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Research paper

Electrochemical fabrication and optoelectronic properties of hybrid heterostructure of CuPc/porous GaN

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ABSTRACT

A new hybrid heterostructure of p-type copper phthalocyanine (CuPc) and n-type porous GaN (PGaN) has been fabricated by electrophoretic deposition. The influence of CuPc concentration, electric field intensity, and deposition time on the growth of CuPc film has been explored. The as-prepared CuPc films are made of numerous nanorods. The X-ray diffraction (XRD) spectra revealed that the CuPc films are the β phase and amorphous type on pristine and porous GaN, respectively. Moreover, the prototype devices were fabricated on the basis of the CuPc/PGaN heterostructures. The devices exhibited excellent photodetector performance under ultraviolet (UV) light illumination.

1. Introduction

Organic/inorganic semiconductor heterostructures have attracted a surge of interest due to their unique electronic and optoelectronic properties, which arise from individual components and along with processes occurring at interfaces between components [1–3]. They have showed superior performance of improved carrier mobility, stability, and lifetime relative to those of organic/organic junctions, and been widely used in hybrid devices such as solar cells, electroluminescent devices, and photodetectors [4–6].

It is noted that in previous studies inorganic semiconductors are mainly Si, ZnO, GaAs, and InP [7–10]. Recently, efforts have also been made to study GaN-based materials due to its high thermal capacity, chemical stability, high electron mobility, and excellent UV optoelectronic response. For instance, Kim et al. fabricated and characterized a heavily Si-doped GaN/PEDOT:PSS/Au structure and the Current–Potential (I–V) characteristic of the hybrid structure shows diode-like behavior [11]. Hu et al. reported a prototype device on the basis of P3HT/PGaN heterojunction and the device exhibited obvious rectifying and photoresponse properties in dark and under UV light illumination [12].

In contrast with organic polymers, copper phthalocyanine (CuPc), as a representative type of small-molecule semiconductors, have superior light fastness, resistance to radiation, stability and chemical stability. They also have potential applications in optical and electrical devices, such as light-emitting diodes, solar cells, and field-effect transistors [13–15]. As part of ongoing efforts to explore hybrid heterostructures of CuPc and to improve the performance of GaN-based devices have been investigated. Kim et al. reported on progress and features on the charge transport between GaN and CuPc and demonstrated efficient transport of photo-generated electrons and holes across the hybrid interface [16–18]. Janardhanam et al. investigated the electrical properties of the Au/*n*-GaN Schottky structure modified using CuPc interlayer and it is effective in modification of Schottky barrier of the Au/*n*-GaN Schottky diode [19,20]. The previous studies reported the thermal evaporation method to form heterostructures, which was a great amount consuming of energy and materials. However, to date, few reports have used the electrochemical method though its facile and low-cost processing [21].

Herein, we report the fabrication of heterostructures of CuPc and PGaN by a facile electrophoretic deposition method. The influence of CuPc concentration, electric field intensity, and deposition time on the growth of CuPc film was thoroughly explored. The as-prepared heterostructure was directly used for the fabrication of prototype devices. The devices have obvious rectifying effect in dark, and photoelectric response under UV light illumination.

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2. Experimental

Si-doped n-type GaN(0001) films were grown on sapphire (0001) substrates by hydride vapor phase epitaxy. The GaN layer was 5 μm thick, 5 mm × 10 mm, and with a carrier concentration of 10^{18} cm^{-3}. CuPc was purchased from Aldrich. Sulfuric acid, acetone, ethanol, chloroform and trifluoroacetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Before each experiment, The GaN layer was cleaned with ultrasonication sequentially in acetone, ethanol, and deionized water (>18 MΩ) for 20 min.

UV light-assisted electrochemical etching was carried out in a three-electrode cell using a CHI660D potentiostat/galvanostat (Shanghai Chen Hua Co., Ltd). GaN substrate was used as working electrode, and Pt wires were counter and reference electrodes. The electrolyte is 0.5 M sulfuric acid solution, and the applied voltage was 6 V. The GaN was etched for 15 min, treated with aqua regia, and washed with deionized water.

Electrophoretic deposition was performed with a potentiostat and a DC regulated power supply. The cathodes were GaN and PGaN, the anode was Pt wire, and the electrolyte was a mixture of chloroform, CuPc and trifluoroacetic acid. The concentration of CuPc was 1 mg/mL, the electric field intensity was 100 V/cm, and the deposition time was 10 min. The as-deposited CuPc films was further vacuum annealed at 150 °C for 2 h. Indium point was soldered onto GaN and PGaN substrate, while Au point was deposited on P3HT layer. For simplicity, such devices were denoted by In/GaN/P3HT/Au and In/PGaN/P3HT/Au. Fig. 1 illustrates the cross sectional schematic of the fabricated hybrid device.

The morphology of samples was investigated by means of scanning electron microscopy (SEM, Hitachi S4800). The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance power X-ray diffractometer using Cu Ka radiation ($\lambda = 1.5406$ Å). The energy dispersive X-ray spectroscope (EDX) was performed on a Quanta 400 FEI SEM at 10 kV. Raman spectrometer (excited at 532 nm) was characterized by Laser confocal Raman spectroscopy (Labram HR 800). The ultraviolet–visible (UV–vis) absorption spectroscopy was recorded on UV–vis absorption spectrometer (LAMBDA 750 UV/Vis/NIR). The I–V characteristics in dark and under UV light illumination were recorded with an Agilent 4200 semiconductor parameter analyser.

