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Role of conductive nitrogen incorporated diamond nanowires for enhancing the UV detection and field emission properties of ZnO nanotubes

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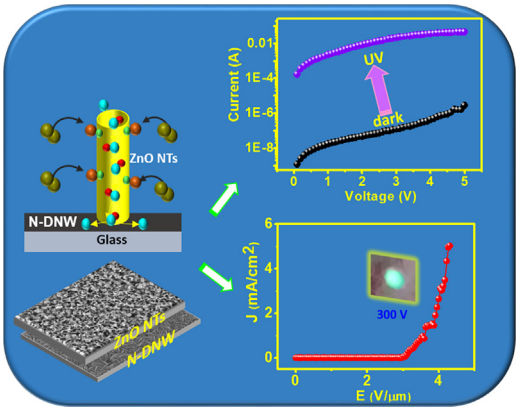
HIGHLIGHTS

- Weak stability of ZnO nanotubes (ZNTs) requires a suitable combination.
- Diamond nanowires (DNW) could be afford high adsorptivity and robustness to ZNTs.
- The integration of DNW enhanced the UV detection and Field emission properties of ZNTs.
- The interface of ZNTs/DNW n-N junction has been confirmed to play a vital role.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we focus on the preparation of a nanocarbon and ZnO based hybrid with the incorporation of nitrogen to form diamond nanowires (N-DNW) and ZnO nanotubes (ZNTs) using simple routes. The potential of the carbon enriched hybrid material for application as UV photodetectors (PDs) or electron field emitters (EFE) is evaluated. Firstly, the ZNT/N-DNW based UV PDs with their multifinger anode cathode configuration offer a high photoresponse ratio of 1930, which is superior to that of bare ZnO PDs (12.6). The obtained photoresponse values also have greatly enhanced stability and photoresponsivity of 49.2 AW^{-1} compared with the ZNRs (0.4 AW^{-1}). In addition, EFE study of the ZNT/N-DNW hybrid device reveals an electron emission at voltage as low as 2.59 V/μm with a high current density of 5.2 mA/cm^2. This striking improvement in the multifunctional measurements of the annealed ZNT/N-DNW - based device can be attributed to its fast adsorptivity and oxygen vacancies. Moreover, the respective band model of this hybrid structure was also proposed to demonstrate its heterostructure. Furthermore, the outstanding feature of this combination are its cost-effective synthesis routes, reliability, and long-term stability, which makes it a potential applicant for multifunctional opto-electronic devices.

1. Introduction

UV photodetectors (PDs) have gained extensive attention in multiple areas for industrial, military, ecological and biological applications

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[1–5]. UV radiation has increased day by day as a consequence of the depletion of the polar *stratospheric* ozone layer. Such UV radiation is very dangerous to human beings and can cause many diseases such as skin cancer, aging effects, and skin disorders. Hence UV PDs are desirable to detect the level of UV radiation which can affect the human body. Furthermore, UV PDs have also been recognized as valuable in environmental security detectors, UV multi-functional emitters, UV photovoltaic cells, gas detection, and UV bio-imaging [6–12]. The electron field emitters (EFE) also have many remarkable applications such as in vacuum amplifiers, field emission X-ray sources, electron microscopes, marketable display panels, and bioelectronics and space applications [13–16]. Numerous researchers are keen to develop a new generation of materials to improve the properties of the existing EFE materials (CNT, Mo and graphene) [17,18]. The solution to these issues requires the incorporation of multi-task materials within a single device for production for commercial markets. Fascinatingly, wide band gap semiconductor materials have shown the desired photodetecting and field emitting properties with improved response [9–12].

For this purpose, ZnO is a low cost and reliable material that has a wide bandgap of 3.37 eV with exciton binding energies, which can be used for multifunctional device applications such as field emitters, logic circuits, solar cells, sensors, and photodetectors [4,19–21]. In particular, the ZnO nanotube (ZNT) has the effective properties of a porous structure with well etched areas and a large surface-to-volume ratio, due to the formation of a large number of defects and vacancies, especially when compared to ZnO nanowires and films [22–24]. However, the stability of ZNT for various applications remains a challenge to overcome, requiring the formation of a heterostructure or surface doping. Of these two options, the formation of a heterostructure has appreciable advantages for both PD and EFE applications because surface doping cannot effectively transport electrons [25–33].

It has been found that nanohybrid combinations of ZnO and carbon materials have exhibited stable responses for certain applications. Relevant examples are ZnO/diamond [24], ZnO/CNT [34], ZnO/SWCNT [35], ZnO/graphene [36] and ZnO/rGO [37]. Among them, diamond-based devices exhibit reliable performance with high robustness, low turn-on voltages, and long life time stability [38]. As is well-known, diamond has fascinating properties such as a wide bandgap, negative electron affinity surface, good thermal conductivity, chemical inertness, and a high degree of hardness. The ultra-nanocrystalline diamond films (UNCD) especially have many attractive properties, and sp^3 bonded ultrananosized grains that give high reliability accompanied with multifunctional properties [39]. The incorporation of N_2 with the CH_4 plasma treatment produces electrically active needle structured ultradiamond nanowires that possess low resistivity and enriched electrical conductivity [40]. The addition of nitrogen stimulates the formation of sp^2 bonds and conducting nanocarbon materials in diamond films, which helps to increase the number of charged electrons and O_2 residuals. The N-DNW films generate the electron travel pathways that result in considerable improvement of the charge carriers, and they have already been used in several applications [41].

