Vertical-Type Ni/GaN UV Photodetectors Fabricated on Free-Standing GaN Substrates

Bing Ren 1,2, Meiyong Liao 3,*, Masatomo Sumiya 3, Jian Huang 1, Linjun Wang 1, Yasuo Koide 4 and Liwen Sang 2,4,*

1 School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China
2 International Center for Materials Nanoarchitecnotics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
3 Research Center for Functional Materials, National Institute for Materials Sciences, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
4 Amano-Koide Collaborative Research Lab, National Institute for Materials Science, (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
* Correspondence: jianhuang@shu.edu.cn (J.H.); SANG.Liwen@nims.go.jp (L.S.)

Received: 3 June 2019; Accepted: 15 July 2019; Published: 19 July 2019

Abstract: The authors report on a vertical-type visible-blind ultraviolet (UV) Schottky-type photodetector fabricated on a homoepitaxial GaN layer grown on free-standing GaN substrates with a semi-transparent Ni Schottky contact. Owing to the high-quality GaN drift layer with low-density threading dislocation and high electron mobility, the UV photodetector shows a high specific detectivity of more than $10^{12}$ Jones and a UV/visible discrimination ratio of $1530$ at $-5$ V. The photodetector also shows the excellent self-powered photo-response and a high signal-to-noise ratio of more than $10^4$ at zero voltage. It is found that a relatively lower growth rate for the GaN epilayer is preferred to improve the performance of the Schottky-type photodetectors due to the better microstructure and surface properties.

Keywords: GaN; Schottky contact; vertical-type photodetectors

1. Introduction

Ultraviolet (UV) detection is widely demanded in different applications, such as environmental monitoring systems, flame monitoring, gas detection, or medical inspection systems [1]. The III–V nitride semiconductors, with a tunable direct bandgap (3.4 eV for GaN and 6.2 eV for AlN), good chemical and thermal stability, and radiation hardness, are highly promising for the fabrication of photodetectors in UV regions [2,3]. Different structures for GaN-based detectors have been reported, including the Schottky-type, metal-semiconductor-metal (MSM) structures, $p$–$i$–$n$ diodes and avalanche types [4–7]. Among them, Schottky-type photodetectors exhibit the merits of fast response speeds, low-level noises, and self-powered operation, which are attractive for UV detection in remote or extreme conditions. Early Schottky-type GaN UV photodetectors were mainly fabricated on foreign substrates, such as sapphire or Si, and high-density surface states with native disordered oxides or vacancies exist on the GaN layers. The surface states lead to a low Schottky barrier height (SBH) and high leakage currents due to the Fermi-level pining effect, which greatly degrades the device responsivity and reliability [8,9].

Recently, the rapid progress on free-standing GaN substrates offers a good opportunity for the fabrication of high-performance vertical-type opto-electronic devices. A total threading dislocation density (TDD) lower than $10^6$/cm$^2$ has been obtained for commercialized GaN substrates. The homoepitaxial growth and properties of GaN-on-GaN have been investigated by our group.
The surface state density as low as $\sim 10^{11}$ cm$^{-2}$eV$^{-1}$ in the metal-oxide-semiconductor structures were obtained by the two-step pre-treatments [10]. Nearly ideal Schottky barrier diodes with an ideality factor close to unity were also achieved on GaN epilayers grown on GaN substrates with optimized growth rates [11]. However, there is no report on the photo-response properties of vertical-type detectors fabricated on free-standing GaN substrates. In this study, vertical-type Schottky photodetectors on GaN-on-GaN are fabricated with 5-nm-thick Ni as the Schottky contact. The electrical and photo-response properties are characterized by analyzing the carrier transport mechanisms across metal/semiconductor interfaces. The photodetector shows a good spectra selectivity between UV and visible light, and a high detectivity, even at zero voltage. The effects of growth rate in the GaN epilayers on the performance of the photodetectors are also illustrated.

