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ZnO nanorods/graphene/Ni/Au hybrid structures as transparent conductive layer in GaN LED for low work voltage and high light extraction

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ABSTRACT

In this paper, by virtue of one-dimensional ZnO nanorods and two-dimensional graphene film hybrid structures, both the enhanced current spreading and enhanced light extraction were realized at the same time. A 1 nm/1 nm Ni/Au layer was used as an interlayer between graphene and pGaN to form ohmic contact, which makes the device have a good forward conduction properties. Through the comparison of the two groups of making ZnO nanorods or not, it was found that the 30% light extraction efficiency of the device was improved by using the ZnO nanorods. By analysis key parameters of two groups such as the turn-on voltage, work voltage and reverse leakage current, it was proved that the method for preparing surface nano structure by hydrothermal method self-organization growth ZnO nanorods applied in GaN LEDs has no influence to device's electrical properties. The hybrid structure application in GaN LED, make an achievement of a good ohmic contact, no use of ITO and enhancement of light extraction at the same time, meanwhile it does not change the device structure, introduce additional process, worsen the electrical properties.

1. Introduction

In the field of solid state lighting, signal lights, large screen display and so on, GaN based LED applications are more and more widely. Because of its shock resistance, low energy consumption, long life, high brightness and other advantages, it is gradually replacing the traditional light source [1–4]. But due to the GaN material growth technical limitations, p-type doping concentration of GaN can't achieve high enough. Furthermore, the holes mobility is low, making that the conductivity of pGaN is very poor and need a transparent conductive layer (TCL) to afford an auxiliary conductivity [5,6]. In the current commercial products, indium tin oxide (ITO) is the TCL materials. But the main element indium of ITO is rare earth elements whose earth's reserves are limited, and the price is increasingly expensive. Since its discovery, graphene has attracted extensive research interest because of its unique electrical and optical properties [7]. Graphene is a two-dimensional single atomic layer material composed of carbon atoms arranged in hexagon. The transmittance of monolayer graphene can reach 97.7%, while the carrier mobility can be as high as 15,000 cm^2/V-s or even higher [7,8]. Graphene, which has the characteristics of electric conductivity and transparency, is very suitable to be used as a transparent conductive layer in optoelectronic devices. Kim et al. [9] reported the application of graphene as a transparent conductive layer in GaN LED, obtained the surface uniform illumination of the optical micrograph, and verified the feasibility of the application of graphene as a transparent conductive layer in GaN LED. However, due to the graphene's work function and other reasons, the contact between graphene and pGaN is not ohmic contact [8]. On the other hand, GaN crystal refractive index is 2.43, resulting in photon in the LED difficult to escape from the GaN crystal to external space, which makes the low Light extraction efficiency (LEE) and wall-plug efficiency (WPE) of GaN LED [10,11]. In order to improve the extraction efficiency of GaN LED light, researchers have tried many methods, including using flip-chip LED, special shape LED. But by far the most studied and most promising

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method is texture or nano-structure processing on the surface of the LED. However, graphene is a two-dimensional single atomic layer material, which is not easy for texture processing on the surface. Our research group has done a lot of work about graphene as TCL application in GaN LED, including that, employ ITO nano layer to be interlayer between graphene and GaN to reduce the opening voltage and operating voltage of the device [12]; employ nano structure to improve LEE [13]. At present, the nano structures directly prepared on the GaN all have some damage to the GaN, resulting in an increased leakage current of the device [13,14]. And it is difficult for fabrication. The intrinsic absorption peak of ZnO is 380 nm, transparent for blue light. The preparation of ZnO nanorods, greatly increased the surface area of ZnO, can improve the light extraction efficiency of the device effectively. The ZnO nanorods can be easily obtained by hydrothermal method, and the cost is low, which is suitable for large scale application. In the face of this problem, we propose a new hybrid electrode structure, using two-dimensional graphene and one-dimensional ZnO nanorods, and using Ni/Au as an interlayer, that is, Ni/Au-graphene-ZnO nanorods structure.

In this paper, by using Ni/Au-graphene hybrid transparent conductive electrode spread the surface current on pGaN. ZnO nanorods were successfully prepared on graphene and it increased the probability of photon emission. In order to compare the experiment results, the device was prepared using Ni/Au-graphite hybrid electrode without the growth of zinc oxide. Meanwhile, a normal device with ITO TCL was also prepared for electrical analysis. It turned out to be, the ZnO nanorods can effectively improve the graphene-GaN LED LEE, increase the WPE. In the Ni/Au-graphene-ZnO nanorods structure, Ni/Au was the ohmic contact layer for graphene and pGaN, which confirmed the low turn-on voltage and operating voltage. Due to its self-organization crystal growth, without any etch process, it has no damage to GaN crystal and no change for device structure and electrical properties.