In this context, it is envisioned that ZNT and N-DNW would be a good combination for the formation of integrated devices on a single chip. The inner and outer sites of well-etched ZNT can efficiently transport electrons from the N-DNW heterojunctions, which can afford long-term stability. Hitherto, no effort has been devoted to the use of this combination for the fabrication of high performance UV photodetectors and field emitters. Thus, in this study, nanohybrid ZNT/N-N-DNW-based materials were designed and fabricated with multifinger electrodes for UV photodetectors and field emitters. The devices were found to possess excellent photoresponsivity and lower field emission threshold voltage. Systematic observations revealed the as-fabricated ZNTs/N-DNW to be a promising material that can overcome the deficiencies of the existing UV photodetector and field emitter materials.

2. Experimental method

The N-DNW films were synthesized using microwave plasma enhanced chemical vapor deposition (MPE-CVD-IPLAS, CYRANNUS) on glass substrates with high proportions of nitrogen (N_2). To facilitate the nucleation process, the glass substrates were subjected to ultrasonication for 1 h in a methanol solution consisting of diamond (0.05 g) and titanium (0.05 g) powders. After ultrasonication, the substrates were cleaned well and loaded into the MPE-CVD system. The N-DNW films were grown with gas ratios (H_2:CH_4: Ar and N_2 = 5: 15: 45 and 150 sccm) for 20 min at a power of 1200 W with a pressure of 60 Torr. To obtain the needle-like morphology, the as-prepared samples were plasma post-treated in a H_2 (100 sccm) atmosphere for 5 min. The combinations of ZNR/N-DNW and ZNT/N-DNW were acquired by the deposition of ZNRs and ZNTs on diamond coated glass substrates using a simple hydrothermal method. Initially, a ZnO seed layer was prepared using spin coating, and then the above samples were annealed under the ambient temperature and pressure along with N_2 for 30 min.

The Au interdigitated anode/cathode multifinger electrodes were fabricated on the N-DNW substrates by photolithography and sputtering methods. The interdigitated anode/cathode electrodes contained ten fingers 100-μm in length and 15-μm wide with gaps about 5 μm wide between the fingers. Then the lift-off process was carried out to etch the ZnO seed layer in which the place has no interdigitated Au electrodes as shown in the supplementary material (scheme S1). The integrated multifinger electrodes significantly enhanced the UV response performance of the PD. The ZNRs and ZNTs were synthesized hydrothermally by immersion in a pre-modified solution of zinc acetate (ZnAc, Zn $(CH_3COO_2)\cdot 2H_2O$) and hexamethylenetetramine (HMT, $C_6H_{12}N_4$) with a 35 millimolar (mM) concentration at 90 °C for 3 h. The ZNTs were acquired by leaving the above sample in the same solution for 2 to 6 h at 50 °C. Finally, the ZNT coated substrates were taken from the solution, washed with DI water, and heated for 1 h at 120 °C in an air ambient. The complete synthesis and fabrication process is shown in the schematic diagram in Fig. 1.

The morphology of the ZnO nanotubes and ZnO/N-DNW hybrids was characterized using a field-emission scanning electron microscope (FESEM, JSM-6500F) with an acceleration voltage of 15 kV. The bonding structure of the ZnO nanotubes and ZnO/N-DNW hybrids was investigated by typical Raman spectroscopy with an excitation wavelength of 514 nm. The crystal structure of the samples was characterized by X-ray diffraction (XRD) (D2 PHASER-X-ray Powder Diffraction, BRUKER) using CuKα1 radiation (λ = 1.54056 Å). X-ray photoelectron spectroscopy (XPS) was used to analyze the material composition. He-Cd laser (Kimmon, 1 K series) was used to examine photoluminescence characteristics with a wavelength of 325 nm at room temperature. The I–V characteristics of the dark current and UV photocurrent and photoresponses were measured with a 365-nm illumination laser using a source measuring unit (Keithley 237) at a laser intensity of 1 mW/cm^2. The photoresponsivity of the as-fabricated samples was calculated using I_{photo}-I_{dark}/P x A, where P is the laser power and A is the area of the sample. The electrical conductivity of the N-DNW films was investigated by Hall measurement in a van der Pauw configuration (ECOPIA HMS-3000). EFE measurements and EFE display studies were carried in high vacuum chamber at the pressure of 2×10^{-7} Torr. A mutable voltage was applied between the parallel-plate structured ZNTs/N-DNW cathode and Cu anode at a distance of 150 μm.

3. Results

3.1. Material characterization

Fig. 2 shows the FESEM micrographs of the (a) N-DNW (b) ZNRs, (c) ZNTs, (d) ZNRs/N-DNW, (e) ZNTs/N-DNW, and (f) annealed ZNTs/N-DNW (150 °C). The N-DNW synthesized using 70% N_2, as shown in Fig. 2a, exhibits the tiny needle like morphology that is due to the