 nm-1100 nm. It decreases to below $1 A/W$ and in the visible range and shows minima of $R \approx 0.5 A/W$ for $\lambda \approx 450 nm$. The contribution of the plasmonic Au NPs can be best appreciated in this range. In the bare array without the Au NPs, R drops rapidly in the visible range of the spectrum and goes down even as low as $10^{-2} A/W$ as compared to $0.5 A/W$ for the Au NPs decorated detector. In UV region ($\lambda \leq 375 nm$) $R \sim 2 A/W$ for Au NPs decorated photo-detector. It is noted that this performance is much improved over a typical Si detector available commercially. The comparison Table SI is given in supporting information. Responsivity (R) is function of measurement bias and increases as the bias V increases and is also dependent on the illumination power P and it decreases as P is increased. The dependence of R on these two parameters for bare n-ZnO/p-Si NWs and Au NPs decorated n-ZnO/p-Si NWs core shell arrays are shown in the contour plot in Figure 7(b) and (c) respectively. It can be seen for Figure 7(c) that at a small bias of 1V and up-to $3 \mu W$ illumination power it is possible to get a $R \geq 1 A/W$.

Figure 7. (a) Spectral responsivity (R) of ZnO/p-Si NWs core shell arrays with Au NPs and without Au NPs under different wavelength. Contour plot of responsivity R as a function of bias V and illumination power P of (b) n-ZnO/p-Si NWs (c) Au NPs decorated n-ZnO/p-Si NWs core shell arrays.

Thin film and heterostructures based photo-detectors have a wide dynamic range where the photocurrent I_{PC} has dependence on the incident power P which is generally expressed by the relation $I_{PC} \propto P^\beta$, where typically the power exponent $\beta < 1$. The value β depends on the existence of localized traps near the band edges that controls the process of recombination and the energy distribution of the localized states near the conduction band edge.²⁶ Since the responsivity $R = \frac{I_{PC}}{P}$, variation of R with incident power P is given by the relation $R \propto P^{-(1-\beta)}$. β being < 1 , R decreases as the incident power P on the device increases. This is shown in the contour plot of Figure 7 (b) and (c) as well as in Figure 8 (a) and (b). Figure 8 (a) shows the P dependence of value of responsivity R for illumination with light of $\lambda = 500$ nm for without and with Au NPs decorated devices and Figure 8(b) shows the corresponding data for illumination at $\lambda = 900$ nm. For $\lambda = 500$ nm $\beta \approx 0.78$ - 0.90 for the devices and are significantly higher than those seen at $\lambda = 900$ nm where $\beta \approx 0.66$ - 0.70 . In general, β depends on the distribution of trap states around the Fermi Level E_F and band edges. For a more uniform distribution $\rightarrow 1$. Since β does not change much when Au NPs is added to the device, these traps that control this exponent, are likely to lie within ZnO shell or Si NW core or at their interface. β being smaller at longer

wavelength (900nm) , where the excitation and carrier generation by illumination is controlled by Si NW, it is expected that there are non-uniform trap distribution within Si NW. Small value of β has been seen in Si single NW photo-detectors before where the Si NW had been grown by same method.¹²

Figure 8. (a) Variation of responsivity with incident power before and after Au NPs decoration on ZnO/p-Si NWs for $\lambda = 500$ nm and (b) $\lambda = 900$ nm of wavelength. Values of exponent β are shown in inset boxes.

The sensitivity of the photodetector and the limit of detection sensitivity are important factors which are often measured and parameterized by the spectral dependence of the specific detectivity, $D^*(\lambda) = \frac{R(\lambda)}{(2eJ_d)^{1/2}}$. Briefly, one can find the minimum power that can be detected by a photodetector, from the observed value of responsivity and the detectivity. For a detection band width of 1.66 Hz (integration time ~ 0.3 s) the observed value of $R \sim 1$ A/W at 900 nm, for Au NPs decorated ZnO/p-Si NWs can detect $\approx 1.5 \times 10^{-12}$ W. The value of detectivity limits ($D^*(\lambda)$) for the wavelength of 500 nm and 900 nm at the bias voltage of 1 V of the n-ZnO/p-Si NWs core shell arrays without and with Au NPs are tabulated in Table I.

