Effect of annealing on performance of PEDOT:PSS/n-GaN Schottky solar cells*

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We develop a heterojunction-based Schottky solar cell consisting of n-type GaN and PEDOT:PSS and also investigate the effect of annealing on the performance of the solar cell. The results show that the open circuit voltage (V_{oc}) increases from 0.54 V to 0.56 V, 0.71 V and 0.82 eV while decreases to 0.69 eV after annealing at 100 °C, 130 °C, 160 °C, and 200 °C, respectively, which can be ascribed to the change of barrier height of PEDOT:PSS/GaN Schottky contact induced by variation of the work function of the PEDOT:PSS. Furthermore, the conductivity and surface roughness measurements of the PEDOT:PSS indicate that annealing can increase the grain size and improve the connectivity between PEDOT and PSS particles, and cause thermal degradation at the same time, which leads to the rise in short-circuit current density (I_{sc}) up to 160 °C and the dropoff in I_{sc} after annealing at 200 °C.

Keywords: gallium nitride, PEDOT:PSS, Schottky solar cell, post-annealing

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1. Introduction

Optoelectronic devices based on III-nitride semiconductors have been widely studied, for example, light emitting diodes (LEDs), photodetectors and solar cells.[1–3] In particular, the ternary InGaN alloy becomes a significant candidate for the application of high efficiency photovoltaic devices, for its energy band gap can vary from 0.7 eV to 3.4 eV, which nearly covers the whole solar spectrum, and it has a high optical absorption of $\sim 10^5$ cm^{-1} near the band edge and a superior radiation resistance as well.[4,5] Although the theoretical calculation has indicated that a high solar energy conversion efficiency greater than 40% can be obtained in the InGaN solar cell, up to now, the conversion efficiency is still very low.[6] One of the most serious problems in the fabrication of solar cells is the low doping efficiency and activity of Mg in p-type III-nitride semiconductors, while the InGaN based solar cell requires a highly conductive front layer on the top of the p-type layer to collect the photo-generated carriers.

To solve the above-mentioned problem, transparent conductive polymers such as PEDOT:PSS and PANI, which have the advantages of high conductivity (> 500 S/cm), high transparency (> 80%) for short-wavelength light and a high work-function comparable to those of Ni (5.1 eV) and Au (5.2 eV), were investigated to form a transparent Schottky contact.[7–11] This suggests that the Schottky contact based on transparent conductive polymers can be a novel window layer for III-nitride solar cells as an alternative to a p-type layer. Recently, Matsuki *et al.* reported that the heterojunction, which is fabricated by using PANI and PEDOT:PSS to form the Schottky contact on n-GaN thin film, exhibited good rectifying properties and photovoltaic characteristics.[10,11]

In this paper, Schottky solar cells based on PEDOT:PSS are fabricated and the effect of annealing on the photovoltaic characeteristics is investigated to improve the performance of the device. Furthermore, the diode characteristics, the variation in work function, conductivity and the surface morphology of the PEDOT:PSS are analyzed.

2. Device fabrication

The 2 μm-thick silicon-doped gallium nitride (GaN) film was grown on 5 cm c-face sapphire substrate by metal–organic chemical vapour deposition (MOCVD). The measured room temperature carrier concentration was 4.3×10^{17} cm^{-3}.

Figure 1(a) shows the molecular structure of PEDOT:PSS in which the π-conjugated system is responsible for the hole transport in PEDOT. Figure 1(b) shows the schematic diagram of a sapphire/n-GaN/PEDOT:PSS Schottky diode. The p-type polymer PEDOT:PSS was spin-coated (3000 rpm, 30 s) three times on the GaN film. The ohmic contact Ti/Al (20/120 nm) was formed on the GaN film by electron-beam evaporation. The obtained uniform polymer films were processed into 4 mm^2 configurations of isolated cells. The PEDOT:PSS Schottky diodes were annealed at 100 °C, 130 °C, 160 °C, and 200 °C for 30 min under N_2 ambient respectively. The properties of the solar cell devices were measured at room temperature. The light intensity was measured to be about 100 mW/cm^2 on the sample surface by using a photo detector, and the short current and open circuit volt-

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age were recorded. The parameters of the Schottky barrier were determined by measuring the current–voltage (I–V) and capacitance–voltage (C–V) curves, and the surface morphologies of the devices were investigated by using tapping mode atomic force microscopy (TM–AFM) and ultraviolet photo electron spectroscopy (UPS) measurements were carried out in a UHV chamber with a base pressure of $\sim 10^{-10}$ Torr. He I (21.2 eV) radiation was used in UPS with an experimental resolution of 0.1 eV.

