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Self-powered High Responsivity UV Detector based on Porous GaN/silver Nanoparticle Composite

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Abstract

Photodetectors with Ag NPs/porous GaN composite structure were prepared by using $NaNO_3$ solution as etching solution and porous GaN material prepared at 20 V voltage as substrate, and silver nanoparticles (Ag NPs) were deposited on the surface of it by electrochemical method. Based on the principle of localised surface equipartition excitations to improve the performance of the UV photodetector, the responsivity reaches 14.3 A/W, which is 18 times higher than that of the porous GaN device. At zero bias, the detector shows a low dark current of 2.21×10^{-11} A, and the device has a fast response with a rise time of 0.3 s and a fall time of 0.5 s. The photodetector has a high response with a rise time of 0.3 s and a fall time of 0.5 s.

Keywords

Porous Gallium Nitride; Localized Surface Plasma Excitations; Ultraviolet Detectors.

1. Introduction

Ultraviolet photodetector (UV PD) is an optoelectronic device that converts ultraviolet light signals into electrical signals, which is commonly used in optical fibre communications, image sensors, ozone sensing, radiation leakage detection, missile detection, astronomical research, and remote control, etc. [1-3]. Although PDs based on the first and second generation semiconductors are relatively mature and commercially available in some fields, they still require expensive external filters for ultraviolet detection, so many scholars have focused on the research of wide-band semiconductors. Since the third-generation semiconductor materials such as diamond, ZnO, SiC, etc. have significant drawbacks in terms of technology cost, doping, and light absorption, GaN, which has a direct bandgap and high chemical stability, has become the preferred material for the preparation of UV PDs.

In order to improve the performance of GaN UV photodetectors, reduce the defect density, and lower the stress caused by lattice mismatch, GaN with nanopillars[4], nanoflowers[5], and porous structures[6] have been fabricated.Among them, one of the materials that are considered as highly promising for UV photodetector preparation is the porous GaN, which possesses a high surface-area-to-volume ratio and excellent optical properties. It shows great potential in optoelectronic devices due to its large surface ratio, high electron mobility, strong light collection, easy preparation and low cost. Under light illumination, the high-density surface states of the pore sidewalls can trap carriers and prolong the carrier lifetime. Therefore, the detector with porous structure can obtain large responsivity [7].

Although porous-structured GaN UV detectors already have excellent detection performance, large surface ratios due to the trap effect reduce the response speed of the detectors. Currently, the slow response speed of GaN-based PDs severely limits their application in communications and other high-

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speed systems. The above single-semiconductor-based photoconductive UV photodetectors suffer from high dark current, slow response speed, and single-band detection.

In order to achieve improved light detection, metal nanoparticles with Localised Surface Plasmon Resonance (LSPR) effect are used to enhance light absorption and thus increase the production of photoinduced charge carriers. Enhancing the performance of optoelectronic devices by injecting metal nanoparticles has received much attention in applications such as solar cells, LEDs and UV PDs.

The localised surface plasma (LSP) enhancement effect can be achieved by applying incident light to metal free electrons, which induces collective oscillations between electrons and photons. If the frequency of the collective oscillations is similar to that of the excitation light wave, resonance occurs, the extinction efficiency of the metal nanostructures increases, and the local electromagnetic field is greatly enhanced [8]. This phenomenon has been used to improve the responsivity of GaN UV detectors with commonly used metals such as Ag, Au, and Al. The use of plasma is an effective way to achieve both high sensitivity and high speed in photodetectors due to the localised surface plasmon resonance (LSPR) effect that induces strong light trapping and efficient carrier transport processes at the metal/semiconductor interface.

2. Experiment

2.1 Preparation of Porous GaN/Ag NPs Composites

The GaN films were cut into 1 cm×0.5 cm size, and the cut films were sequentially cleaned by ultrasonic cleaning in 0.5 mol/L sulfuric acid, deionised water, acetone and ethanol for 10 min, and then blown dry with nitrogen. The samples were wet etched using photoelectrochemical method. The etchant used in the etching process was 0.3 mol/L $NaNO_3$ solution, the applied voltage was 20 V, and the etching process was irradiated with a UV lamp.

