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RESEARCH ARTICLE

Green light-emitting diode based on graphene-ZnO nanowire van der Waals heterostructure

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Abstract The rectifying behavior between graphene and semiconductors makes novel type of solar cells, photodetectors and light emitting diodes (LEDs). The interface between graphene and ZnO is the key for the performance of the optoelectronic devices. Herein, we find that green light emission is very strong for the forward biased graphene/ZnO nanowire van der Waals heterostructure. We correlated the green light emission with the surface defects locating at the ZnO nanowire surface through the detailed high resolution transmission electron microscopy and photoluminescence measurements. We pointed out engineering the surface of ZnO nanowires could bring a dimension of designing graphene/ZnO LEDs, which could be extended to other types of graphene/semiconductor heterostructure based optoelectronic devices.

Keywords ZnO nanowire, van der Waals heterostructure, light-emitting diode (LED)

1 Introduction

Graphene has attracted a great attention since discovered in 2004 [1]. It is a semi-metal two dimensional (2D) material with extremely high mobility, high transmittance, and excellent electrical conductivity [2,3]. The invention of graphene brought a novel family of heterostructure diode based devices, which can function as solar cells [4,5], photodetectors [6–8] and light emitting diodes (LEDs) [9]. On the other hand, semiconductor solid-state lighting is replacing traditional incandescent lamps. The commercial blue LEDs are based on GaN materials system [10]. It is generally believed that ZnO could replace GaN based on: 1) ZnO material can be grown in large scale at low temperature [11]; 2) The exciton binding energy of ZnO can reach 60 meV [12], which is twice that of GaN; 3) Zn is abundant in nature and Ga is scarce. However, the lack of stable, low resitivity, single crystalline p-type ZnO hindered the development of ZnO homojunction LED [13]. Building heterojunctions with ZnO using p-type materials, such as graphene, could solve this problem. In fact, comparing with semiconductor homojunctions, graphene/semiconductor heterostructure has its unique advantage as the junction is located at the surface, which permits a high external quantum efficiency. Up to now, graphene/ZnO heterostructure based LED has been reported [14–16]. Other than UV emission, it is common to see green light emission in the reported graphene/ZnO heterostructure LED. However, it remains unclear where the green light emission comes from. The green light emission may come from the intrinsic defects inside the crystal or from the surface of ZnO contacting with graphene.

While most of graphene/ZnO LEDs are based on ZnO single crystal or ZnO film we use single ZnO nanowires to build graphene-ZnO heterojunction LEDs for revealing the origin of green light emission. We chose mechanical exfoliated single crystal graphene as the hole injection layer. The relationship between the green light emission and the defects locating at the ZnO nanowire surface is extensively studied with transmission electron microscopy (TEM) and photoluminescence (PL) measurements. We point out that the surface of ZnO nanowires is the major source of green light emission. Thus, engineering the surface of ZnO may bring a dimension of designing graphene/ZnO LEDs, which could be extended to other types of graphene/semiconductor heterostructure based optoelectronic devices.

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2 Experimental

2.1 Growth of the ZnO nanowire

ZnO nanowire was prepared by physical vapor deposition method in a tube furnace [17–19]. ZnO powders were used as the evaporation source and the sapphire substrate was used as the substrate. When the temperature of the tube furnace reached 1500°C, nitrogen was introduced for about one hour with a constant flow of 60 sccm. Then, the samples were taken out and cooled down in the air. Monolayer graphene was prepared by mechanical exfoliation method [1,20]. Highly oriented pyrolytic graphite (HOPG) was stripped to single layer graphene by repeated mechanical exfoliation. The monolayer graphene was then transferred to the SiO_2 (300 nm)/P^+-Si substrate.

2.2 Integration of the van der Waals LED

ZnO nanowires were dispersed in the alcohol solution and further sonicated for 5 min. Then the alcohol solution containing ZnO nanowires was dripped onto the target substrate. After the evaporation of alcohol solution, ZnO nanowires were moved onto graphene by a nanoprobe which was attached to a three-dimensional micro-nano platform. Silver pastes were attached on graphene and ZnO nanowire to act as electrodes.

2.3 Materials characterizations and device measurements

Raman spectra were measured by a Reinishaw system with an excitation laser of 532 nm. The morphology and microstructure of the ZnO nanowires were examined by TEM (Tecnai F-20 operating at 200 kV). PL measurements were performed on a FLS920 fluorescence spectrometer Edinburgh Instruments at temperature ranging from 20 to 290 K with a closed cycle helium cryostat. PL was detected through a Jobin Yvon HR 640 monchromator using a cooled GaAs photomultiplier and conventional lock-in techniques. The sample was excited under low excitation density condition using the 300 nm light produced by a Xe lamp [21]. Current-voltage (*I-V*) characteristics were carried out by Agilent B1500A semiconductor device analyzer. Electroluminescence (EL) spectra were measured by QE pro spectroscope.

