High Performance Nanoplasmonic UV/VIS/NIR Photodetector Fabricated in Ambient Condition

Debika Banerjee

École de Technologie Supérieure

Ivy Asuo

Institut National de la Recherche Scientifique

Francois-Xavier Fortier

École de Technologie Supérieure

Alain Pignolet

Institut National de la Recherche Scientifique

Sylvain Cloutier (✉ SylvainG.Cloutier@etsmtl.ca)

École de Technologie Supérieure

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Abstract

Surface plasmon based techniques are widely used to promote the exciton generation and light absorption in solar cells and photodetectors. In this work, a feasible approach for UV-VIS-NIR photodetection using plasmon induced silicon nanowires (SiNWs) and amorphous TiO_2 heterostructure is presented. The photodetector shows excellent photoresponse up to 3.5 orders of magnitude enhancement with a rise/decay time constants of 0.75/0.5 μs . Under small bias (1V), the photodetector exhibits very high responsivity up to 49 A/W at 532 nm irradiation over a broadband wavelength range from 300–1100 nm. These figures of merits represent the excellent performance over the reported heterojunction based photodetectors. Our finding offers new opportunities to engineer plasmon-based nanostructures in different fields like chemical sensors, optoelectronics and nanophotonics applications.

Introduction

Nanoplasmonics is the resonant interaction of light with metal nanoparticles, has gained lots of attention thanks to its unique capability of light manipulation in the sub-wavelength regions^{1,2}. It has unprecedented optical properties and a huge range of applications starting with the early work of Michael Faraday on gold nanocolloids³ to the cutting edge device applications such as nanoscale lasing, optical and photonics devices, biomedical imaging, energy storage and so on^{4–7}. Till now, several chemical and physical techniques are used to synthesize the plasmonic nanoparticles such as seed induced nucleation, ion exchange methods, galvanic displacement methods etc^{8–10}. Seed mediated nucleation relies on the degree of the lattice matching between different components which are challenging to achieve. Galvanic displacement employs all solution based chemical redox reaction where metallic nanoparticles reduced and deposited and the substrate gets oxidized. This technique offers precise control over the nanostructures length, diameter and other important parameters^{10–12}.

Silicon nanowires (SiNWs) have gained lots of attention since past two decades due to its fascinating chemical and physical properties^{13–15}. The confluence of the confinement of one dimensional nanostructure with the plasmonic effect of metallic nanoparticles makes the best use of the SiNWs in sub wavelength regions. The surface functionalization of SiNWs using Ag nanoparticles enhances the UV-NIR absorption through the nanoplasmonic effect, collecting and transporting the photo excited electrons to the electrodes^{16,17}.

Crystalline TiO_2 gained much attention for its metal-oxide-semiconductor nature since decades. The large band gap of TiO_2 makes it a suitable material for UV detection^{18–20}. The amorphous phase of TiO_2 has not been explored as extensively before, despite of having similar electronic properties as the crystalline phase²¹. In our previous studies, we have optimized similar behavior from amorphous TiO_2 based photodetectors in an energy efficient manner which is comparable to anatase TiO_2 based devices^{22,23}. Making a heterojunction with amorphous TiO_2 in conjunction with plasmonic SiNWs extends its detection ability in a broadband wavelength range from UV to NIR.

A novel broadband photodetector architecture using plasmon sensitized SiNWs / amorphous TiO₂ heterostructure has been presented in this manuscript. The geometry of the SiNWs enhances with the Ag nanoparticles which further increase the UV and NIR absorption through the nanoplasmonic effect. Plasmonic nanoparticles have unprecedented optical properties which further enhance the performance of the photodetector for various applications such as sensing, detection, night vision, and spectroscopy and so on.

Results And Discussions

Plasmon sensitized SiNWs are fabricated using galvanic displacement method (GDM). The details of the synthesis process are described in the materials and method section. Figure 1a shows the surface morphology of the as synthesized plasmon sensitized SiNWs. The 45° tilted cross-sectional SEM images are depicted in the Fig. 1b and 1c. Commercially available amorphous TiO₂ sol-gel are spin coated on top of the plasmon sensitized SiNWs. The surface and 45° tilted cross-sectional SEM images of the heterojunction are depicted in the Fig. 1d and 1e respectively.

The plasmonic nanowires structure on Si substrate contributes in generating more electron hole pairs (EHPs) by trapping more of the incident light. As suggested by the literature^{2,24,25}, the nanoplasmonic SiNWs have increased scattering cross-section and optical path length which further helps in light harvesting and light trapping. As a result, these nanoplasmonic SiNWs produces more EHPs. The UV/VIS/NIR spectroscopic plot in Fig. 2 reveals the enhanced near UV and NIR absorption of the nanoplasmonic SiNWs to benefit the creation of EHPs.