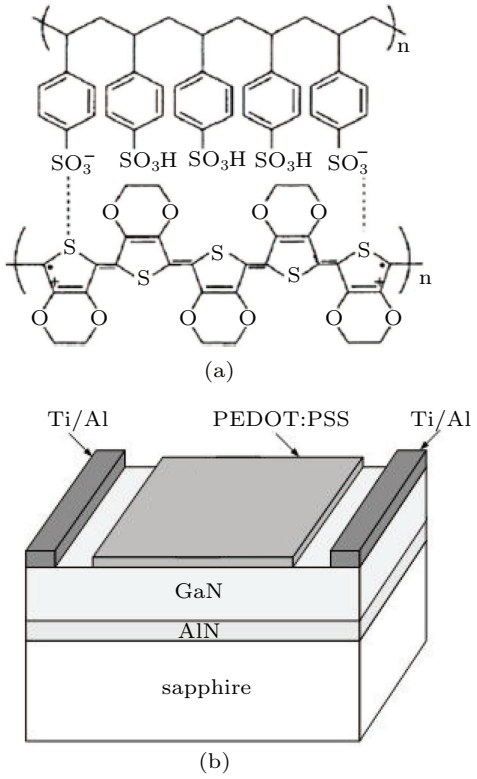


Fig. 1. Schematics of the molecular structures of PEDOT:PSS (a) and sapphire/GaN/PEDOT:PSS multilayers (b).

3. Results and discussion

Figure 2(a) shows the photovoltaic characteristics of the sapphire/GaN/PEDOT:PSS samples and the variations of parameters, such as the open-circuit voltage V_{oc} and short-circuit current density (I_{sc}), are investigated for ten groups of samples, each group consisting of five samples corresponding to different annealing conditions as shown in Fig. 2(b). The results show that the open circuit voltage V_{oc} increases from 0.54 V to 0.56 V, 0.71 V, and 0.82 eV while decreases to 0.69 eV after post-annealing at 100 °C, 130 °C, 160 °C, and 200 °C, respectively. On the other hand, the short circuit current presents a gradual increase as the annealing temperature increases to 160 °C and decreases after 200 °C annealing.

In order to explain the improvement in the performance, the characteristics of the Schottky contact are studied by measuring the I–V and C–V curves[12,13] as shown in Fig. 3. The

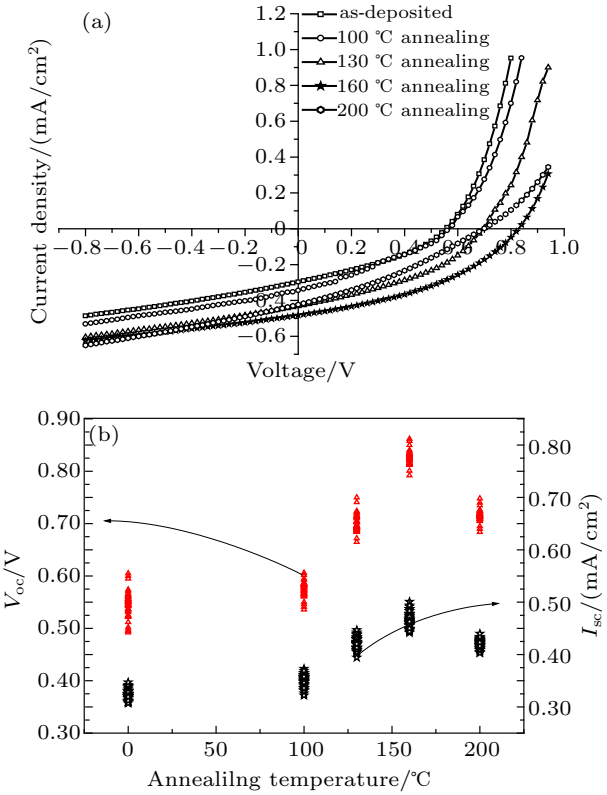


Fig. 2. (color online) (a) The I–V characteristics of the sapphire/GaN/PEDOT:PSS Schottky contacts. (b) The I_{sc} and V_{oc} each as a function of annealing temperature.

Table 1. Schottky barrier heights and ideality factors of PEDOT:PSS Schottky diodes on n-GaN at different annealing temperatures.