In the electrodeposition work, 0.01 mol/L $AgNO_3$ solution was used as the plating solution, sodium citrate was added as buffer, and the reagent ratio of $NaNO_3$ as catalytic solution to $AgNO_3$ ionisation properties was 5:1. Before electroplating, the etched porous GaN was pre-immersed in $AgNO_3$ solution for ultrasonic vibration. The samples were rinsed with ethanol and dried and preserved in a vacuum bag after 4 min of electrodeposition using 8 V. The samples after 4 min of electrodeposition appeared yellowish brown.

2.2 Device Preparation

The prepared films were placed into a Zeiss Crossbeam electron beam/ion beam dual beam electron microscope, and two Pt electrodes of 100 μm × 100 μm in size were deposited on their surfaces, with a spacing of 50 μm between the two electrodes. Figure 1 shows a schematic diagram of the device structure.

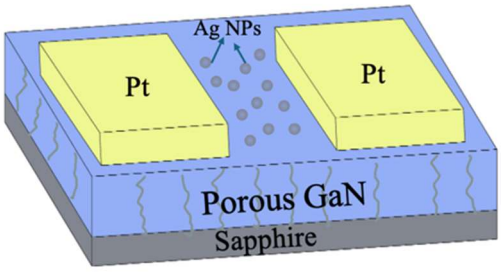


Figure 1. Device Structure Schematic

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3. Results and Discussion

3.1 Characterisation of Porous GaN/Ag NPs Composite Structures

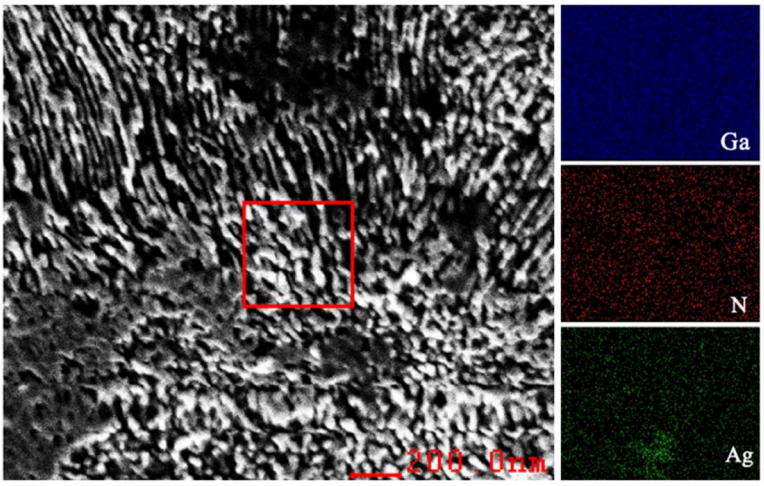


Figure 2. SEM secondary electron image of porous GaN/Ag NPs electrodeposited at 8 V for 4 min (SEM accelerating voltage 10 kV)

Figure 2 shows the SEM secondary electron image of porous GaN/Ag NPs deposited by electrodeposition technique in 4 min under 8 V voltage condition. From the image, it can be clearly observed that many Ag NPs are attached to the branches of the porous GaN structure.These nanoparticles are not uniformly distributed in the porous structure of GaN, especially in the centre of the pores formed by etching, where the number of Ag nanoparticles is more concentrated.