Aiming at increasing optical absorption in nanoplasmonic SiNWs, the volumetric proportion of Ag nanoparticles are controlled by the cleaning process after GDM. The big dendrite layer of Ag are removed using dilute HNO₃ leaving the minute amounts of Ag nanoparticles on the top and the sidewalls of the SiNWs. The reduced reflection of the nanoplasmonic SiNWs after removing the dendrite layers can be attributed to the increased absorption due to a strong interaction between the free electrons in the Ag nanoparticles and the incident electromagnetic radiation. However, the nanoplasmonic SiNWs with the dendrite layers (before cleaning) results in increased reflection (shown in the figure S2 in the supplementary information section) as the larger density of Ag leads to the percolation effect²⁶, hence acquiring a strong metallic character that inhibits refraction into the layer. In addition to the reflection spectrum of SiNWs, it is evident that the addition of nanoplasmonic Ag results a remarkable reduction of the reflection. This behavior can be ascribed to the higher imaginary value of the refractive index that further contributes to the increased optical absorption by the Ag nanoparticles. Moreover, the maxima and minima values of reflectance are getting shifted due to the changes of the complex nature of the effective refractive index in the spectrum. This effect can be attributed to GDM which deposits Ag nanoparticles and creates pores as well.

The schematic of the photodetector device has been illustrated in Fig. 3a. The photoresponse properties of the photodetector are systematically investigated by probing the current vs. voltage characteristic

under dark and 1.5 G illumination as shown in Fig. 3b. It clearly shows that the current of the device increases significantly up to 3.5 orders upon illumination with A.M. 1.5 G incident light.

Due to having a wide bandgap of around 3.2 eV, TiO₂ produces photo generated carriers under UV illumination. Similarly, the nanoplasmonic SiNWs produced photo generated carriers under near UV + VIS + NIR illuminations thanks to the plasmonic effect and relatively narrow band gap of Si. Surface plasmons can trigger plasmonic hot carriers with higher energy than those induced by direct excitations. SiNWs have a wider band gap than bulk Si because of the nanostructure. Since the Fermi level of the SiNWs is higher than the Si substrate, electrons will flow from SiNWs to Si and a depletion region will be formed in SiNWs region. The band diagram of the photodetector device is shown in Fig. 4. Hence the photodetector is capable of detecting UV + VIS + NIR range of wavelengths.

The transient photoresponse behavior of the photodetector device is analyzed as demonstrated in the Fig. 5a and 5b. The rise and decay time measured from the photodetector device are found to be 0.75 μs and 0.5 μs respectively which indicates the fast response behavior from the nanoplasmonic photodetector devices. The small rise/decay time assures rapid detection for several applications like portable equipment, biomedical or optical communications.

To complete the evaluation of the nanoplasmonic photodetector devices, the external quantum efficiency, responsivity and detectivity of the devices are probed using 1V external bias. Figure 6a shows the high EQE in a broadband wavelength range from 300–1100 nm. The peak value of the EQE reaches up to 85% at 475 nm. Another crucial parameter is the spectral responsivity which determines the spectral behavior of the photodetectors. The spectral responsivity is characterized by the method described in the materials

and method section and used the formula: $D^* = R(A)^{1/2} / (2eI_d)^{1/2}$ to calculate the detectivity (where A denotes the active area (0.021 cm²) of the device, R is the responsivity, I_d is the dark current, and e is the elementary charge). Figure 6b illustrates the spectral responsivity and detectivity of the nanoplasmonic photodetector device from 300–1100 wavelength range under 1 V external bias. The peak responsivity reaches up to 11 A/W in the near UV region, and 34 A/W and 49 A/W in the VIS and NIR region respectively. The detectivity of these photodetector devices reaches up to 6.84 E¹¹ Jones, 2.16 E¹² Jones and 3.11 E¹² Jones in the near UV, VIS and NIR regions respectively. Simply adding these minute amounts of Ag nanoparticles extends the photodetection from UV-VIS region to UV-VIS-NIR region as compared to the pristine SiNWs/ amorphous TiO₂ devices as shown in our previous report²². Hence, the superior performance of the photodetector as compared to our previous report²² can be attributed to the nanoplasmonic effect. The peak values of responsivity, EQE and detectivity at different wavelengths are illustrated in the Table 1.

Table 1
EQE, responsivity and detectivity values at different wavelengths
(near UV, VIS, NIR).

