Enhancing Responsivity of Porous GaN Metal–Semiconductor–Metal Ultraviolet Photodiodes by Using Photoelectrochemical Etching

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In this paper porous and as-grown GaN metal–semiconductor–metal photodiodes with Ni contact electrodes were fabricated. Structural and optical properties were studied of the both samples. Both detectors show a sharp cut-off wavelength at 370 nm, with a maximum responsivity of 0.14 A/W and 0.065 A/W achieved at 360 nm for porous GaN and as-grown metal–semiconductor–metal photodetectors, respectively. The metal–semiconductor–metal photodiode based on porous GaN shows enhanced twice magnitude of responsivity relative to the as-grown GaN metal–semiconductor–metal photodiode. Enhancement of responsivity can be attributed to the relaxation of stress and reduction of surface pit density in the porous sample. The porous sample showed a significantly low dark current at 5 V as compared to as grown sample.

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1. Introduction

In recent years, many researchers have been focusing on semiconductor-based ultraviolet (UV) photodiodes. Gallium nitride (GaN) is one of the most promising materials for the fabrication of high-responsivity and visible-blind UV detectors, since it has a large direct band-gap energy (3.41 eV) and a high saturation electron drift velocity (310 cm/s) \cite{1, 2}. The superior radiation hardness and high temperature resistance of GaN also make it the suitable material for UV detectors working in extreme conditions \cite{3, 4}. In the past few years, various types of GaN-based photodetectors have been proposed, such as \textit{p–n} junction diode \cite{5}, \textit{p–i–n} diode \cite{6}, \textit{p–π–n} diode \cite{7}, Schottky barrier detector \cite{8}, and metal–semiconductor–metal (MSM) photodetector \cite{9}. Among these, MSM photodetectors exhibit superior performance in terms of the response speed, device noise, and fabrication simplicity.

Porous semiconductors have stimulated much interest recently, primarily due to the potential for intentional engineering of properties not readily obtained in the corresponding bulk solids. These materials exhibit unique chemical and physical properties due to their extremely small size and large surface to volume ratio; therefore it opens possibilities for various potential applications in optoelectronics photodetectors. From the literature, there are a few reports using porous GaN as photodetectors. To achieve a large Schottky barrier height on GaN, one can choose metals with high work functions such as gold (Au), platinum (Pt), palladium (Pd), and nickel (Ni). Ni is an interesting metal that has recently been used as a stable Schottky contact due to its high metal work function.

In this work, porous GaN was used to fabricate Ni Schottky MSM photodetector contacts. For comparative study, a reference MSM photodetector was also fabricated on the as-grown sample from the same wafer using the same processing tools under identical parameters.

2. Experimental procedures

The samples used in this study were commercial \textit{n}-GaN grown by metalorganic chemical vapor deposition (MOCVD) on \textit{Al}_{2}\text{O}_{3} substrate. The electron concentration (Si doped) obtained by the Hall measurements was \( n = 1 \times 10^{17} \text{ cm}^{-3} \). The samples were cleaned first with acetone and methanol, then second in 1:20 NH\(_4\)OH:H\(_2\)O for 10 min, followed by a third cleaning in 1:50 HF:H\(_2\)O solution to remove the surface oxides. This was followed by a fourth cleaning in 3:1 HCl:HNO\(_3\) at 80°C for 10 min. Between the cleaning steps, the samples were rinsed in deionized water. Aluminum was then partly evaporated on the face of GaN using a thermal evaporation system under a pressure of 3.4 \times 10^{-3} Torr, to provide an ohmic contact. By using a home-made teflon cell, we fixed the GaN sample as an anode and Pt wire as a cathode. The electrolyte was a mixture of HF solution and nitric acid HNO\(_3\) (1:4). In the electrochemical etching process...
we used constant current density of $J = 5 \text{ mA/cm}^2$ for 20 min (supplied by a Keithley 220 programmable current source), under a low power UV lamp ($\approx 4 \text{ W}$). After the etching, the samples were rinsed in deionized water, and dried in ambient air. The surface morphology of the samples was examined by scanning electron microscopy (SEM), the optical properties were investigated by high-spatial resolution Raman and photoluminescence (PL) spectroscopy. To fabricate MSM photodetectors, Ni Schottky contacts were deposited onto samples using thermal evaporating system.