Table I: The details of devices characteristics value measured at wavelength of 500 nm and 900 nm at 1 V bias

Devices (n-ZnO/p-Si NWs)	Responsivity (R) at 1 V bias (A/W)		Detectivity (D^*) at 1 V bias ($\text{cmHz}^{1/2}\text{W}^{-1}$)	
	$\lambda = 500$ nm	$\lambda = 900$ nm	$\lambda = 500$ nm	$\lambda = 900$ nm
W/O Au NPs	0.14	0.75	$\sim 5 \times 10^9$	$\sim 6 \times 10^{10}$
With Au NPs	0.55	1.0	$\sim 3 \times 10^{10}$	$\sim 2 \times 10^{11}$

The detectivity of ZnO/p-Si NWs with Au NPs is found to be higher as compared to that for the bare ZnO/p-Si NWs arrays. We have tested six devices for bare ZnO/p-Si NWs and six for Au NPs decorated

ZnO/p-Si NWs devices which shows excellent reproducibility in broadband (UV-visible-NIR) region and deviation of responsivity (R) in photodetectors is less than $\pm 5\%$.

We have monitored the photoresponse of the devices at an interval of 30 days for a period of six months. The data are shown in Figure S4 (given in supporting information). The decrease in responsivity of photodetector is $< 10\%$ over a period of 180 days which shows good stability and a good self-life of detectors. A comparison of the devices in our work with others reported photodetectors have been summarized in Table II. As seen in Table II the performance of the device reported in the present investigation can be seen to be comparable or even better than the performances of devices reported in literatures.

Table-II: Comparison of present photodetector characteristics value with previous reported values in literatures.

Photodetectors	Wavelength range	Power dissipation	Bias voltage	Peak Responsivity (R)	Ref.
ZnO/p-Si NWs	300 – 1100 nm	1.5 μ W	1 V	1.4 A/W	Present work
Au NPs- ZnO/p-Si NWs	300 – 1100 nm	2.8 μ W	1 V	2 A/W	Present work
n-ZnO/p-Si NWs	325 – 660 nm	> 100 mW	5 V	0.98 A/W	7
n-ZnO/n+-Si NWs	400-1100 nm	-	0 V	0.54 A/W	8
Al NPs- ZnO NRs	300 – 400 nm	150 μ W	5 V	1.59 A/W	15
Ag NPs- ZnO NTs	320 – 400 nm	400 μ W	2 V	-	16
Ni NPs-ZnO NRs	325 nm	210 μ W	1 V	0.124 A/W	17
ZnO/Pt NPs/ZnO	220 – 400 nm	-	60 V	0.4 A/W	18
Au NPs- ZnO NWs	350 – 625 nm	1 μ W	1 V	0.4 A/W	19
Au NPs- ZnO NWs	300 – 600 nm	-	5 V	1.9 A/W	20

Absorption and Responsivity: Role of plasmonic Au NPs

Decoration of the bare core-shell array by Au NPs enhances the absorption α and also enhances the responsivity R . To establish a direct connection between α and R due to the Au NPs decoration we plot in Figure 9, the excess absorption $\Delta\alpha_{NP}$ due to the Au NPs, obtained by subtracting out the absorption of the bare device from that of the Au NPs decorated device (see Figure 5), and the excess responsivity ΔR_{NP} obtained by subtracting out R of the bare device from that of the Au NPs decorated device (see Figure 7 a). The large enhancement of the responsivity occurs for $\lambda \leq 550$ nm, when the absorption gets enhanced and is dominated by the surface plasmon resonance of the Au-NPs. There is also enhancement of R when the wavelength is in the UV region due to tandem effect of ZnO fundamental edge absorption along with the enhanced absorption due to Au NPs (see inset of Figure 5).

Figure 9. Variation of enhanced responsivity (ΔR_{NP}) with the enhanced absorption ($\Delta\alpha_{NP}$) of n- ZnO/p-Si NWs due to decoration of Au NPs.