3 Results and discussion

3.1 Structure and electrical properties of the heterojunction

The ZnO nanowires were moved upon graphene with a nanoprobe and a heterojunction can be formed between locating at the interface between graphene and surface of ZnO. Figure 1(a) shows the optical image of cross-formed ZnO nanowire/graphene heterojunction. The quality of graphene was confirmed by Raman test, as presented in Fig. 1(b). The almost invisible D peak indicate the high-quality of monolayer graphene [22], while the Raman G peak of graphene locates at 1587 cm^{-1}, which demonstrates graphene is p-type doped [23]. The ohmic contacts with the graphene and ZnO nanowire are achieved by silver pastes [24]. The typical electrical property of a single ZnO nanowire contacted by silver paste is shown in Fig. 1(c), where the linear *I-V* curve demonstrates ohmic contact has been achieved between silver paste and ZnO nanowire. One typical heterojunction LED formed between graphene and ZnO is shown in Fig. 1(d), which is marked as LED 1#.

3.2 Light emitting properties of the heterojunction

The *I-V* curve of LED 1# is shown in Fig. 1(e), which is asymmetrical, indicating heterojunction between graphene and ZnO nanowire has been formed [25]. When a forward bias of 6 V is applied, green light emission of 512.5 nm was observed as shown in Fig. 1(f). There is a limited ultraviolet emission from the LED, which means that most the injected holes from graphene recombine with defects on ZnO nanowire surface or inside ZnO nanowire while the exact origin stays unclear.

3.3 PL spectrum of the ZnO nanowire

As ZnO nanowire is naturally n-type material, the heterojunction formed between graphene and ZnO nanowire is expected. To check the origin of green light emission from LED 1#, the PL spectrum of ZnO nanowires was measured and shown in Fig. 2, where a strong defect related emission locating around 510 nm can be found. The emission band near 510 nm in the PL spectrum agrees well with the 512.5 nm line emitted from the graphene/ZnO nanowire heterostructure LED, which means that the injected holes from graphene recombine with the electron locating near the defects of ZnO. Considering the large surface area of ZnO nanowire, it is naturally to deduce that the defects should locate on the ZnO surface.

3.4 Influence of the forward bias voltage on the performance of LED

For further investigating the dependence of emitted light of the LED on the forward bias voltage, we have integrated another device (LED 2#) with the optical image shown in Fig. 3(a). The *I-V* curve is shown in Fig. 3(b), which is asymmetrical and similar with the LED 1#. The dependence of light emission behavior on the forward bias voltage is shown in Fig. 3(c). At a zero bias, there is no light emission from the LED 2# and when the forward bias increases to 15 V, a strong green light emission near 529 nm is observed while there is a very weak ultraviolet emission locating around 385.7 nm. As the forward bias

