Fabrication of NiO/AlGaN heterojunction UV photodetector by low temperature aqueous method

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Abstract
A NiO/Al0.1Ga0.9N heterojunction structure was prepared using aqueous method. It was composed of NiO nanosheets and Al0.1Ga0.9N film. The device based NiO/Al0.1Ga0.9N heterojunction structure was sensitive to ultraviolet (UV) light illumination. It showed fast decay time of 34 ms and rise time of 30 ms. Moreover, high responsibility of 0.65 A W⁻¹ was achieved at 365 nm UV illumination. The results showed high performance NiO/AlGaN heterojunction UV-photodetector can be obtained using simple way. Meanwhile, it may be promising candidates for novel nanostructures design and high performance device fabrication.

Introduction
In the last few years, many UV detectors have been achieved using p–n junctions and Schottky junction diodes [1–4]. As wide bandgap (3.5 to 6.2 eV) materials, AlₓGa₁₋ₓN was assumed to be possible materials for UV photodetectors applications [5–7]. However, the detectors based on the AlGaN film always have impurities due to difficulties growing high quality p-type material. Thus, the devices based on AlGaN materials often show persistent photoconductivity, which means that they have long decay time after the light source is removed [8, 9]. Persistent photoconductivity behavior has a significant effect on the performance of UV photodetectors. This has limited the development of AlGaN-based detectors for different applications [10–12].

Meanwhile, in order to form AlGaN p–n junction, a different p-type material was always needed to create the junction. As a naturally p-type semiconductor, nickel oxide (NiO) has been widely investigated and it has attracted much attention for electronic device applications [13–15]. Moreover, NiO has similar energy bandgap and closely matched lattice constants (~8%) with AlGaN-based materials, which makes it promising for applications in AlGaN-based electronic devices [16, 17]. Combining the properties of NiO nanostructures with AlGaN film can give full play to their respective advantages. However, it has the large thermal mismatch between AlGaN and NiO materials (~142%), which makes the NiO/AlGaN heterostructure is hard to be achieved by high temperature way. In recent years, the aqueous method has been developed to produce metal oxide materials on various substrate [18, 19]. It has low-cost and low growth temperature, which can obtain high quality NiO layer on AlGaN.

In this paper, a highly sensitive UV sensor based on NiO/Al0.1Ga0.9N heterostructure was fabricated. It composed of NiO nanostructures and Al0.1Ga0.9N film, which displayed high performance UV detection response. The results demonstrated that it can construct high performance NiO/Al0.1Ga0.9N device using aqueous method.
Experimental

In our experiments, the metal-organic chemical vapor deposition (MOCVD) was applied to grow Al$_{0.1}$Ga$_{0.9}$N films. As-grown Al$_{0.1}$Ga$_{0.9}$N film served as the substrate for the subsequent growth of NiO layer. The thickness of Al$_{0.1}$Ga$_{0.9}$N film was 800 nm. Subsequently, The NiO structure was grown using aqueous way, the same growth way has been reported previously [20, 21]. The Al$_{0.1}$Ga$_{0.9}$N film was firstly grown NiO seeding layer. The seeding solution contained 50 mM nickel acetate (Ni(CH$_3$COO)$_2$) with ethanol as the solvent. Then, 30 mM aqueous solution of Ni(CH$_3$COO)$_2$ and hexamethylenetramine (C$_6$H$_{12}$N$_4$) was used to grow NiO layer. The Ni(CH$_3$COO)$_2$ and C$_6$H$_{12}$N$_4$ were dissolved in distilled water under stirring. Then, the seeded Al$_{0.1}$Ga$_{0.9}$N film was placed into the prepared reaction solution, and the temperature was kept at 90 °C. After 3 h of growth, the sample was rinsed with deionized water and dried in air. Meanwhile, NiO nanostructure was also grown on sapphire with the same growth condition for reference.

The structural characteristics of the NiO nanostructures were investigated using x-ray diffraction (XRD). The morphology was examined using scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, Philips CM-200). For the TEM characterization, NiO nanostructure was scratched from AlGaN film. X-ray photoelectron spectroscopy (XPS) was acquired using a Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectrometer. Photodetector devices based on NiO/Al$_{0.1}$Ga$_{0.9}$N heterojunction structure and NiO nanostructures were fabricated using simple methods [22–24]. The UV photoresponse measurements were illuminated under a portable UV LED lamp (λ = 365 nm, 7 mW cm$^{-2}$). A Xe-arc lamp connected with monochromator was acted as the light source to characterize the photoresponsibility.

Results and discussion

Figure 1 depicts the XRD pattern for NiO/Al$_{0.1}$Ga$_{0.9}$N heterostructure. Both the AlGaN and NiO diffraction peaks can be seen. For the NiO nanostructure layer, the weak peaks observed at 37.3° and 42.4° correspond to the (111) and (200) crystal planes, respectively.

Figure 2(a) shows the morphology of the as-grown NiO/Al$_{0.1}$Ga$_{0.9}$N heterostructure with plan view. According to Figure 2(a), the Al$_{0.1}$Ga$_{0.9}$N surface is uniformly covered by sheet-like structure. It can be clearly seen that the NiO nanostructures form interconnected and densely packed morphology. Figure 2(b) displays the cross-sectional image of NiO/Al$_{0.1}$Ga$_{0.9}$N, the thickness of the NiO layer is 800 nm. Figure 2(c) demonstrates the TEM image of NiO nanostructure, sheet-like structure can be clearly seen. Figure 2(d) showed the high-resolution TEM image of marked region in the figure 2(c), the distinct lattice fringes correspond well to the (111) plane of cubic phase NiO with a spacing of 0.25 nm.