Photo- gating effects in the Au NPs decorated device:

The device presented in this paper is innovated around an n-ZnO photoconductive channel which shows response for wavelengths shorter than its fundamental absorption edge of ZnO at $\sim 375\text{nm}$. The core-shell structure with Si NW array as the core and Au NPs decoration, led to the broad band response of the optical device extending from UV to NIR region. In a photo-conductive type detector, which has a metal-semiconductor-metal (MSM) structure, the response is generally controlled by electron-hole pair generation in the active channel and thus its fundamental absorption edge will determine the longest wavelength of response. In a gated photo-detector, carriers are introduced into the channel by induction through the gate when a voltage is applied.⁹ In photo-gating the carrier are introduced through “gate” materials that can be photoexcited and can introduce the photoexcited carriers into the channel without any gate bias being applied. This ensures that the response of the detector will not be limited by the fundamental absorption edge of the channel and it will be enabled for response in other wavelength regions as well that will be decided by the opto-electronic properties of these “gate” materials that are being excited by illumination introduce carriers into the channel. In the specific context of this paper the n-ZnO channel receives photo-excited carriers from the core of Si NWs as well as AuNPs when they are illuminated. This is illustrated through a schematic in Figure 10. In the wavelength range 1100 nm to 450 nm the illumination creates electron-hole pair in p-Si and the electrons transfer to n-ZnO from p-Si which increases the conductivity in ZnO. In the wavelength range 600nm to 400nm additional electrons come from Au NPs which are excited by plasmonic excitation. For wavelength $< 400\text{ nm}$ it is usual ZnO photoconductivity.

Figure 10. A schematic illustration of photo-gated device where the n-ZnO channel receives carriers from the core of Si NWs as well as Au NPs when they are illuminated.

Proposed model for charge transfer:

Enhanced photo-response is based on transfer of photo excited carriers from Si NW and Au NPs to the n-ZnO. The transfers of carriers are proposed to be explained on the basis a model shown schematically in Figure 11. The model shows the band alignments. The electron affinities of ZnO (χ_{ZnO}) and Si (χ_{Si}) are taken as 4.35 and 4.05 eV, respectively.²⁷ While the band-gaps of ZnO and Si are taken as 3.3 and 1.12 eV, respectively. The band-gap discontinuity at conduction band and valence band is therefore equal to $\Delta E_c = \chi_{\text{ZnO}} - \chi_{\text{Si}} = 0.3 \text{ eV}$ and $\Delta E_v = E_{g\text{ZnO}} - E_{g\text{Si}} + \Delta E_c = 1.88 \text{ eV}$. At the n-ZnO and p-Si interface, which is an interface of a p-type and an n-type material, the conduction and valence bands in the p-type material bend- down and those in n-type material bend-up. This allows transfer of electrons from the conduction band of p-type Si NW to the conduction band of n-ZnO and transfer of holes from valence band of ZnO to valence band of Si without application of any bias. The electron-hole pairs are generated with the UV and visible-NIR absorption of ZnO and Si NWs respectively. The band bending at the interface leads to an effective carrier separation mechanism and leads to accumulation of electrons in the conduction band on ZnO. This leads to enhancement of photoconduction of ZnO. Additional carriers (electrons) in the conduction band of ZnO that is needed for the enhanced photo-response in the visible range come from the plasmonic Au NPs. The enhancement of the absorption due to the Au NPs arises from two mechanisms: (i) the surface plasmon resonance in the visible centered around $\lambda \approx 510 - 530 \text{ nm}$ depending on NPs particle size and shape and (ii) the inter- band transition in Au (d band $\rightarrow$ sp band) that starts in the visible at $\lambda \approx 650 \text{ nm}$ and extends to shorter wavelength. These two absorption mechanisms have over lapping wavelength regime leading to strong absorption in the visible starting from 650nm peaking at the SPR wavelength

and extending to UV region as shown in inset of Figure 5. Due to both the mechanisms the conduction band of Au NP gets populated when illuminated. Since the conduction band (CB) minimum in ZnO has lower energy than the excited electrons in the *sp*-band of Au (in the conduction band) these excited electrons get transferred to conduction band of Au without any applied bias. This charge generation process needs no intermediary chemical bonds for charge transfer of electron to semiconductor from Au NPs and which can work without any functionalization of semiconductor. There are recent suggestions²⁸ that due to plasmonic excitation one can have direct transfer of electrons to conduction band of ZnO leaving a hole in Au NP. Both the charge transfer mechanisms lead to large photo-current in ZnO particularly in the visible range.

Figure 11. Schematic of energy band diagram of ZnO/p-Si NWs decorated with Au NPs.