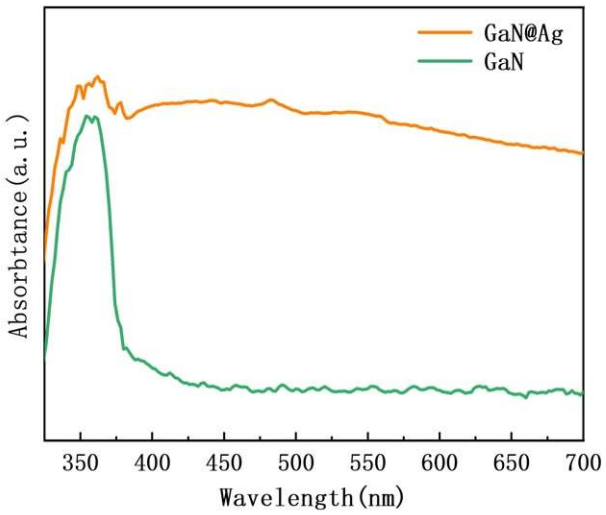


Figure 3. UV absorption spectra of Ag NPs composite porous GaN samples

Figure 3 shows the UV absorption spectra of porous GaN and Ag NPs composite porous GaN measured by UV-visible spectrophotometer, both materials have a significant cut-off wavelength around 375 nm due to band-edge absorption of GaN.The absorption peaks of Ag particles are usually located in the range of 400-500 nm, and the appearance of absorption peaks around 458 nm in the spectra of the silver-plated samples confirms the Ag NPs formation and that they have been successfully compounded on the surface of porous GaN.

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3.2 I-V Characteristic Curve of Porous GaN/Ag NPs UV Detectors

Figure 4 shows the I-V characteristic curve of the porous GaN device at -5 V to 5 V. The photocurrent generation of the device is not obvious under the light condition, and the lowest dark current is 2.21×10^{-9} A. The device responsivity is calculated from the responsivity formula to be 0.8 A/W at a bias voltage of -5 V. The reason for the larger dark current of the porous device at the positive bias voltage may be due to the fact that the porous structure forms additional electronic traps (interfacial states) at the grain boundaries of the material or pore walls form additional electron traps (interface states). These interfacial states can be activated in the absence of external light, promoting carrier generation and complexation, thus increasing the dark current.

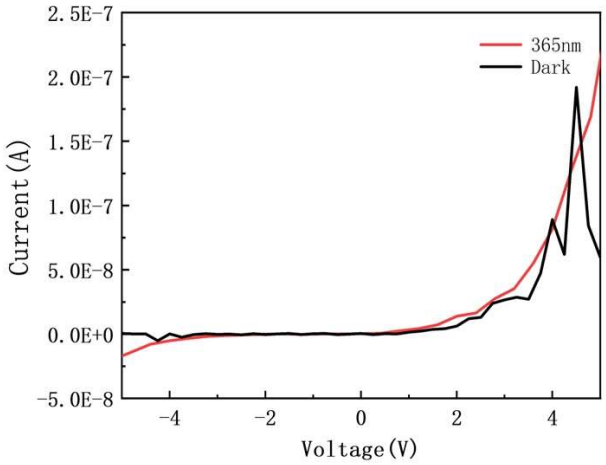


Figure 4. I-V curves of porous GaN photodetectors under light and dark conditions

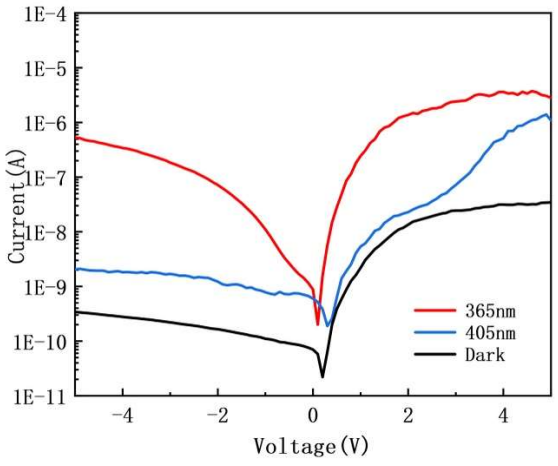


Figure 5. I-V logarithmic curves of Ag NPs composite porous GaN photodetectors

Figure 5 shows the I-V characteristic curves of the Ag NPs composite porous GaN device for 365 nm and 405 nm illumination at voltages ranging from -5 V to 5 V. The detector has a large photoelectric response to 365 nm UV light, which corresponds to the cutoff wavelength of the GaN material. The detector also has a photoelectric response to illumination at wavelengths greater than 365 nm because defects within the semiconductor shorten the energy band gap, thereby increasing the cutoff wavelength.