The chemical binding energies of the fabricated NiO/Al$_{0.1}$Ga$_{0.9}$N heterostructure were studied by XPS. As shown in figure 3(a), the Ni 2p$^{3/2}$ binding energy locates at 855.4 eV with multiple splitting characteristics [25]. It also showed shake-up structures which are characteristic of NiO (indicated by the arrows). The O 1s peak is shown in figure 3(b) and indicates that oxygen peaks are from the NiO layer.
Figure 4 shows the I-V curve of a NiO/Al0.1Ga0.9N device. The curve is symmetrical due to the symmetrical ITO electrode structure being adopted. The aim of using symmetrical ITO/glass structure is to enhance the contact area between the electrode and NiO nanostructures. Under dark conditions, the current was $2.2 \times 10^{-6}$ A at 3 V. When the device under 365 nm UV light illumination, the photocurrent increases dramatically to be $3.7 \times 10^{-5}$ A.

Figures 5 (a) and (c) show the UV detector device schematic diagram based on NiO/AlGaN/sapphire and NiO/sapphire structures, prepared. The top surface of both samples were contacted with the ITO/glass substrate. ITO coated glass was used as a transparent electrode to cover the NiO/Al0.1Ga0.9N heterojunction structures and ensure full contact with the top NiO layer. Figures 5(b) and (d) show the photoresponse for both devices under the same UV periodic illumination with 30 s on and off. It can be seen that the two devices present different response profiles. Rectangular profile was observed for the NiO/Al0.1Ga0.9N heterojunction structure, which indicated the device had a rapid response behavior.

The time-dependent response curves of the NiO/Al0.1Ga0.9N structure with a 1 s on/off was also obtained to characterize the response properties of the device, which was shown in figure 6(a). The magnified rise and decay edges of device current were demonstrated in figures 6(b) and (c), respectively. A fast UV response was observed for the NiO/Al0.1Ga0.9N photoconductor device. The rise time ($t_r$) is $\approx 30$ ms, which is defined as the time to
move from 10% to 90% of the maximum photocurrent value. The decay time \( t_d \) is \( \approx 34 \) ms, which is defined as the time it takes for the current from 90% to 10%. These results indicated rapid UV response characteristics for the NiO/Al\(_{0.1}\)Ga\(_{0.9}\)N structure.

Figure 7 displays the photoresponse spectrum of NiO/Al\(_{0.1}\)Ga\(_{0.9}\)N structure. It can be observed that the device showed strong UV light detection selectivity between 300 and 400 nm. This meant that the device can be used as photodetector for UV-A (320–400 nm) applications. Meanwhile, the maximum photoresponsivity was obtained at 360 nm and the maximum of photoresponsivity was about 0.65 A W\(^{-1}\).

Figure 8 shows the time-resolved photocurrent response under 365 nm illumination with various light power intensities. The photocurrent increased with the incident optical power. The results showed that the NiO/Al\(_{0.1}\)Ga\(_{0.9}\)N based device is sensitive to the UV illumination power.
The connection between the current and UV intensities is shown in figure 9. The curve meets the power law function, \( I_{\text{light}} \propto P^k \). The fitting results show \( k \) (the power law factor) is 0.8. The non-unity of \( k \) law factor can be linked with the photoresponse process, which is always observed for semiconductor nanostructures [26].

The energy band diagram of the NiO/Al\(_{0.1}\)Ga\(_{0.9}\)N heterostructure was illustrated in the figure 10. For the NiO/Al\(_{0.1}\)Ga\(_{0.9}\)N structure, the electron affinity of Al\(_{0.1}\)Ga\(_{0.9}\)N is 3.84 eV, which is assumed to be linearly dependent on \( x \) and to lie between 0.6 eV for AlN and 4.2 eV for GaN. The electron affinity of NiO is assumed to 1.8 eV. The \( \Delta E_c \) can be calculated using \( \Delta E_c = \chi_{\text{AlGaN}} - \chi_{\text{NiO}} = 2.04 \text{ eV} \). \( \Delta E_v \) can be calculated using \( \Delta E_v = (\chi_{\text{AlGaN}} + E_g\text{AlGaN}) - (\chi_{\text{NiO}} + E_g\text{NiO}) = 2.02 \text{ eV} \). \( \chi_{\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}} \) and \( \chi_{\text{NiO}} \) are the electron affinities of Al\(_{0.1}\)Ga\(_{0.9}\)N and NiO, respectively.
affinities of Al$_{0.1}$Ga$_{0.9}$N and NiO (1.8 eV), $E_{g}$,Al$_{0.1}$Ga$_{0.9}$N (3.68 eV for $x = 0.1$) and $E_{g}$,NiO (3.7 eV) are the band gaps of Al$_{0.1}$Ga$_{0.9}$N and NiO. Under bias voltage with UV light, electron-hole pairs will be generated in the NiO layer due to the lower valence band offset. The sheet-like structure of NiO can enhance the surface area and
charge mobility which result in the device’s high response speed. Thus, high performance NiO/Al$_{0.1}$Ga$_{0.9}$N photoresponse device can be achieved.

Conclusions

In conclusion, low temperature aqueous way was adopted to construct NiO/Al$_{0.1}$Ga$_{0.9}$N heterostructure. The heterostructure displayed excellent UV response properties. This work demonstrated that it can construct NiO/Al$_{0.1}$Ga$_{0.9}$N device using aqueous method. Meanwhile, it may be promising candidates for novel nanostructures design and high performance device fabrication.

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