Introducing CuO films as hole transport materials to GaN-based heterojunction LED

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Abstract

The basic structure of p-CuO/n-GaN heterojunction light emitting diodes (LEDs) were demonstrated using CuO films as the hole transport material by frequency reactive magnetron sputtering. The current-voltage (I-V) characteristics of the diodes revealed a typical p-n diode nature with a turn-on voltage of 2.0 V and leakage current of 10^-6 A. The electroluminescence spectra from the p-CuO/n-GaN diodes at different forward bias voltages exhibited blue-light emissions peaked around 446 nm, which was corresponding to the radiative combination between electrons and holes in the depletion region. The blue-light emission was strong enough to be clearly seen by the naked eye at the forward bias voltage of 8 V. Moreover, the working mechanism of the blue emission was preliminary discussed in terms of the energy band diagram of the diode.

1. Introduction

GaN-based materials with excellent opto-electrical performance has been used in light emitting diodes (LEDs) in the past decades. The GaN-based LEDs has the advantages of high carrier mobility and excellent thermal conductivity [1]. The emission of n-GaN based LEDs covered a whole visible range from red to ultraviolet [2]. The hole transport material has been chosen from organic and inorganic material [3]. While the organic material has certain drawbacks for LED applications such as low lifespan, damage in humid environment, screen burn-in, and high-power consumption [4]. To improve the stability of LED diodes and reduce the fabrication cost, some researchers turned their attention to the inorganic material. Mo et al [4] used p-GaN as the hole transport material to fabricate n-ZnO/p-GaN heterojunction diodes. And Wu et al [5] chose Mg-doped p-GaN to fabricate InN-based infrared light emitting diodes. However, the Mg-doped GaN [6] always has the problem of high cost and complicated growth process [7, 8]. Under such conditions, Biswas et al [9] fabricated ZnO-based LEDs by using CuO as the hole transport material. The as-prepared LEDs exhibited prominent near infrared emission peaked at 710 nm under different forward bias voltage. So, the transition metal oxide (for instance CuO [10], ZnO [11, 12], NiO [13–16] etc) are on the search list, which are widely used in optoelectronics due to their stability and easy fabrication [17]. Compared with other transition metal oxide material, the CuO is a stable p-type semiconductor with an indirect band gap and the energy of 1.2–1.9 eV [18, 19]. And also, the CuO has excellent performance [20], such as: chemically stable, cheap, non-toxic and electrochemical activity, etc Hence, in this study, we chose p-CuO as the hole transport material to fabricate GaN-based LED with a simple device architecture and low production cost. The blue-light electroluminescence (EL) spectrum had been realized under different forward bias voltages. Moreover, the structural properties of the CuO films and the modulation of the current-voltage (I-V) and EL characteristics of the p-CuO/n-GaN heterojunction diodes were discussed in detail.
more uniform. Furthermore, the texture coef-

2. Experiments

The CuO thin films were deposited by using the Cu target (99.99% pure, 50 mm diameter and 3 mm thickness) with the high purity (99.9%) sputtering gas (Ar, 40 sccm) and reactive gas (O2, 2 sccm). The growth of the CuO layer was optimized in our previous work under the sputtering temperature of 400 °C, sputtering pressure of 2.1 Pa, sputtering power of 120 W and growth time of 1 h [21, 22]. The internal diameter and height of the vacuum chamber was 350 and 280 mm, respectively. And the bass pressure of the chamber was kept at 2.0 × 10−3 Pa. The commercial n-GaN with the thickness of 2 um was fabricated on the 2 cm × 2 cm sapphire substrate with the c-axis growth orientation ((002)-oriented) for 1 h by metal organic chemical vapor deposition (MOCVD). The Au and In electrodes were fabricated by evaporations and grinding methods on the CuO and GaN layer, respectively. And then, the heterojunction diodes were annealed for 3 min by infrared quick annealing furnace in order to consolidate the connection between the electrodes and films. Finally, the schematic diagram of the p-CuO/n-GaN heterojunction diode was shown in figure 1.

The crystal structure of the CuO films grown on the Al2O3 and GaN-based substrates were examined by x-ray Diffraactometer (XRD, Bruker Advanced D8) in θ–2θ continuous scan using a CuKα (λ = 1.5406 Å, at the work current of 35 mA and work voltage of 35 kV). And the surface morphology and cross-section of CuO films grown on the GaN-based substrates were examined by field emission scanning electron microscope (FE-SEM, JSM-7800F). The electrical properties of CuO films were measured in the van der Pauw configuration by Hall system (ACCENT HL5500PC Hall system with the magnetic field of 0.520 Tesla). And the absorption and transmittance (T) spectra in the 300–900 nm range were acquired using the ultraviolet and visible spectrophotometer (Shimadzu, UVvis-2600) at the room temperature. And the band gap energy was calculated by the Tauc’s formula [18]. Moreover, the current-voltage (I-V) of the diode was measured by sourcemeter 2400 (Keithley 2400). The photoluminescence (PL) spectrum of GaN layer and the electroluminescence (EL) of the p-CuO/n-GaN diode were detected using a He–Cd laser (central wavelength of 325 nm) and home-made acquisition equipment consisting of photomultiplier tube and lock-in amplifier system. All the measurements were performed at room temperature.

