Hybrid solar cell based on polythiophene and GaN nanoparticles composite*

Feng Qian(冯 倩)[a)b)†], Shi Peng(时 鹏)[a)b)], Li Yu-Kun(李宇坤)[a)b)], Du Kai(杜 锴)[a)b)]
Wang Qiang(王 强)[a)b)], Feng Qing(冯 庆)[a)b)], and Hao Yue(郝 跃)[a)b)]

[a)] *School of Microelectronics, Xidian University, Xi'an* 710071, *China*
[b)] *Key Laboratory of Wide Band-Gap Semiconductor Materials and Devices, Xidian University, Xi'an* 710071, *China*

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Hybrid solar cells based on poly(3-hexylthiophene) (P3HT) and Galium nitride (GaN) nanoparticle bulk heterojunction are fabricated and analyzed. The GaN nanocrystal is synthesized by means of a combination of sol–gel process with high temperature ammoniation using $Ga(OC_2H_5)$ as a precursor. Their characteristics are determined by X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy. With the addition of GaN nanoparticle to P3HT, the device performance is greatly enhanced.

Keywords: gallium nitride nanocrystal, hybrid solar cell, P3HT

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1. Introduction

There has been great interest in hybrid organic–inorganic solar cells due to the low cost of their material and solution-based processing techniques, creating the potential for large-scale, cost-effective solar cells. In recent years, various solutions for processed bulk-heterojunction solar cell devices have been reported using p-type conjugated polymers with n-type inorganic semiconductor nanoparticles. These nanoparticles include TiO_2,[1–5] PbS,[6,7] PbSe,[8] $CuInS_2$,[9] CdS,[10] CdTe,[11] and ZnO.[12–15] These hybrid polymer/inorganic nanoparticle bulk heterojunction solar cell devices are more advantageous over the devices fabricated with solution processing of polymer semiconductor and high electron mobility of inorganic semiconductor.

In order to obtain high currents and fill factor devices, both electron and hole mobility must be optimized and balanced. This can be achieved by improving electron transport through the inorganic component in the conjugated polymer. Some studies indicated that hybrid solar cells could be fabricated using a combination of a semiconducting polymer and ZnO nanoparticle via a solution-based approach.[16–18]

Gallium nitride (GaN) has a direct and wide bandgap of 3.39 eV at room temperature, and is a well-known semiconducting material for short wavelength optoelectronic devices. The conduction band minimum (CBM) of GaN has a more negative conduction bandedge than that of TiO_2. The electron mobility is higher in GaN than in other n-type metal oxides.

The present study focuses on the synthesis of GaN nanoparticles by the sol–gel method. The nanocrystal characteristics are determined by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM), and then the GaN and poly(3-hexylthiophene) (P3HT) solution process bulk heterojunction solar cell can be achieved. The *I*–*V* characteristic of the solar cell is measured.

2. Experiment

2.1. Synthesis of GaN nanoparticles

GaN nanoparticles were prepared by sol–gel process. 5-g Gallium was dissolved in mixture of concentrated hydrochloric acid and concentrated nitric acid with a blend volume ratio of 1:1 (both of them are 30-mL). After a strong reaction with smoke and heat release, a light yellow solution was generated. With ammonia added, the PH value of the solution was between 7.2∼8.0 in this process, and sol appeared. The solution was transparent until we poured citric acid into the solution. Then, 2-g more acid was dropped into the solution. The solution was heated with an alcohol lamp for 2 hours before mass gel appeared. The samples were cooled to room temperature. A two-hour calcination in Muffle furnace at 400 °C made the gel into dark grey multilayer. Finally, we obtained the grey dry Ga_2O_3 gel powder after grinding. For the nitridation process, the prepared Ga_2O_3 was placed in a horizontal quartz tube under a flowing NH_3 atmosphere and annealed at proper temperature (in this paper, three temperature were taken) for 80 min. The samples were then cooled slowly to room temperature in an environment of flowing N_2. Yellow colored GaN nanoparticles were produced.