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The results from the dark-state I-V test in Figure 5 shows that the lowest dark current of the Ag NPs composite porous GaN device is 2.21×10^{-11} A, which is a two-order-of-magnitude decrease in dark current compared with the porous GaN device.The Ag NPs composite device exhibits an asymmetry under forward and reverse bias, which is typical of the Schottky barrier-induced rectification effect [10]. The dark current can be effectively suppressed within 5×10^{-10} A when negative bias is applied, and the current increase is significantly accelerated when switching to positive bias. The dark current of the device under -5 V/5 V bias is 3.4×10^{-10} A/3.45×10^{-9} A, respectively, and the rectification ratio is 101.5. The test results of I-V under 365 nm illumination (500 μW/cm^2) are basically consistent with the change rule of dark-state I-V. When a positive bias of 5 V is applied to the device, the photocurrent of the device is 2.8×10^{-6} A. When a negative bias is applied to the device, the photocurrent is 2.8×10^{-6} A. When a negative bias is applied to the device, the photocurrent of the device is 2.8×10^{-6} A. When negative bias is applied to the device, the photocurrent increases slowly with the increase of the bias voltage (the absolute value of the bias voltage, regardless of positive and negative), and when the bias voltage reaches -5 V, the photocurrent is 5.3×10^{-7} A. At this time, the ratio of the photocurrent to the dark current can reach 1.56×10^{3}, and the high ratio of the photocurrent to the dark current indicates that the device has a smaller noise. When the UV light at 405 nm (500 μW/cm^2) is switched on, the maximum photocurrent can reach 1.39×10^{-6} A. In principle, there should be no dark current when the device is operated at 0 V. However, due to the influence of the test equipment and other circuit noises, a certain amount of dark current will be measured in the actual test even at 0 V. The device can be operated at 0 V with a high ratio of photocurrent to dark current, which indicates that the device has more noise.

3.3 Responsivity and Detectivity of Porous GaN/Ag NPs UV Detectors

The responsivity (R) of a photodetector is defined as follows:

$$R = \frac{I_{photo} - I_{dark}}{P_{light} * S} \quad (1)$$

I_{photo} denotes the photocurrent, I_{dark} denotes the dark current, P_{light} denotes the incident optical power, and S is the effective surface area of the detector. For photoconductive devices, the photogenerated electron-hole pairs generated in the region between the two electrodes are capable of producing photoconductive effects, so S is taken to be the entire area between the electrodes.

In addition to the responsiveness of its detection ability is also very important, the detection rate as a characterisation of the detector's ability to detect the smallest optical signals, usually denoted by the symbol D *, according to the detection rate calculation formula:

$$D^* = R * \sqrt{\frac{A}{2qI_{dark}}} \quad (2)$$

where A is the effective light area and q is 1.6×10^{-19} C [9].

The device responsivity and detectivity values were calculated from the I-V curve data and the R and D* equations, as shown in Figure 6(a)(b). Between 0 V and 5 V, the maximum value of the responsivity under 365 nm illumination is 14.3 A/W, which is 18 times the responsivity of the porous GaN device, and the detectivity is 3.2×10^{12} Jones; the maximum value under 405 nm illumination is 4.3 A/W, and the detectivity is 9.15×10^{11} Jones. between 1 V and 5 V, the responsivity under 365 nm increases from 0.96 A/W to 11.1 A/W. The significant increase in responsivity indicates that the device has a large photoconductivity gain. In practice, changes in responsivity with external variable conditions may lead to detection bias, which manifests itself as a slight non-linear behaviour of the increment, which can be further improved by linearising the response curve by optimising materials, optimising the device fabrication process, or adding an external correction mechanism [11].