3. Results and discussion

The XRD spectrum of CuO films grown on GaN/Al2O3 and Al2O3 substrates under the same conditions are shown in figure 2(a) and (b), respectively. None of the Cu or Cu2O related diffraction peak was detected. As seen from figure 2(a), according to GaN: JCPDS Cards no.76-0703 [23] and CuO: JCPDS Cards no.45-0937 [22, 24], the XRD pattern revealed some diffraction peaks around 2 theta ~34.56°, 32.496°, 35.495° and 38.730° corresponding to GaN (002), CuO (−110), CuO (002) and CuO (111) crystal orientation, respectively. Compare figure 2(a) and 2(b), one can observe that the CuO (−110) diffraction peak of the sample grown on GaN/Al2O3 substrate disappeared, which illustrated that the crystal orientation of CuO grown on the GaN substrates was more uniform. Furthermore, the texture coefficient (TC), regarded as the determining parameters of the crystal orientation, were calculated from the XRD spectrum according to the formula [25, 26]. The TC(002) for the CuO films grown on GaN and Al2O3 substrates was 1.72895 and 0.87457, respectively. The TC(hkl) value of 1 represented a random orientation and the value above 1 meant a preferential orientation of the (hkl) plane [26]. This TC(002) value showed that the CuO grown on GaN-based substrates has (002) preferred crystal orientation.
Those results indicated that the structural quality of CuO films grown on GaN/Al₂O₃ substrates was better than that grown on Al₂O₃ substrates. In addition, the morphologies of CuO thin films deposited on GaN/Al₂O₃ substrates were also investigated as shown in figure 2(c). The FE-SEM image exhibited that the CuO film had a relatively crystal structural and uniform surface. The grain size was measured about 140–250 nm, which were in agreement with the result of XRD spectra at 153–250 nm by Scherrer’s formula [27]. The inset of figure 2(c) showed the cross-sectional image of the CuO film grown on the GaN layer. The CuO layer with a thickness of ∼800 nm was consisted of columnar structure. The transmittance spectrum of CuO film grown on Al₂O₃ substrate was measured and shown in figure 2(d). The result displayed that the transmittance of CuO sample was very low below the wavelength of 500 nm. While the transmittance was above 50% in the wavelength range of 800–900 nm. Moreover, the inset of figure 2(d) displayed the absorption spectrum of CuO sample, which demonstrated that the energy band gap was about 1.43 eV according to the Tauc’s formula [18]. This result was conformed to the energy band gap of CuO [19]. In addition, no PL was observed from the CuO layer in the region of 500–1000 nm. Besides, the electrical characteristic of the CuO layer was analyzed by Hall effect system. The results showed that the CuO films had a high hole concentration of 3.32 × 10¹⁸ cm⁻³ with a mobility of 0.238 cm² V⁻¹ s⁻¹ and the resistivity of 7.924 Ω·cm. This result demonstrated the feasibility of the CuO film as a hole transport layer [27].

The corresponding I-V characteristics of the p-CuO/n-GaN heterojunction diode were shown in figure 3(a). The illustrated showed the contact between the electrode and the membrane. The Au-electrode with p-CuO layer exhibited a quasi-linear behavior, because of the Schottky barriers at both source and drain contacts [28]. It was observed that a typical diode-like nonlinear rectifying behavior with the turn-on voltage of 2.0 V was detected in figure 3(a). Thus, it can be deduced that the rectification behavior origins from the p-CuO/n-GaN heterojunction. In order to investigate the I-V behavior in more obvious detail, we plotted the data on a logarithmic scale in figure 3(b). The I-V curves clearly showed a nonlinear increase of current under the forward bias voltage, and the leakage current of heterojunction diodes was below 10⁻⁶ A, which was the better than that of the result by Jeong’s report [29]. The linear-like increasing trend above 5 V may be due to the presence of the series resistances (Rs) [30]. In the presence of a Rs, the electron emitted some energy by the heat and photons.