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†Corresponding author. E-mail: qfeng@mail.xidian.edu.cn
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2.2. Preparation of solar cell devices

ITO-coated glass substrates were first cleaned by ultrasonic agitation in detergent, de-ionized water, acetone, and ethanol sequentially. Then, the substrates were dried by flowing N_2, followed by oxygen plasma treatment for 5 min. The PEDOT:PSS solution was dropped and coated on the substrates and dried at 120 °C for 10 min. Then, the substrates were taken into a glove box. Before preparing the mixture solution of P3HT and GaN, P3HT solution (20 mg/mL) and GaN solution (5 mg/mL, 10 mg/mL, 15 mg/mL, and 20 mg/mL) in chlorobenzene were first prepared, respectively. Then, the P3HT and GaN solutions were mixed together and spin-coated onto the surface of PEDOT:PSS followed by being annealed for 10 min at 120 °C in the glove box. Al film was electron beam-evaporated through a shadow mask. The schematic illustration of the device is shown in Fig. 1.

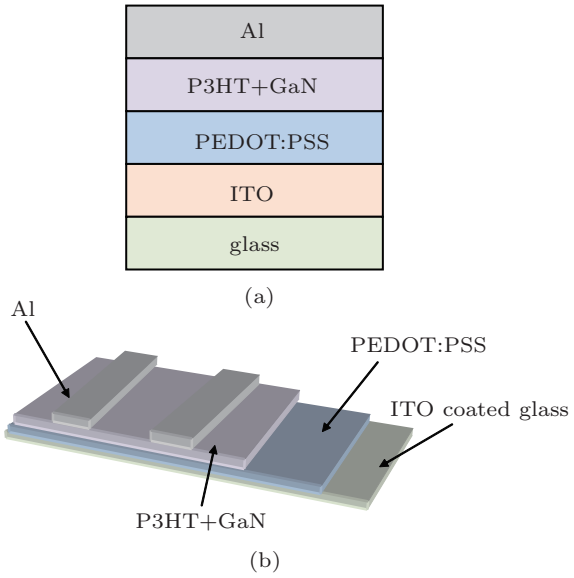


Fig. 1. (color online) Schematic (a) side view layer structure and (b) a part of the device on the ITO-coated glass.

2.3. Characterization of material

The GaN nanocrystal analysis was conducted using XRD, SEM, and XPS. The XRD pattern was recorded using an X-ray diffractometer using Cu Kα radiation of wavelength $\lambda = 1.5406$ Å in the scan range $2\theta = 10°$–$80°$.

2.4. Testing of photovoltaic device

The current–voltage characteristics of the solar cell devices were measured at room temperature. The light intensity was about 100 mW/cm^2 on the sample surfaces measured with a photo detector and the short current and open circuit voltage were recorded.

3. Results and discussion

Figure 2 shows XRD patterns of the GaN nanoparticles under different nitridation processes at (a) 950 °C, (b) 1050 °C, (c) 1100 °C. As shown in the figure, the sizes and purities of samples are different, and the observed peaks clearly suggest that 1050 °C is the optimum temperature. At a lower temperature of 950 °C, the Ga_2O_3 could not turn into GaN absolutely, so GaOOH is present, while at a higher temperature of 1100 °C, some of the GaN decomposes and the intensity of the GaN pattern reduces to some extent. The XRD peaks indicate that GaN nanoparticles have wurtzite structure well matched with standard GaN according to the Joint Committee on Powder Diffraction Standard (JCDS) card. Traditionally, the broadening of the peaks in the XRD patterns of solid powder indicates that the sizes of GaN particles are in a nano range.