CONCLUSIONS

To summarize, a high the performance n-ZnO/p-Si NWs core-shell array decorated with ligand-free plasmonic Au NPs has been developed. The photo-detector works at low bias of 1V and consumes power $< 3 \mu\text{m}$. The device uses n-ZnO as the active photoconductive channel that is sensitive in UV region. However, using photo-gating as well as favourable band alignments the carriers generated at longer wavelengths in visible and NIR in Au NPs and Si NWs array were introduced into the conduction band of ZnO leading to its broad band performance. The optical detector combines the visible and NIR detectability of Si NW with the UV detectivity of ZnO through the core-shell structure and broad band detectivity to bridge the gap in the visible was achieved by decorating with ligand-free Au NPs that contributes enhanced absorption and carrier generation at wavelength range $< 650 \text{ nm}$. The ligand-free decoration of Au NPs was done by using pulsed laser ablation in liquid (water) method. We observed significant enhancement of responsivity R not only in visible range but also in UV and NIR region. The responsivity of the detector $\sim 1 \text{ A/W}$ from 700nm to longer wavelength (at bias of 1V) and in the visible region the responsivity of the photo detector with Au NPs is $> 0.5 \text{ A/W}$ and increases to $> 1 \text{ A/W}$ at UV region.

ASSOCIATED CONTENT

Supporting Information

XRD of Au NPs decorated ZnO/p-Si NWs core shell heterostructure, STEM-HAADF image, elemental compositions and STEM-EDS mapping of the device, Comparison of device characteristics value with commercial Si photodetector.

AUTHOR INFORMATION

Corresponding Author

*E-mail: barnali@bose.res.in

Notes

The authors declare no conflicts of interest.

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TOC Graphic

Schematic of Variation of spectral responsivities of individual components (ZnO, Si NWs and Au NPs) and that of the Au NPs decorated core-shell arrays.

A schematic diagram of fabrication process of Au NPs-ZnO/p-Si NWs core shell heterostructure arrays. The process starts from a p-type wafer thickness 0.45 mm.

176x111mm (150 x 150 DPI)

A schematic of photoresponse measurement set up.

151x70mm (96 x 96 DPI)

STEM-HAADF image of Au NPs decorated on ZnO/p-Si NWs arrays

157x137mm (150 x 150 DPI)

STEM-HAADF image of Au NPs decorated on ZnO/p-Si NWs arrays

171x161mm (150 x 150 DPI)

Cross sectional SEM image of Au NPs decorated ZnO/p-Si NWs core shell arrays

180x166mm (150 x 150 DPI)

HRTEM image ZnO/p-Si NWs decorated with Au NPs. Inset (upper left) is the SAED pattern and lower right is HRTEM image of Au NPs.

180x180mm (150 x 150 DPI)

Absorption spectra of ZnO/p-Si NWs core-shell array and Au decorated core shell arrays. Inset is the absorption Au NPs alone synthesised by PLAL method.

239x181mm (150 x 150 DPI)

Photo-current (I_{PC}) under different illumination of light of wavelength ranging from 400-1100 nm at a fixed power of 1.5 μ W. The illumination was turned ON and OFF.

Plot of I_{PC} at different wavelengths for the n-ZnO/p-Si core-shell array with and without Au NPs. The right hand scale shows the change in gain (ΔG) on decoration by ligand-free Au NPs.

237x162mm (150 x 150 DPI)

Spectral responsivity (R) of ZnO/p-Si NWs core shell arrays with Au NPs and without Au NPs under different wavelength.

Contour plot of responsivity R as a function of bias V and illumination power P of n-ZnO/p-Si NWs

Contour plot of responsivity R as a function of bias V and illumination power P of Au NPs decorated n-ZnO/p-Si NWs core shell arrays.

Variation of responsivity with incident power before and after Au NPs decoration on ZnO/p-Si NWs for $\lambda = 500$ nm of wavelength. Values of exponent β are shown in inset boxes.

Variation of responsivity with incident power before and after Au NPs decoration on ZnO/p-Si NWs for $\lambda = 900$ nm of wavelength. Values of exponent β are shown in inset boxes.

Variation of enhanced responsivity (ΔR_{NP}) with the enhanced absorption ($\Delta \alpha_{NP}$) of n- ZnO/p-Si NWs due to decoration of Au NPs.

A schematic illustration of photo-gated device where the n-ZnO channel receives carriers from the core of Si NWs as well as Au NPs when they are illuminated.

75x82mm (150 x 150 DPI)

Schematic of energy band diagram of ZnO/p-Si NWs decorated with Au NPs.

243x114mm (150 x 150 DPI)