Figure 2. (a) XRD pattern of the CuO layer deposited on n-GaN/Al₂O₃ substrate. (b) XRD pattern of the CuO film grown on Al₂O₃ substrate. (c) SEM image of the CuO layer deposited on n-GaN layer. The inset displays the cross-sectional images of the CuO layer. (d) The transmittance spectra of the CuO sample grown on Al₂O₃ substrate. Inset is the absorption spectra of the CuO sample grown on Al₂O₃ substrate.
with electricity. The $R_s$ of the diode could be determined from the slope of the curve ($I \sim 1/(dI/dV)$) in the high-voltage region as shown in the inset of figure 3(b). The $R_s$ was calculated to be 34.2 $\Omega$ by the fitting curve according to the formula from Yao’s [31] and Shi’s [32] report.

The EL spectrum of the p–CuO/n–GaN heterojunction diodes under different forward bias (FB) voltage at room temperature were shown in figure 4(a). No emission occurred at reverse bias (RB) voltage and no obvious peak appeared on the other wavelength. From the EL spectra, the profiles of the EL spectra present well Gaussian distribution and relatively low linewidth (20–30 nm), which was in good agreement with Deng’s report [33]. A strong blue-light emission peaked around 446 nm was observed. No signal intensity on the side of CuO layer were detected because of the lower transmittance CuO below the wavelength of 500 nm [34]. The EL intensity was increased as the FB voltage was increased from 5 to 11 V. The inset in figure 4(a) displays the magnified EL spectrum of the heterojunction diodes under FB voltage of 4–6 V. The obvious EL signal intensity was detected when the voltage was above 5 V. And the shape and peak location were almost unchanged even at the higher FB voltages. The ratio between the peaks intensity of light output under 11 and 10 V voltage was about 3.59, which indicated the possible of application in the visible light communication (VLC) by modulating the light output [35]. Furthermore, the blue-light emission was strong enough to be clearly seen by the naked eye at the FB voltage of 8 V as shown in the illustration in figure 4(b). The work current and peak intensity as a function of voltage were shown in figure 4(b). The increasing trend of luminance intensity was similar with that of the work current. The electrons were accelerated to a given energy, and subsequently excite (or ionize) the luminescent centers, which was corresponding to the rapid increase in the luminance [36]. This result leads to the disproportionate increase for the work current and emission intensity because of the effect of series resistances.

Figure 3. (a) Room temperature I-V characteristics of the p–CuO/n–GaN heterojunction diodes. The inset displays I-V characteristics of the Au contactn on CuO and In contactn on GaN layer. (b) The leakage current of the heterojunction diode on a logarithmic scale. The inset displays $I \sim 1/(dI/dV)$ curves showing the series resistances of the p–CuO/n–GaN heterojunction diodes.

Figure 4. (a) EL spectra of the p–CuO/n–GaN heterojunction under forward voltages. The inset displays the EL spectra of the diode under the forward voltage of 4–6 V. (b) Work current and peak intensity as a function of voltage. The inset displays the corresponding EL emission photograph of the diode in a dark environment at 8 V.
The working mechanism of the p-CuO/n-GaN heterojunction diodes under FB voltage was illustrated in figure 5. Herein, the p-CuO/n-GaN heterojunction diodes had type-II band alignment, determined by the Anderson model [8]. The electron affinity $\chi_{\text{GaN}}$ and $\chi_{\text{CuO}}$ were 4.2 eV and 4.07 eV, respectively, and the band gap of GaN and CuO were 3.4 eV and 1.43 eV, respectively. Then, the conduction band offset was $\Delta E_C = \chi_{\text{GaN}} - \chi_{\text{CuO}} = 4.2 - 4.07 = 0.13$ eV, whereas, the valence band offset was $\Delta E_V = E_{\text{gGaN}} - E_{\text{gCuO}} - \Delta E_C = 3.4 - 1.43 - 0.13 = 1.84$ eV. Figure 5(a) displays the energy band diagram of p-CuO/n-GaN heterojunction diode under the equilibrium condition. Under FB voltages, as shown in figure 5(b), some of holes from CuO layer turned into GaN corresponding level at the condition of higher valence band offset [37–39]. And then the excitons composed of holes from CuO and electrons from GaN conduction band emitted energy and photons. Finally, the photons were generated and the light signals can be detected from the back of the Al$_2$O$_3$ substrate.

4. Conclusion

The GaN-based heterojunction diode using CuO as hole-transport materials were fabricated by magnetron sputtering method. The crystal structure and surface morphology of CuO films exhibited a monoclinic phase and a type of columnar growth. The I-V curves of the p-CuO/n-GaN diode showed a typical rectification behavior and the turn on voltage was about 2.0 V. Moreover, the EL spectra of the diodes revealed stable blue-emissions peaked around 446 nm and the peak intensity steeply increased with the applied voltage increasing from 5 to 11 V. The blue-light emission could be clearly seen by the naked eye at the voltage of 8 V. The working mechanism of the diode was demonstrated from the hole-electron radiative recombination in the depletion region of GaN layer. This study indicated that the CuO films could be a promising hole transport material in the application of GaN-based LEDs.
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