2. Experimental Section

The GaN layers used for the photodetectors were grown on free-standing GaN substrates by metalorganic chemical vapor deposition (MOCVD). The free-standing GaN substrates were in c-axis orientation. The donor concentration and resistivity of the GaN substrate was 1 $\times$ 10$^{18}$ cm$^{-3}$ and 0.01 $\Omega$·cm, respectively, measured by the Hall effect. Trimethylgallium (TMG) and ammonia (NH$_3$) were used as precursors, while the mixed nitrogen and hydrogen were served as the carrier gases. The homo-epitaxial GaN layers were deposited at a relatively lower growth rate of 2.61 $\mu$m/h to reduce the incorporation of unintentionally doped impurities and improve the surface morphology [11]. For Schottky-type photodetectors, a semi-transparent Schottky contact with 5-nm-thick Ni, was deposited by E-beam evaporation patterned by laser lithography and a standard lift-off process. The multiple layers of Ti/Al/Au (20/100/100 nm) were deposited on the backside of the substrates as the Ohmic contacts by sputtering deposition. The schematic structure of the Schottky-type photodetectors is shown in the inset of Figure 1a. The current-voltage ($I$–$V$) measurements were performed using an Advantest picoammeter R8340A and a DC voltage source R6144. The photoresponse was measured in the range from 630 to 300 nm by using a 500 W Xenon lamp. The incident light power was calibrated by a commercial Si photodiode.

![Figure 1](image-url)

Figure 1. (a) I-V characteristics for device-A (5-nm-thick Ni) and device-B (Ni (20 nm)/Au (80 nm)). The reverse I-V curves can be well seen by the TFE model. The inset depicts the schematic structure of device-A. (b) The reverse dark current and photo-current under 350 nm illumination for device-A. The fitting curves governed by TFE are shown.

3. Results and Discussion

In our previous study, a low growth rate of the GaN epitaxial layer is preferred to reduce the incorporation of unintentional impurities such as C or O. The mobility of the GaN drift layer at a growth rate of 2.61 $\mu$m/h was estimated to be 1370 cm$^2$/Vs, and the nearly ideal Schottky contact with an ideality factor $n = 1.04$ and SBH of 0.97 eV were obtained using the Schottky contact of Ni
(20 nm)/Au (80 nm) (named device-B) [12]. However, as a photodetector, to obtain the sufficient UV light absorption, the thickness of the Schottky contact should be less than 10 nm, while this may degrade the $I - V$ properties. The thickness of the Schottky contact of device-B is too thick (Ni (20 nm)/Au (80 nm)), and this device cannot be regarded as the detectors since the electrode is not transparent to the UV light. Therefore, we only compare the $I - V$ characteristics between device-A and device-B. The optical performances are compared among device A, C, and D. Figure 1a is the $I - V$ characteristic of the photodetector with a 5-nm-thick Ni Schottky contact (device-A), in comparison to device-B. As can be seen, the thinner Schottky contact degrades the $I - V$ property both in the forward and reverse regions. The leakage current density is increased by ~2 orders of magnitude, but it still shows a low value of $10^{-7}$ A/cm$^2$ at the applied voltage of ~5 V. In the forward region, the rectifying characteristics of the device-B is also better than that of device-A. The forward $I - V$ characteristic of the Schottky contact can be described by the modified thermionic emission (TE) theory, which is given by [12]:

$$J = J_s \left[ \exp \left( \frac{q(V - IR)}{nkT} \right) - 1 \right]$$

(1)

where $q$ is the electronic charge, $k$ the Boltzmann constant, $T$ the absolute temperature, and $n$ the ideality factor. The saturation current density $J_s$ is expressed by:

$$J_s = AA^* T^2 \exp \left( \frac{-q\phi_B}{kT} \right)$$

(2)

where $A$ is the effective area of the Schottky contact, $A^*$ the Richardson constant (26 A/(cm$^2$·K$^2$) for GaN), and $\phi_B$ the Schottky barrier height. For device-A, the ideality factor $n$ is ~1.8, which is much higher than that of device-B ($n = 1.04$). This is because of the barrier inhomogeneities at the metal–semiconductor interface with the super-thin Schottky contact [13].