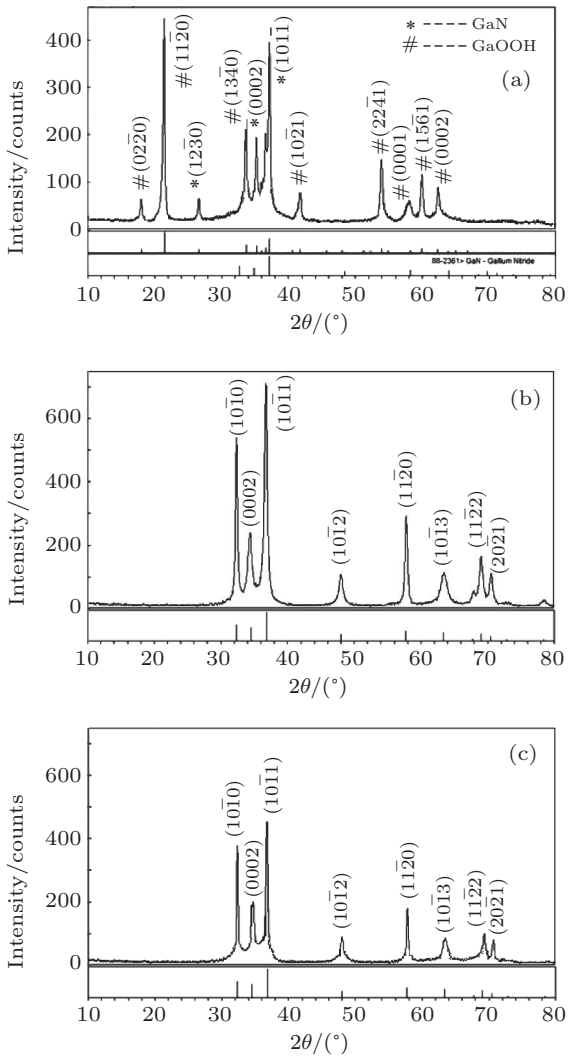


Fig. 2. XRD patterns of the GaN nanoparticles at (a) 950 °C, (b) 1050 °C, and (c) 1100 °C.

The crystalline domain diameters of the GaN particles are estimated from the full widths at half maximum (FWHMs) of the XRD peaks according to the Debye–Scherrer formula[19,20]

$$d = \frac{K\lambda}{B\cos\theta},$$

where d is the particle size, λ the wavelength of X-ray radiation, B the FWHM of the peak, θ the angle of diffraction,

and K the correction factor contributed from the geometry of the crystallites. Borchert *et al.*,[21] Klug and Alexande[22] modified the above equation for more accurate calculations by adopting geometrical factor $K = 0.9$ of the nanoparticles, the average particle sizes of the GaN nanoparticles, calculated from the diffraction peaks observed through the Scherrer formula, are in a range of 15 nm–20 nm.

A typical SEM image is presented in Fig. 3, showing the sample at 1050 °C for 80 min in nitridation process. The sizes of the particles are in a range of about 15 nm–20 nm. Their surfaces are very smooth.

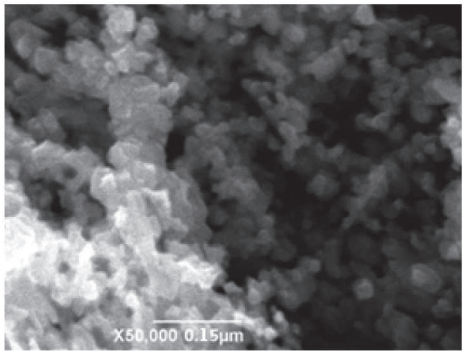


Fig. 3. SEM micrograph of GaN nanoparticles.

Figure 4 shows the XPS patterns of binding energies ranging from 0 eV to 1400 eV for the sample at 1050 °C for 80 min in nitridation process. We can conclude that the elements of the martial are Ga, C, N, and O, more details of the samples are presented in Table 1.

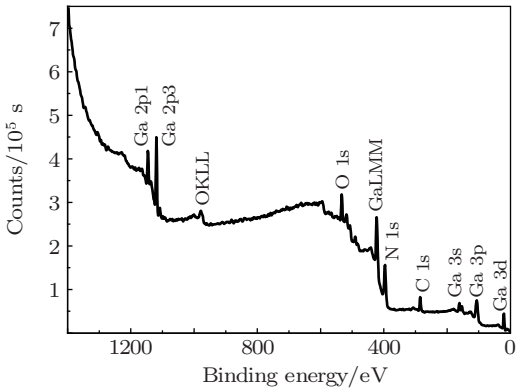


Fig. 4. XPS patterns of sample b.