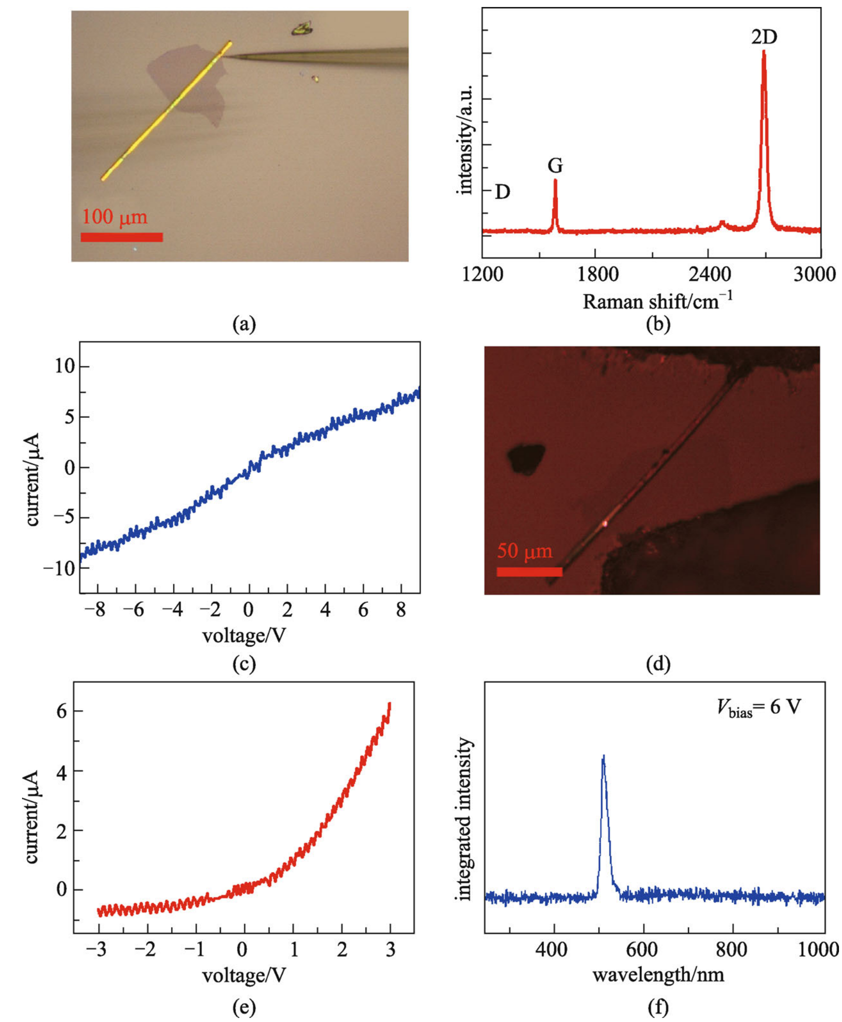

Fig. 1 (a) Optical image of the graphene-ZnO nanowire heterojunction; (b) Raman spectrum of the graphene; (c) *I-V* curve of a ZnO nanowire with Ag paste contacting at both ends; (d) microscopic image of the graphene-ZnO heterojunction marked as sample LED 1# at a forward bias of 6 V; (e) *I-V* curve of LED 1#; (f) light emission spectrum of LED 1# at a forward bias of 6 V

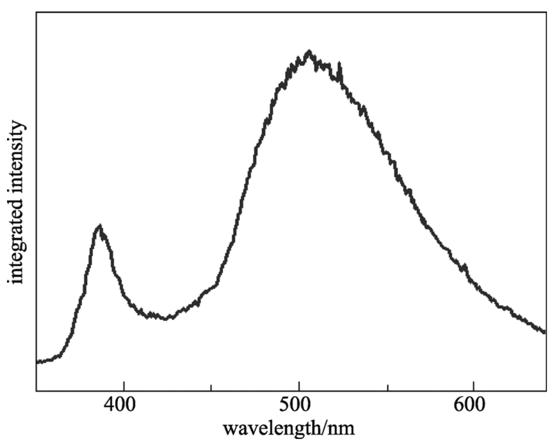

Fig. 2 PL spectrum of the ZnO nanowire

increases further up to 20 V, the intensity of the ultraviolet (385.7 nm) and green light (528.8 nm) band are enhanced. The green emission does not saturate as the forward bias increases, which means that there are a lot of surface defects locating between graphene and ZnO nanowire [26]. The typical optical image of the LED 2# under forward bias is shown in Fig. 3(d), which shows the light emission exhibits a white-like color, as the mixed effect from the ultraviolet-blue band and the green-yellow band. It should be noticed that the LED 2# has weak UV emission, which is different from LED 1#. This is due to the difference of the local defect density at the junction part of the ZnO surface.

3.5 Surface microstructure of the ZnO nanowire

The representative high resolution TEM (HRTEM) image of ZnO nanowire surface is shown in Figs. 4(a) and 4(b), which reveals that the surface are very rough with many ZnO quantum dots. The rough surface permits the high density of surface defects. As a comparison, we have

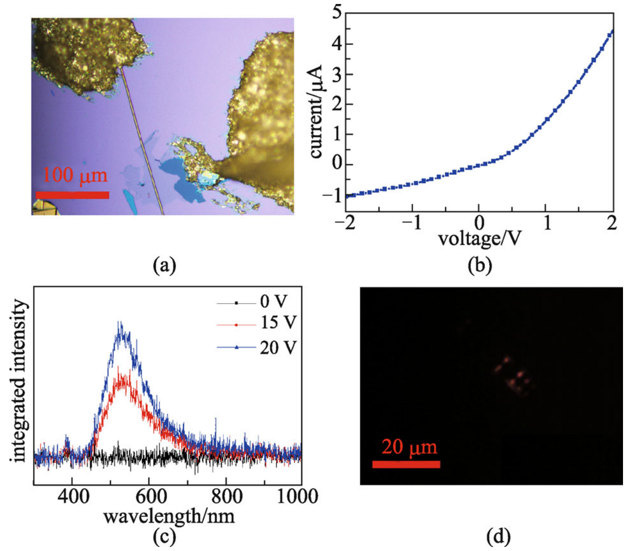

Fig. 3 (a) Microscopic image of the graphene-ZnO heterojunction labeled as LED 2#; (b) *I-V* curve of the LED 2#; (c) spectrum of emitted light at different forward bias voltages; (d) microscopic image of the device with forward bias at 20 V