Sample	Schottky barrier height (SBH), ϕ_b/eV			Ideality factor n
	I–V	Norde	C–V	
as-deposited	0.64	0.68	0.62	1.76
100 °C	0.66	0.73	0.64	1.71
130 °C	0.77	0.83	0.74	1.68
160 °C	0.90	0.95	0.91	1.41
200 °C	0.81	0.86	0.80	1.53

Norde method is also employed[14] because series resistance can hinder an accurate evaluation of barrier height from the standard ln(I)–V plot. The extracted barrier height and ideality factor of the PEDOT:PSS Schottky contact are listed in Table 1 (the value is the average over the values of five group samples). It is noted that barrier height extracted from the Norde method is higher than from the other two methods, so the series resistance is large enough to affect the results. However, we can conclude that the barrier height increases with annealing temperature rising to 160 °C compared with the as-deposited one and results in the improvement of the open circuit voltage (V_{oc}). It is also consistent with the measurements on leakage current. Furthermore, the ideality factor of the PEDOT:PSS Schottky diodes is found to gradually decrease from 1.76 to 1.41 after 160 °C annealing, while increases to 1.53 after 200 °C annealing and the ideality factor is greater than one, suggesting transport mechanisms other than thermionic emission. In order to explain the variation of the Schottky contact after annealing at different temperatures, the

PEDOT:PSS films on the GaN substrates are subsequently annealed at different temperatures in an ultra high vacuum chamber and then the valence band structures and work functions of PEDOT:PSS are characterized using UPS without breaking the vacuum state (as shown in Fig. 4). Work function values of as-deposited and annealed PEDOT:PSS films are calculated using the energy difference between $h\nu$ (21.2 eV) of He I and the binding energy from the Fermi energy to the secondary cut-off of spectra.[16–18] The calculated work function of the PEDOT:PSS film is dependent on annealing temperature. After annealing at 100 °C, 130 °C, and 160 °C, the work function of PEDOT:PSS film increases from 4.93 eV to 5.01 eV, 5.12 eV, and 5.23 eV, respectively, while after annealing at 200 °C, the work function decreases to 5.15 eV. Thus the barrier height of the PEDOT:PSS/n-GaN gradually increases for annealing at 100 °C, 130 °C, and 160 °C and decreases at 200 °C and the V_{oc} also increases from 0.54 V to 0.56 V, 0.71 V, and 0.82 eV while decreases to 0.69 eV after post-annealing at 100 °C, 130 °C, 160 °C, and 200 °C, which is consistent with the variation of the barrier height.

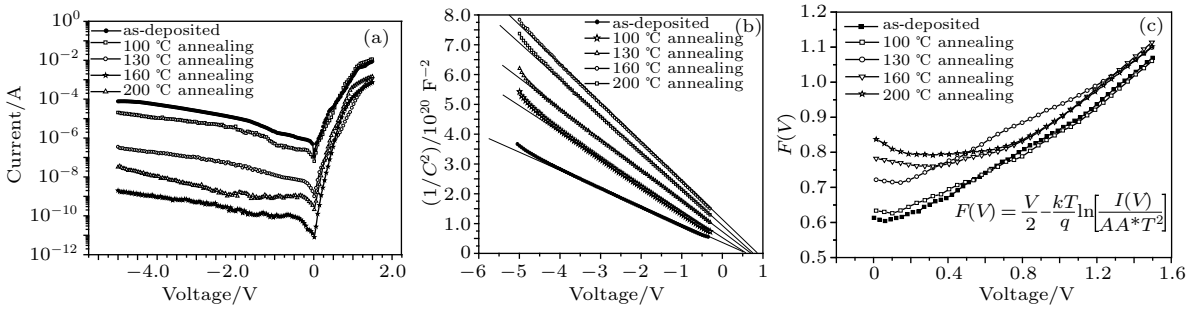


Fig. 3. (a) Typical I–V characteristics for the PEDOT:PSS Schottky contacts to n-GaN, (b) plots of $1/C^2$ versus V for the PEDOT:PSS Schottky contact, and (c) plots of $F(V)$ versus V for the PEDOT:PSS Schottky contacts at different annealing temperatures.

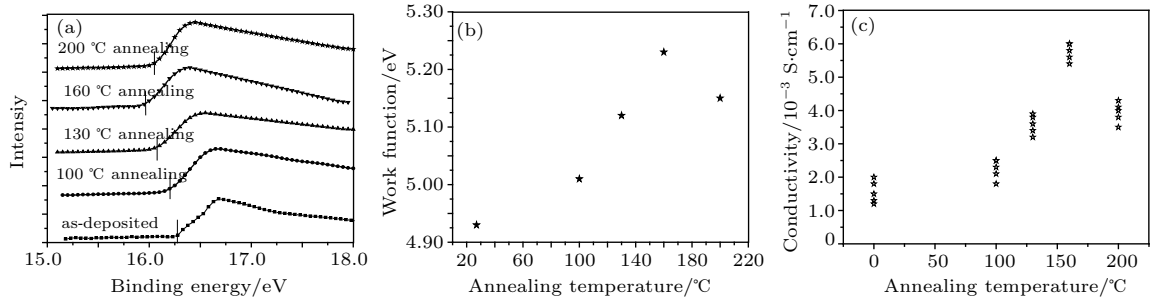


Fig. 4. (a) UPS spectra of PEDOT:PSS annealed at different temperatures, and (b) work function and (c) conductivity of PEDOT:PSS as a function of annealing temperature.