Table 1. Percentages of elements in samples.

Sample	Ga	N	C	O
a	40.15	38.05	10.17	11.63
b	45.58	46.92	3.64	3.86
c	38.54	37.02	11.21	13.23

The pattern shows the peak of the Ga 3d at 19.8 eV and the peak of Ga 2p3 at 1117.4 eV, which can be assigned to the Ga–N bonding. Furthermore, the peak of N 1s is at 397 eV but not at 399 eV, which can also be assigned to the Ga–N bonding. On the other hand, there is a peak of O 1s at 530.8 eV and no peak of Ga 3d appears at 20.8 eV, so there is no Ga–O bonding[23–25] and the presence of oxygen is in a chemical adsorption state.

The I–V behaviors of the solar cells are investigated under the irradiation of the solar simulator. Figure 5 shows the photovoltaic responses of the devices of ITO/P3HT/PEDOT:PSS/Al and ITO/P3HT-GaN/PEDOT:PSS/Al, respectively. In P3HT-only devices, the lack of an electron-accepting material means that any built-in potential must arise from the junction with the electrode, so the P3HT device exhibits little photoactivity. The photovoltaic response based on P3HT/GaN composites is greatly enhanced. I_{sc} can be improved significantly to reach 3.5 mA/cm^2 and the V_{oc} to 0.71 V. The enhancement of photovoltaic response can be explained in the following way. GaN nanoparticles with nanometer diameters are dispersed in the P3HT phase and act as electron accepting species. When excitons are produced in P3HT polymer during irradiation, the excitons in P3HT may migrate to the interfaces of P3HT and GaN nanocrystals, at which charge separation could take place. The increase in interfaces between electron donor (P3HT) and electron acceptor (GaN) enhance the excitation separation. This causes the photocurrent of the device to be enhanced. The effect can be made more significant by increasing the GaN nanoparticles in the P3HT/GaN nanocomposites.

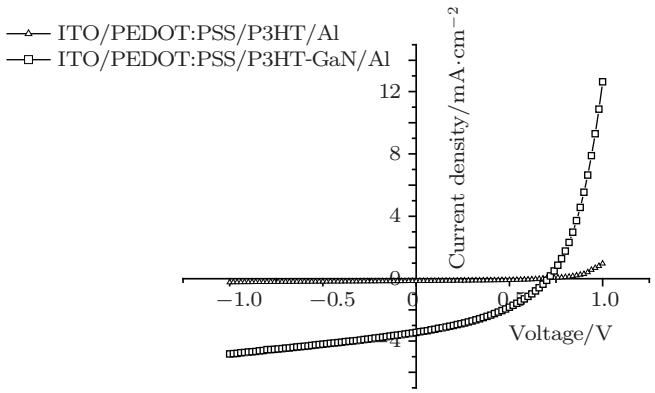


Fig. 5. Current density and voltage characteristics of ITO/PEDOT : PSS/P3HT/Al and ITO/PEDOT : PSS/P3HT-GaN/Al devices.

In bulk heterojunction solar cells, charge transport is also responsible for the device performance. In order to study the influence of the concentration on device characteristics, the GaN solutions with different concentrations of 5 mg/mL, 10 mg/mL, 15 mg/mL, and 20 mg/mL are prepared. Figure 6 shows the I–V behaviors of four devices with different concentrations and the device parameters are presented in Table 2. It is obvious that, with the increase of concentration, the values of V_{oc} change slightly, but the values of I_{sc} increase dramatically. When the concentration is 15 mg/mL, we obtain