3. Results and discussion

Fig. 2a shows a typical SEM image of PGaN, which was prepared by UV light-assisted electrochemical etching. It can be seen that porous structures have been formed over the entire surface. These features are different from pristine GaN, which have flat and smooth surface (the inset in Fig. 2a). Due to the increase of surface roughness of PGaN, the illumination area is increased, the reflection of light is decreased, and thus the photoelectric conversion efficiency is greatly improved.

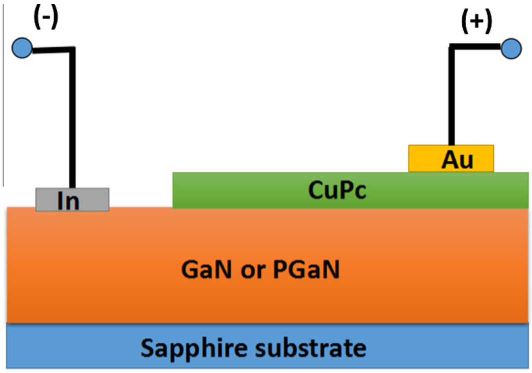

Fig. 1. Cross-section schematic diagram of the hybridstructure.

Meanwhile, CuPc molecule has eight N atoms (the inset in Fig. 2b). Under acidic environment, the four periphery N atoms are easily combined with H, and the N atoms are protonated. As described previously, the degree of protonation depends on the pH value of the acidic media [22–24]. Under the strong acidic media, such as sulfuric and hydrochloric acids, the four periphery N atoms of the phthalocyanine can be combined with the H and fully protonated. Under the weak acidic media, for example trifluoroacetic acid, the four periphery N atoms can be protonated partly. After protonation, the phthalocyanine molecules are positively charged, and the surface potential of the particles is increasing. The particles can move to the cathode under an external electric field and a typical electrophoretic deposition occurs.

Moreover, many factors can affect the morphology of CuPc film, such as deposition time, solution concentration, and electric field intensity. Fig. 2b is the SEM image of CuPc/PGaN. There is a layer of uniform and dense CuPc film, which consists of cross-linked nanorods and distributed on the surface. The average diameter of nanorods is about 50 nm, and the length is tens of nanometers. Similar morphology had also been observed for the CuPc/GaN. The concentration of CuPc is 0.1 mg/ml, the electric field intensity is 100 V/cm, and the deposition time is 10 min. Further increasing the deposition time, microrods will occur (Fig. S1). In addition, both the electric field and the concentration of CuPc could affect the growth of CuPc films (Fig. S2).

Fig. 3a shows the XRD spectra of CuPc films deposited on GaN and PGaN, respectively. The 2θ peaks at 7.09 can be indexed as the (001) peak of the β phase of CuPc [25]. In comparison, there is no obvious diffraction peaks of CuPc/PGaN. i.e., amorphous deposit is obtained. Similar phenomenon has also been observed in the literature. Mallik et al. found the CuPc film on quartz glass showed obvious α phase and on the quartz glass surface with coating a layer of gold nanoparticles is amorphous [26]. The reason of CuPc crystal type transforming is mainly caused by the roughness of the substrate surface and the nature of the base material. For the CuPc/PGaN, the large roughness of PGaN can change the density of charge distribution when applying an electric field, forming a tiny local electric field on the surface of PGaN and the electric field intensity and direction are different from the smooth surface. The protonated CuPc molecules move along the different power line direction to the surface of PGaN and deposited. Hence, the arrangement direction of CuPc molecules on PGaN is various and form anomalous crystal structure. Fig. 3b shows the UV–vis absorption spectrum of CuPc/PGaN. There is an obvious absorption features in the visible light region and the Q bands of CuPc film are blue-shifted to 614 and 694 nm. Fig. 3c shows Raman spectra of CuPc/PGaN. Characteristic peaks of CuPc are observed and has the same feature as that of the source powder of CuPc, which indicates that there is no any chemical modification at the interface of the CuPc/PGaN [27,28]. Meanwhile, there is no characteristic peak (1244 cm^{-1}) of C–F bond, which confirms no trifluoroacetic acid molecules in CuPc film [29]. Fig. 3d is the EDX spectrum of CuPc/PGaN, It can be seen that the GuPc film are only composed of Cu, C, and N elements. No other elements are observed in the EDX spectrum, implying no trifluoroacetic acid molecules. In addition, the peaks of GaN and Au elements result from GaN substrate and pre-deposited Au for SEM imaging, respectively.

Fig. 4a shows the typical I–V curves of the device based on PGaN (In/PGaN/In) in dark and under UV light illumination. The linear I–V curves of In/PGaN/In device suggest that ideal Ohmic contact is formed between PGaN and In electrode. Fig. 4b shows the I–V curves of the device based on the CuPc (Au/CuPc/Au). The nonlinear I–V curves of Au/CuPc/Au device indicate that there is a Schottky barrier at the contact between the CuPc film and the Au