The reverse leakage current of the photodetectors can be well fitted by the thermionic field emission (TFE) model [14]:

$$J_{TFE} = J_s \exp \left[ \frac{q(V_R + V_n)}{\varepsilon'} \right]$$

(3)

$$J_s = \frac{A^* T}{\sqrt{\pi \hbar}} \frac{E_{00}}{k} \frac{q}{E_0} \exp \left[ -\frac{q(\phi_B - V_R)}{E_0} + \frac{q(\phi_B - V_n)}{\cosh^2 (qE_{00}/kT)} \right]$$

(4)

$$\varepsilon' = \frac{E_{00}}{E_{00}/kT - \tanh(\E_{00}/kT)}$$

(5)

$$E_{00} = E_0 \cot h(\E_{00}/kT)$$

(6)

$$E_{00} = \frac{q\hbar}{4\pi \sqrt{m^* \varepsilon_s}}$$

(7)

$$V_n = \frac{kT}{q} \ln \left( \frac{N_e}{N_c} \right)$$

(8)

where $m^*$ is the effective electron mass, $V_R$ the applied reverse bias voltage and $\varepsilon_s$ the dielectric constant of GaN. $N_c$ and $N_e$ represent the effective density of states in the conduction band and the electron density on the $n$-GaN surface. $E_{00}$ reflects the tunneling probability. From fitting, tunneling factor $E_{00}$ is estimated to be 2.72 meV and 5.61 meV at room temperature, corresponding to the $N_c$ of $4.52 \times 10^{16}$/cm$^3$ and $1.90 \times 10^{17}$/cm$^3$, for device-B and device-A, respectively. The surface electron density obtained from TFE model was higher than the carrier density inside the GaN drift layer extracted by C-V measurement and dependent on different Schottky contacts [11]. The higher surface electron density is attributed to the unintentional donors at the metal/semiconductor interfaces during the Schottky contact deposition. The difference by using different Schottky contact is from the inhomogeneous distribution of the electrons by the local variations of electric field [11,14]. The highly doped surface...
layer could shrink the depletion width and increase the current tunneling probability at the reverse voltage. Correspondingly, a relatively lower SBH of 0.9 eV in device-A was obtained, compared to that of device-B.

The photo-current of device-A under the UV light (350 nm with a power of 1.32 mW/cm²) illumination is shown in Figure 1b. Compared to the dark current on the order of $10^{-11}$ A at the applied voltage of $-5$ V, the photocurrent at 350 nm illumination is greatly increased. A signal-to-noise ratio of $1.6 \times 10^4$ at $-1$ V and $4 \times 10^3$ at $-5$ V are obtained. Through the carrier transport analysis with different models as above, it is found that the photocurrent is driven by the TFE model, in which the tunneling of the photocurrent may be induced by UV-inspired defects [4].

The spectral responsivity of the device-A from 630 to 300 nm at different bias voltages is displayed in Figure 2a. We note that, the transparence of the 5nm-thick Ni Schottky contact is typically higher than 60% for the UV light [15]. The Schottky-type photodetector exhibits a distinct UV response with a cut off wavelength at 370 nm, which is in the visible-blind region. The peak responsivity is located at 350 nm with the value of 0.16 A/W and an external high quantum efficiency (QE) of 56.4% at $-5$ V. Such values are higher than those in the GaN-based photodetector with W, IrO₂, ITO transparent electrodes [16–18].