Wavelength (nm)	EQE (%)	R (A/W)	D* (Jones)
350	38.18	10.78	6.84 E ¹¹
500	84.29	34.04	2.16 E ¹²
1000	50.35	40.65	2.58 E ¹²
Maximum/peak values	85.88	49.16	3.11 E ¹²
	at 475 nm	at 930 nm	at 930 nm

Figure 7 illustrates the histogram of the peak values of the responsivities of 5 photodetector devices. In the near UV region, the photodetector devices demonstrates peak responsivities between 10–11 A/W, in the VIS region, the responsivities lies between 32–34 A/W, while in the NIR region the peak values of the responsivity lies in the range of 46–49 A/W. The histogram discloses good reproducibility and superior performances for all the photodetector devices.

Conclusion

To conclude, we have experimentally illustrates improved UV/VIS/NIR photodetection from chemically synthesized nanoplasmonic heterostructure. Peak performances reach 49 A/W, 85% EQE and 0.75/0.5 μ s rise/decay time at 532 nm. Moreover, these, devices allow operation over a broad spectrum with performances exceeding 10 A/W and 30% EQE from 300 nm to 1100 nm. The superior detectivity can be helpful in the detection of weak optical signals. These all-solution-based syntheses of nanoplasmonic heterostructures have the potential to reduce the cost of future nanoengineered devices.

Materials And Methods

Fabrication procedure

Plasmon sensitized SiNWs are fabricated by employing all solution based GDM. Details of the GDM have been described elsewhere^{27,28}. For this study, we have used low doped n type Si wafer with the resistivity of 1–10 ohm-cm. The etchant solution contains 0.02M silver nitrate (AgNO₃) solution and 4.6M hydrogen fluoride (HF) solution mixed in 1:1 ratio. The Si substrates have cleaved into 1 cm² pieces and cleaned using ultra sonication with acetone and IPA for 15 minutes each. Then the Si pieces have rinsed with deionized (DI) water and dried using nitrogen (N₂) flow. The cleaned samples are transferred immediately into the etching bath at room temperature for 40 minutes. After the etching, vertically aligned SiNWs have been formed covered with Ag dendrites layers. These Ag dendrites layers are removed using diluted nitric acid (HNO₃) solution (1:5 of 70% HNO₃ and DI water) for 30 minutes at room temperature. Vertically aligned SiNWs with Ag nanoparticles on the sidewalls of the nanowires are found after the cleaning. Pure

SiNWs have found without any Ag contamination when the cleaning has been done using concentrated (70%) HNO₃ at room temperature for 1 hour. Hence, the post cleaning protocol after the fabrication of the nanowires plays the key role to achieve plasmon sensitized SiNWs. These nanowires vary from 800-1000nm in length and 40–50 nm in diameter. The etching takes place in the laboratory environment with 40% humidity and 30 °C of room temperature. Then, a thin film layer (~120 nm) of amorphous TiO₂ sol-gel purchased from Solaronix is deposited using spin-coating technique to form the heterojunction. Finally, 50µm channels of gold pads are evaporated atop the heterojunction photodetector.

Materials and device characterizations

The morphology of nanoplasmonic SiNWs and TiO₂ thin films are probed using a Hitachi SU30 scanning electron microscope (SEM). X-ray powder diffraction (XRD) measurements are carried out using a Bruker AXS D8 Advance X-ray diffractometer. The reflectance measurements are performed using Perkin Elmer LAMBDA 750 UV/VIS system. A Keithley 2400 source measuring unit (SMU) equipped with a Newport solar simulator is used to characterize the current-voltage behavior of the photodetector device. The transient behavior of the photoresponse is characterized with a 532 nm laser-chopper and Agilent DSO-X 3034 A oscilloscope via a 1 GΩ load resistance. The spectral measurement for the photocurrent from the detector is probed using a TRIAX320 monochromator equipped with a lock-in amplifier and a chopper.

Declarations

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ADDITIONAL INFORMATION

The authors declare no competing interests.

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Figures

Figure 1

(a) Surface (b), and (c) 450 tilted SEM images of the plasmon induced SiNWs, (c) and (d) Surface and (e) 450 tilted SEM images of the plasmon induced SiNWs/amorphous TiO₂ heterojunction.

Figure 2

Optical reflectance of SiNWs arrays and nanoplasmonic SiNWs arrays.

Figure 3

(a) Device architecture and (b) Current vs. voltage characteristics of the plasmon induced SiNWs/amorphous TiO₂ heterojunction photodetector.

Figure 4

Band diagram of the nanoplasmonic photodetector device.

Figure 5

(a) and (b) Transient photoresponse of the plasmon induced SiNWs/amorphous TiO₂ heterojunction.

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Figure 6

(a) EQE and (b) Responsivity and detectivity plot of the plasmon induced SiNWs/amorphous TiO₂ heterojunction.

Figure 7

Histogram of the responsivity in the UV, VIS and NIR region for 5 photodetectors.

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