3. Results and discussion

Figure 1 shows the images of SEM of the as-grown and the porous GaN films. The as-grown GaN (Fig. 1a) showed a smooth surface morphology. Figure 1b showed a coral-like pore morphologies, may be due to the presence of ammonia in HF:HNO$_3$ (1:4), which has been reported before in InP [10].

Fig. 1. The SEM images of (a) as-grown and (b) porous GaN.

Figure 2 shows the room temperature PL spectra of the as-grown and porous GaN films. We observed a strong excitonic related PL peak at 364 nm (3.39 eV) for porous GaN. The intensity of emitted light is proportional to the number of photons emitted. This means that the number of photons emission is much higher for porous GaN than as-grown GaN, due to the surface roughness and the large surface area. The PL intensity of porous sample was about 5 times compared to that of as grown. The full-width-half-maximum (FWHM) of the excitonic-related PL peak was 7.3 nm for as-grown and 8.8 nm for porous sample.

Fig. 2. Photoluminescence spectra of (a) the as-grown and (b) the porous GaN films.

Figure 3 shows the current–voltage ($I$–$V$) characteristics of the as-grown and porous GaN MSM photodiodes with Ni electrodes measured in dark and under illumination. The photocurrent under UV illumination is obviously higher than the dark current. The dark current of porous sample became smaller than that of as-grown whereas the photocurrents for both photodiodes are similar. The dark current is only about 5 nA at 3 V bias for porous sample due to high resistivity. The Schottky type detector presents a very low dark current due to the high material resistivity and high Schottky barrier height. The inset shows the current gain (ratio of light to dark currents) for both devices, whereby the porous device and the as-grown shows the value at 3 V of 1240 and 78, respectively. This indicates that the enhancement of photoresponse in porous sample is about 16 compared to that in as-grown device.

These $I$–$V$ curves can be fitted well by the well-known thermionic emission theory [11, 12] to calculate the value of the Schottky barrier height (SBH) $\phi_b$. Table summarizes dark and photocurrent measured at 3 V, as well as the ideality factor and SBH of the as-grown and porous samples determined from the $I$–$V$ measurements. SBH was found to be influenced by both the illumination and porosity. The SBHs of both under dark and illuminated conditions were observed to be higher for porous sample compared to the as-grown sample. Under illumination condition, the Schottky barrier heights of both as-grown and porous samples became smaller, this translated to higher current of the photodetectors. Let us note that the change of SBH for porous sample was 0.09 eV as compared to 0.03 eV for as-grown sample, which was three times higher than as-grown sample, indicating that porous GaN sample was more sensitive to illumination.

Figure 4 shows the measured spectral responsivities of the as-grown and porous GaN photodetectors between 250 and 500 nm. The photodetector responsivities were increased slightly until they reached maximum value at
The ideality factor, Schottky barrier height, dark and photocurrent and gain of as-grown and porous samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ideality factor (n)</th>
<th>ϕ_B [eV]</th>
<th>Current at 3 V [µA]</th>
<th>Gain at 3 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-grown dark</td>
<td>2.2</td>
<td>0.83</td>
<td>0.28</td>
<td>–</td>
</tr>
<tr>
<td>as-grown UV</td>
<td>1.5</td>
<td>0.8</td>
<td>21.71</td>
<td>77.5</td>
</tr>
<tr>
<td>porous dark</td>
<td>2</td>
<td>0.9</td>
<td>0.02</td>
<td>–</td>
</tr>
<tr>
<td>porous UV</td>
<td>1.9</td>
<td>0.81</td>
<td>18.62</td>
<td>1241</td>
</tr>
</tbody>
</table>

The porous GaN thin film was generated by a simple photoelectrochemical etching. Coral-like porous structures have been produced. The photodetector on porous GaN is much better than that on as-grown by 16 times and the responsivity and efficiency were double. We have shown that by using a simple and cost effective electrochemical etching one can produce high quality GaN films for high performance photodetector.

4. Conclusions

In this work, fabrication and characterization of interdigitated Schottky type MSM photodetectors based on a porous and as-grown GaN thin film have been reported.

References