the best performance, which is likely to be due to the formation of nice transport network in the active layer of the device. Further increasing GaN concentration, such as 20 mg/mL, the current density decreases, which is attributed to poor morphology of the blend film with high GaN concentration limiting charge transport, as shown in Fig. 7. The surface topographies of GaN:P3HT films with different GaN concentrations are investigated with tapping mode atomic force microscopy (TM-AFM). The layer with 20 mg/mL shows a rough topography with a root-mean-square (RMS) surface roughness of 25 nm, which indicates a coarse phase separation, while the film with 15 mg/mL shows a much smoother surface with an RMS surface roughness of only 4.7 nm, implying a better surface morphology. The maximum performance of the solar cell is obtained at a GaN concentration of 15 mg/mL, an open circuit voltage V_{oc} of 0.71 V, and a short circuit current density J_{sc} of 3.5 mA/cm^2. With the increase of GaN content in the blend, the performances of the cells deteriorate.

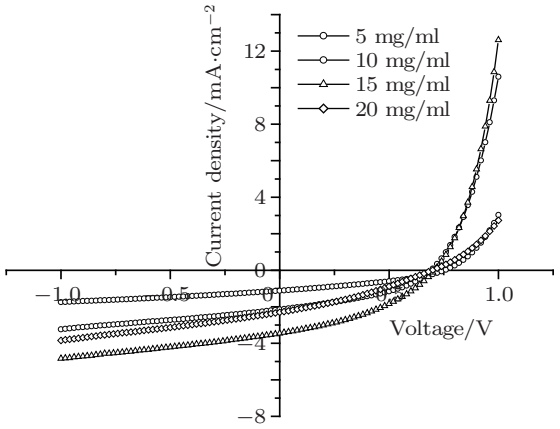


Fig. 6. Current density and voltage characteristics of different GaN concentrations.

Table 2. Performances of P3HT-GaN solar cells with different GaN concentrations.

Device	V_{oc}/V	I_{sc}/(mA/cm^2)	FF/%
5 mg/mL	0.73	1.13	35.5
10 mg/mL	0.7	2.15	39
15 mg/mL	0.71	3.5	44.2
20 mg/mL	0.7	2.30	41.6

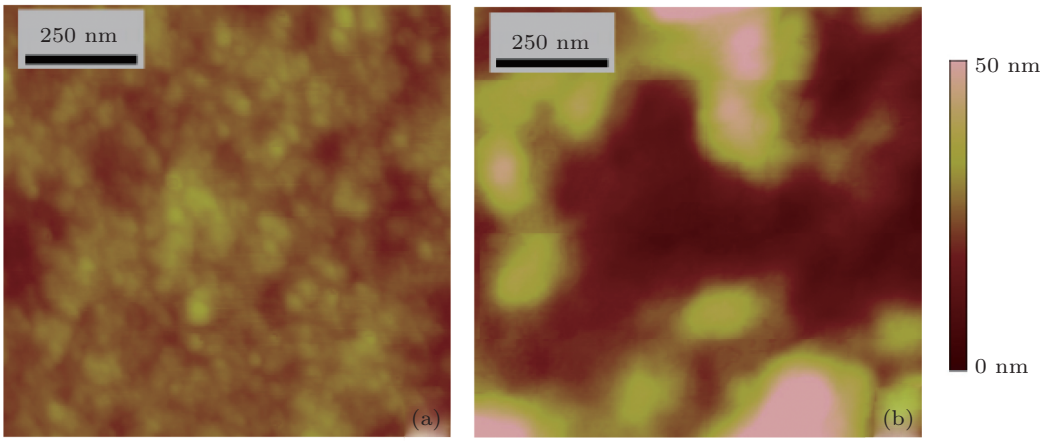


Fig. 7. (color online) AFM height images of GaN:P3HT at (a) 15 mg/mL and (b) 20 mg/mL.

4. Conclusions

In conclusion, hybrid solar cells are fabricated by blending nanocrystal GaN and conjugated polymer P3HT as active layers, where the GaN nanoparticles are synthesized via a solution-based approach. The sizes and element percentages of the particles are quantitatively investigated using XRD and XPS. It can be seen that the performances of this new type of solar cells vary with GaN concentration. At 15 mg/mL, the best results are obtained with an open circuit voltage of 0.71 V and a short circuit current density of 3.5 mA/cm^2.

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