2. Experiment

2.1. Preparation of graphene

The graphene used in the experiment was prepared by chemical vapor deposition (CVD) method. The CVD system was Black Magic graphene deposition system produced by AIXTRON. The catalysts for graphene growth are copper foil with 50 μm in thickness and 99.99% in purity. The growth conditions were as follows: The heater was heated up to 1000 °C and the heating rate was 200 °C/min. H_2 was flowed in and the flow rate was 1000 sccm for 5 min, which was a reduction reaction. Then the H_2 flow rate was reduced, the Ar was increased, until the gas flow rate was 40 sccm, 960 sccm. The deposition of graphene was carried on and the CH_4 was flow in for 5 min and flow rate was 20 sccm. Then the CH_4 was closed, the H_2 and Ar was kept flowing in, the heater was cooled down at 200 °C / min. When the temperature drops to 300 °C, the heater was turned off, naturally cool to 100 °C. The growth was completed.

2.2. Graphene transfer

A layer of PMMA film about 300 nm thick was spun coating on graphene-copper foil with spin time 30 s and spin speed 3000 RPM (round per minute). The PMMA was 960 K in molecular weight and its solution was 4 wt% in weight percentage. The PMMA film was baked on the hot plate at 170 °C for 10 min. The back of copper foil was etched for 2 min by oxygen plasma to remove the graphene on back of the copper foil. The O_2 flow rate was 80 sccm and the plasma power was 75 W. Then the PMMA/graphene/copper foil was placed on the copper corrosive liquid for 2 h. Due to the surface tension of the liquid, the copper foil was floating on the liquid surface. The corrosive liquid is marble solution. After the corrosion, the PMMA/graphene film was transferred to deionized water to remove the ion. The procession was repeated for 3 times. The PMMA/graphene film was transferred to GaN epitaxy wafer, natural air dry. The sample was baked on the hot plate at 170 °C for 15 min. At last, the PMMA was removed by acetone.

2.3. ZnO nanorods growth

Zinc nitrate hexahydrate and hexamethylene tetramine HMTA were used to prepared solution with deionized water. The molar ratio of the two drugs was 1:1 and the solution concentration is 10 mmol/L. The sample was cleaned by acetone, ethanol and deionized water, and baked on hot plate at 200 °C for 5 min. A ZnO seed layer 400 nm in thickness was formed on the sample by magnetron sputtering and the sputtering temperature was 300 °C. The solution was placed in a hermetic container. Then the sample was placed in the solution, meanwhile a holder support the sample suspended in the solution. Then the container was placed in heating box at 80 °C for 8 h. After that, the sample was cleaned by deionized water.

2.4. Preparation of LED device

The GaN LED epitaxial wafer is from the commercial company, the main structure from top to bottom is as follows: 200 nm pGaN, 12 pairs of GaN/InGaN quantum wells as active region, 2 μm nGaN, 2 μm uGaN and sapphire substrate. First, a metal layer Ni/Au (1 nm/1 nm) was prepared as interlayer on GaN LED epitaxy wafer and annealed at 550 °C for 60 s in air. Two layer graphene was transferred to GaN LED epitaxy wafer as current spreading layer. Then ZnO nanorods were grown on graphene. In order to verify the improvement of LEE, two types of LED were prepared. One was the LED with ZnO nanorods, named device 1, and the other one was without, named device 2. For device 1, mesa was defined by lithography, ZnO, graphene, Ni/Au was etched, GaN was etched 1.1 μm in thickness to nGaN. The pad pattern was defined by lithography, and ZnO in the pad area was etched. The patterned pad was prepared. For device 2, the steps of ZnO etching was omitted. Device 3 is a conventional GaN LED with ITO as TCL and the preparation of device 3 was refer to literal [12]. Fig. 1 is the diagram of device 1 and device 2. Device 3 is same to device 2 besides that the TCL of device 3 is ITO. Device 4 is also same to device 2 besides there is no Ni/Au nano layer. The device size is 10 mil $*$ 16 mil.

3. Result and discussion

3.1. Graphene materials

The graphene used in this experiment was single layer graphene with good quality. Fig. 2 is Raman spectroscopy with 488 nm laser as light source. From the Raman spectroscopy, it is can be known that there is no peak around D peak 1350 cm^{-1}. It hints that the defects and boundaries of the graphene growth by this method are few, little response in Raman spectroscopy. At 2680 cm^{-1} and 1584 cm^{-1} there are significant peaks, respectively corresponding to 2D peak and G peak. The ratio of intensity of 2D peak and G peak is 2.6 (2D/G), hinting the graphene is single layer. The sheet resistance was examined by four probe test, which turned out to be 760 Ω/□.