For the variation of I_{sc}, the changes of the ohmic contact resistance and the channel resistance can be neglected for the low annealing temperature and it may be related to the thermally induced change in the PEDOT:PSS. Hence, the conductivity and the surface roughness of the PEDOT:PSS are examined (as shown in Figs. 4(c) and 5). The conductivity and the surface roughness are observed to increase gradually after annealing at 100 °C, 130 °C, and 160 °C while they decrease after annealing at 200 °C. PEDOT:PSS is an aqueous gel in which the hydrated gel particles consist of PSS interlinked by PEDOT chains. The conductivity of PEDOT:PSS film depends strongly on the film morphology and structure, and heating may affect the colloidal particle interactions in the PEDOT:PSS composite. The grain size and the connectivity between particles control the conductivity as in the many granular conductors. Post-annealing will improve the coalescence of PEDOT:PSS particles by softening or melting the PSS and PEDOT particles, increase the grain size of PEDOT:PSS, reduce the number of inter-grain hopping barriers and barrier height, which may lead to the polymer chains forming a more crystalline structure as reported by Aasmundtveit,[18] which will improve the conductivity of PEDOT:PSS and also degrade the surface smoothness. On the other hand, annealing will cause the thermal degradation of PEDOT:PSS, so there is a competition between enhanced crystallization and the material's degradation. If the temperature is lower than 200 °C, the crystallization dominates and the effective colloidal particle size increases, leading to a greater surface roughness and higher conductivity, hence the I_{sc} increases; when the temperature is up to 200 °C, the degradation of the material becomes a severe problem, the surface roughness value reduces and the conductivity falls, which is in agreement with previous AFM studies[19] that suggested that a grain-like structure of PEDOT:PSS film has an inhomogeneous distribution of the PEDOT and PSS species within a single grain, hence the I_{sc} drops.

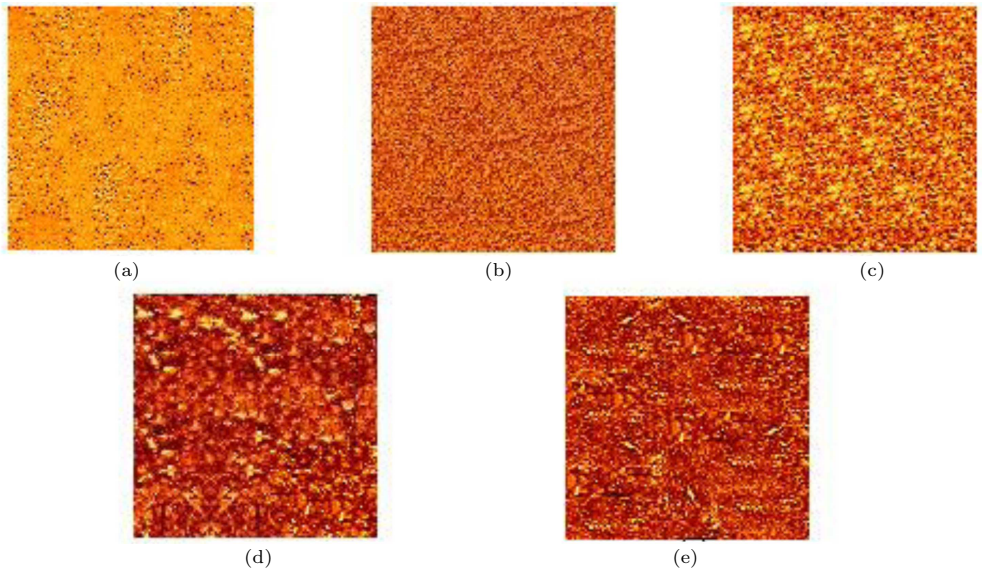


Fig. 5. (color online) AFM images (2 μm × 2 μm) of as-deposited PEDOT:PSS surface (R_{ms} = 1.3 nm) (a) and after post-annealing at 100 °C (R_{ms} = 2.0 nm) (b), 130 °C (3.5nm) (c), 160 °C (5.7 nm) (d), and 200 °C (4.3 nm) (e).

4. Conclusions

The effects of annealing on the performance of PEDOT:PSS/n-GaN Schottky solar cells are investigated; the V_{oc} and I_{sc} increase after annealing at 100 °C, 130 °C, 160 °C and decrease after annealing at 200 °C. The further measurements indicate that the change of the V_{oc} can be due to the work function variations of the PEDOT:PSS and the barrier height of the Schottky contact, while the change of the I_{sc} can be ascribed to the competition between the enhancement of the conductivity and the thermal degradation of the PEDOT:PSS.

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