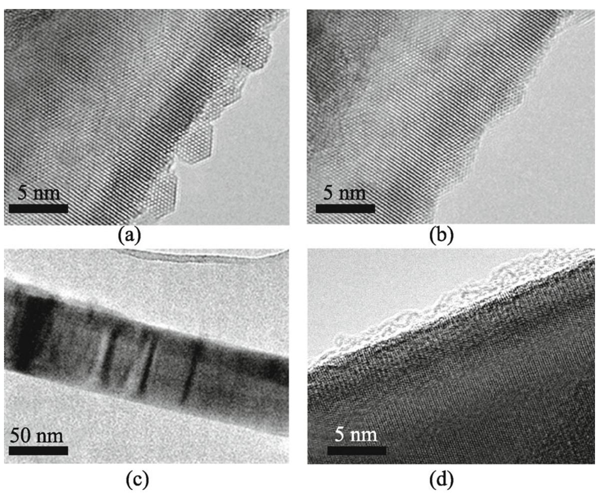

Fig. 4 (a) and (b) HRTEM image of ZnO nanowire with a rough surface; (c) and (d) TEM image of a smooth ZnO nanowire coated with graphene

shown the smooth ZnO nanowire coated with graphene in Figs. 4(c) and 4(d), where the space between graphene and ZnO nanowire is very uniform. There will be much less defects at the interface between graphene and smooth nanowire, compared with the interface between graphene and rough ZnO nanowire.

3.6 Green light emitting mechanism

The mechanism can be qualitatively analyzed with energy band diagrams. As shown in Fig. 5(a), there is a difference between the work function of graphene and ZnO. As graphene contacts with ZnO by the van der Waals force, Schottky contact can be formed between graphene and ZnO, as illustrated in Fig. 5(b) [27]. At a forward bias, the external electric field compensates the built-in electric field and lowers the barrier of the holes. More holes were injected into ZnO nanowire and recombine with electrons near the defects of ZnO nanowire surface, as presented in Fig. 5(c). As the Fermi level of graphene can be widely tuned in a range of –0.9 to 0.9 eV near the Dirac point by a dielectric gating structure [4], we highly believe that the performance of graphene/ZnO nanowire heterojunction based on LED can be enhanced by a more sophisticated device structure.

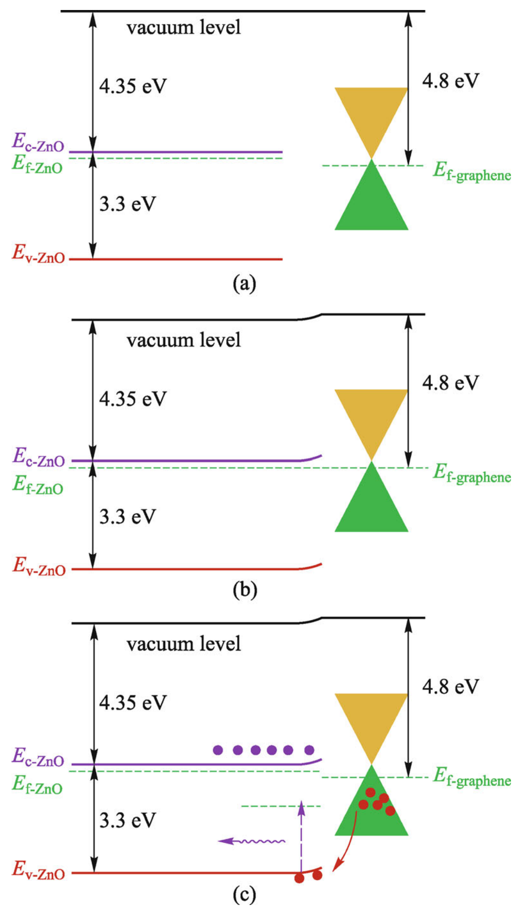

Fig. 5 Schematic electronic band structure of (a) separated ZnO nanowire and graphene; (b) graphene-ZnO nanowire Schottky junction; (c) Schottky junction under forward bias

4 Conclusions

In summary, we have reported that the surface defect engineering of ZnO nanowire could be a very feasible way to produce green light emission from graphene/ZnO nanowire heterojunction. As the forward bias of the LED increases, the green light emission also increases, which means that the surface defects dominates the electron-hole recombination behavior.

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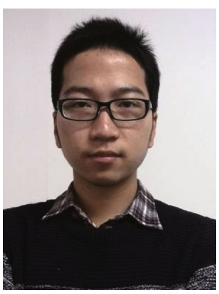

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