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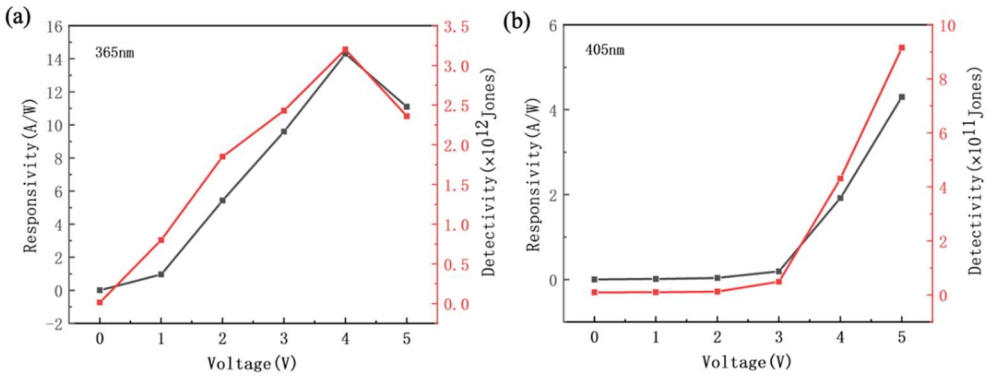


Figure 6. (a) Responsivity, detectivity versus voltage plot of Ag NPs composite device under 365 nm illumination (b) Responsivity, specific detectivity versus voltage plot of Ag NPs composite device under 405 nm illumination

3.4 Comparative Analysis of transient Light Response Characteristics

The time-dependent sequences of photocurrent generation of the device under periodic illumination of 365 nm and 405 nm with different intensities and zero external bias voltage are given in Figure 7 and 8 In each irradiation cycle, the UV lamp is turned on and off for 20 s. With zero bias voltage, the device shows a significant photocurrent when the UV light is turned on, and the device exhibits self-supply performance. The positive and negative currents in the figure represent the direction through the device.

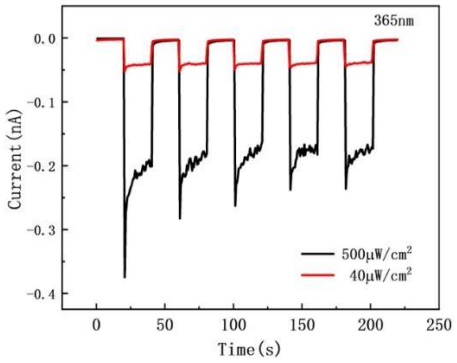


Figure 7. I-t curves of Ag NPs composite porous GaN UV detectors at 365 nm, zero bias

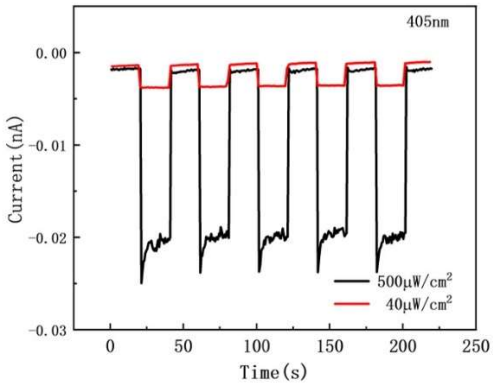


Figure 8. I-t curves of Ag NPs composite porous GaN UV detectors at 405 nm, zero bias

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Figure 7 shows the I-t curves at different light intensities for 365 nm light. When switching on or off the UV light at 365 nm wavelength (500 μW/cm^2), the photocurrent of the device increases rapidly followed by a rapid increase in the current when stabilising at around 0.2 nA, which indicates a rapid generation of photogenerated carriers; and the current decreases rapidly when the light is switched off, which indicates that carrier complexation is also fast. This fast on/off response indicates that the device has good photoresponsiveness and recovery. The fluctuations in current generation could be due to the instability of the light source in the experimental setup or noise in the circuit.