If assuming the shot noise is contributed mainly by the dark current, the specific detectivity ($D^*$) can be given by [19,20]:

$$D^* = \frac{R}{(2qJ_d)^{1/2}}$$  \hspace{1cm} (9)

where $R$ is the responsivity, $q$ the elementary charge of electron and $J_d$ the dark current density. The $D^*$ is calculated to be more than $10^{12}$ Jones at the applied voltage of $-5$ V. The specific detectivity is much higher than that in W/GaN UV detectors, benefiting from low noise level. Low TDD and high Schottky barrier height contribute to the low leakage [16]. The discrimination ratio between the UV and visible light is extracted in Figure 2b. At $-5$ V bias, a high spectra selectivity of 1530 is obtained between 350 and 630 nm. It is noted that this ratio is still more than 900 without the applied voltage, indicating a good self-powered capability of the Schottky-type photodetector.

A comparison of detector properties from device-A in present study and the literatures are listed in Table 1. It is found that UV detector with semi-transparent Ni showed better performance than those with W or Indium tin oxide (ITO) electrodes. Low TDD and high barrier height can suppress the leakage current well, resulting in high specific detectivity and high discrimination ratio. An enhancement of UV responsivity originated from the improved quantum efficiency.
Table 1. A comparison of GaN UV detectors from present study with reports from the literature.

<table>
<thead>
<tr>
<th>Detector</th>
<th>$R @ -5\text{ V (A/W)}$</th>
<th>Peak $D^*$ (Jones)</th>
<th>$R_{350}/R_{630}$ @ -5 V</th>
<th>Peak QE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device-A</td>
<td>0.16</td>
<td>$1.47 \times 10^{12}$</td>
<td>1530</td>
<td>56.4</td>
</tr>
<tr>
<td>R1[16]</td>
<td>0.15</td>
<td>$\sim 10^{10}$</td>
<td>-1000</td>
<td>51.8</td>
</tr>
<tr>
<td>R2[18]</td>
<td>$\sim 0.11$</td>
<td>$2.96 \times 10^{9}$</td>
<td>-100</td>
<td>50.0</td>
</tr>
</tbody>
</table>

The time response characteristics of the device-A are investigated by a mechanical chopping method, in which the 350 nm light was switched on and off alternately. The irradiance power was kept at 1.32 mW/cm². As shown in Figure 3a, during several UV on/off cycles, the device showed nearly identical response and stable photo to dark current ratios. As can be seen, the electrical current drops by 4 orders of magnitude within 0.3 s (the limitation of the measurement system) once the UV light is mechanically turned off, indicating a response time of much lower than 0.3 s. It is noted that a slow component with a much lower amplitude is observed during the decay process. This means a very weak persistent photoconductivity (PPC) still exist after the dark current goes to the relative steady state value. The PPC is probably originated from the defects at the interface of Ni/GaN. The slow components in the time response property can be quantitatively analyzed by the bi-exponential relaxation equation, which is expressed by [21]:

$$I = I_0 + Ae^{-\frac{t}{\tau_1}} + Be^{-\frac{t}{\tau_2}}$$

(10)

where $I_0$ is the initial dark current in the slow components, $t$ the time. $A$ and $B$ are fitting constants. $\tau_1$ and $\tau_2$ are relaxation time constants, corresponding to the shallow and deep traps, respectively. Figure 3c–f depict the slow components in PPC fitted by the above equation. The dependence of the relaxation time constants on the bias voltage is extracted in Figure 3b. For the slow component (I), the relaxation time ($\tau_1$) shows a slight reduction with the bias voltage increasing, indicating a faster electron capture speed by the shallow traps at a higher bias voltage. On the other hand, the relaxation time $\tau_2$ exhibits an increasing trend with the applied voltage increasing from 0 to 5 V. The longer relaxation time ($\tau_2$) is suggested to be derived from the deep traps, which are excited under the high electric field, resulting in a longer relaxation time to fill in the deep traps after the UV light is turned off [4].

The same structured Schottky photodetectors fabricated on the GaN layers with different growth rates from 2.61, 4.72, to 7.78 μm/h (named as device-A, C and D) are further investigated and the performances are compared in Table 2. The device-A fabricated on the GaN epilayer with the lowest growth rate shows the best characteristics, including the highest specific detectivity, highest signal-to-noise ratio and shortest relaxation time. These results indicate the relatively lower growth rate for the GaN layer is preferred for the Schottky photodetector to achieve a high responsivity and spectral selectivity [11].