Figure 8 shows the I-t curves at different light intensities for 405 nm illumination, which shows similar behaviour but with lower current levels than at 365 nm illumination, reaching a maximum current of 0.02 nA, suggesting that the device is more sensitive to ultraviolet light in the UVA band.

Figure 7 and 8 show the photocurrent response under two different intensities of UV light irradiation, the device shows higher photocurrent when the optical power density is higher, the response of the device is related to the light intensity, this is because higher light intensity produces more photogenerated carriers and therefore induces a higher photocurrent. This phenomenon reflects the sensitivity of Ag NPs composite porous GaN UV detectors to different light intensities, a property that can be used to measure light intensity variations and maintain a highly sensitive detection capability in different environments. The lower on/off ratio (i.e., the ratio of photocurrent to dark current) at an optical power density of 40 μW/cm^2 under light irradiation of the same wavelength indicates a degradation of the device performance at low light intensities.

The photocurrent rapidly rises to a maximum value, then rapidly decreases and stabilises, resulting in a sharp peak within the curve. During the photocurrent process, the Ag NPs are able to resonate with the wavelength of the incident light, and the oscillation frequency of their electrons matches that of the incident light. This resonance effect significantly enhances the local electromagnetic field, which in turn couples effectively with the surrounding porous GaN structure, leading to a sharp rise in current. At the same time, the porous GaN structure itself significantly enhances the trapping of the incident light, which contributes to the transient accumulation of a large number of nonequilibrium carriers under light conditions. Some of the non-equilibrium carriers are driven by the internal electric field to separate to the sides of the electrodes before compounding again, and the sample photocurrent starts to decrease, eventually forming a stable photocurrent.

3.5 Working Principle

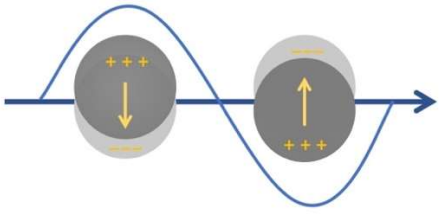


Figure 9. Schematic of localized surface plasmon resonance (LSPR) induced on the metal NPs by incident light

The composite of Ag NPs with GaN firstly generates SPR, where the surface of metallic nanostructures induces the surface plasmon resonance effect when excited by excitation light. The surface plasma is a collective oscillation mode with an electric field strength several orders of magnitude larger than the normal electric field strength. This helps to increase the separation efficiency of the photogenerated carriers and reduces their complexation, thus increasing the effective photovoltaic response.

Furthermore, Ag NPs are able to locally enhance the absorption of UV light due to the localised surface plasmon resonance (LSPR) effect. In porous GaN, this means that more UV light can be

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absorbed, which in turn generates more photogenerated carriers and increases the photocurrent, thus improving the sensitivity and efficiency of UV detection.

4. Conclusion

The LSPR of plasmonic NPs can significantly improve the photoresponse of the photodetectors. Photodetectors with Ag NPs/porous GaN composite structure were prepared by using $NaNO_3$ solution as etching solution and porous GaN material prepared at 20 V voltage as substrate, and Ag NPs were deposited on its surface by electrochemical method. The responsivity of the UV photodetector is improved to 14.3 A/W based on the principle of localised surface equipartition excitations and triggered fast hot carrier injection, which is 18 times higher than the responsivity of the porous GaN device. At zero bias, the detector shows a low dark current of 2.21×10^{-11} A, and the device has a fast response with a rise time of 0.3 s and a fall time of 0.5 s. The photodetector has a fast response with a rise time of 0.3 s and a fall time of 0.5 s.

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