Table 2. The key detector parameters extracted from detector A, C and D. The responsivity, specific detectivity and relaxation time are obtained at $-3\text{ V}$ under the 350 nm illumination.

<table>
<thead>
<tr>
<th>Detector</th>
<th>Responsivity (A/W)</th>
<th>Specific Detectivity (Jones)</th>
<th>$R_{350}/R_{630}$</th>
<th>$I_{350}/I_{\text{dark}}$</th>
<th>Relaxation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.10</td>
<td>$1.47 \times 10^{12}$</td>
<td>1492</td>
<td>8885</td>
<td>1.07 11.20</td>
</tr>
<tr>
<td>C</td>
<td>0.10</td>
<td>$6.19 \times 10^{11}$</td>
<td>1659</td>
<td>1542</td>
<td>1.33 13.59</td>
</tr>
<tr>
<td>D</td>
<td>0.20</td>
<td>$1.19 \times 10^{11}$</td>
<td>891</td>
<td>30.37</td>
<td>1.59 20.9</td>
</tr>
</tbody>
</table>
electric field, resulting in a longer relaxation time to fill in the deep traps after the UV light is turned off [4].

The same structured Schottky photodetectors fabricated on the GaN layers with different growth rates from 2.61, 4.72, to 7.78 μm/h (named as device-A, C and D) are further investigated and the performances are compared in Table 2. The device-A fabricated on the GaN epilayer with the lowest growth rate shows the best characteristics, including the highest specific detectivity, highest signal-to-noise ratio and shortest relaxation time. These results indicate the relatively lower growth rate for the GaN layer is preferred for the Schottky photodetector to achieve a high responsivity and spectral selectivity [11].

Figure 3. (a) Time response of device-A upon the 350 nm light illumination measured by a mechanical chopping method. (b) The relaxation time $\tau_1/\tau_2$ under different bias voltages. (c–f) The slow component during the decay process and its corresponding fitting curve by bi-exponential relaxation equation.

4. Conclusions

In summary, we fabricated vertical-type Schottky-type photodetectors on homoepitaxial GaN layers with semi-transparent Ni contacts. Although the leakage current and the ideality factor of the Schottky contact are degraded as a result of the thin contact compared to the thicker ones, the photodetector still shows good performance as a result of the high-quality GaN drift layer grown on free-standing GaN substrate. A high responsivity of 0.16 A/W and high specific detectivity of more than $10^{12}$ Jones at 350 nm are obtained for the devices fabricated on the GaN epilayer with a relatively lower growth rate. The detectors show the excellent visible-blind spectral selectivity with a cutoff wavelength of 370 nm and a high discrimination ratio (1530 at $-5$ V) between the UV and visible light (350/630 nm). The signal-to-noise ratio at zero voltage is more than $10^4$, indicating a good self-powered capability. The high performances of the photodetectors are beneficial due to the
high-quality GaN drift layer with a high electron mobility and low-density dislocations. A relatively lower growth rate for the GaN epilayer on the GaN substrate is preferred to obtain a high-performance Schottky-type photodetector.

Author Contributions: B.R. did the experiment and measurement; B.R. and L.S. analyzed the experimental results and wrote down the paper; L.S. and J.H. revised the paper; M.L. and L.W. helped on the discussion, paper revision and review; M.S. and Y.K. helped on the discussion, paper review and editing.

Funding: This work was funded by the National Natural Science Foundation of China (No. 11875186), Science and Technology Commission of Shanghai (No. 16010500500), the Ministry of Education, Culture, Sports, Science & Technology (MEXT) in Japan, and JSPS KAKENHI (18K14141).

Conflicts of Interest: There are no conflicts of interest to declare.

References


© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).