Ultraviolet light-emitting diodes and photodiodes grown by plasma-assisted molecular beam epitaxy

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Abstract. We demonstrate a Schottky ultraviolet photodiode (UV-PD) and a UV light-emitting diode (UV-LED) based on AlGaN heterostructures grown by plasma-assisted molecular beam epitaxy. The spectral responsivity of the Schottky UV-PD is 3 mA/W at 271 nm at zero bias and decreases by two orders of magnitude for the spectral range of longer wavelengths (> 300 nm). The sub-monolayer digital alloying technique was used for growing the AlGaN quantum wells in UV-LEDs emitting a single electroluminescence peak at 273 nm.

1. Introduction
Ultraviolet photodiodes and light-emitting diodes (UV-PD and LEDs, respectively) are used in many civilian and military areas, the former including water and air purification, medicine, curing and printing, etc. For the latter, the development of advanced non-line-of-sight covert UV-communications, solar-blind detectors of UV-radiation, and sensors for chemical and bioagents are of great importance.

At present, most AlGaN UV-PD and UV-LED heterostructures with an operating wavelength $\lambda < 300$ nm are grown by using both metal-organic chemical vapor deposition (MOCVD) and plasma-assisted molecular-beam epitaxy (PA MBE) [1-7]. The maximum values of the output power and external quantum efficiency (EQE) as large as 150 mW and ~5%, respectively, have been achieved in the UV-LEDs grown on bulk AlN substrates [8]. Unfortunately, UV-LEDs grown on commercially available c-plane sapphire substrates possess an output power of several mW and the EQE of a few percent, which are related to a high density of non-radiative recombination centers in the active area. Previously, only threading dislocations (TDs) were supposed to be the origin of the non-radiative centers. However, a rather modest improvement of the EQE for the devices grown on TD-free AlN substrates led to a conclusion about the influence of other non-radiative centers [9]. Most probably, different point defects in AlGaN heterostructures can also restrict the EQE of UV-LEDs, and their influence is actively studied now [10]. Therefore, PA MBE operating in the ultra-high vacuum growth environment could be considered as a very attractive growth technique for reducing point defects. Moreover, this technology allows one to grow the AlGaN quantum wells (QWs) in the active area with a sub-monolayer control of the thickness, sharp interfaces, and various composition profiles for the improvement of carrier localization in QWs.
In addition, fabrication of UV-LEDs with a high Al content is hindered by the low doping efficiency of $p$-type layers, high ohmic contact resistance and electron leakage through an electron blocking layer (EBL). The latter leads to a decrease in the EQE and the appearance of a second long-wavelength emission peak originating from a $p$- (Al,Ga)N cladding layer [1].

In our previous works, UV-LEDs emitting at $\lambda = 320$ nm have been grown by PA MBE on standard $c$-Al$_2$O$_3$ substrates by using a new sub-monolayer digital alloying (SDA) technique to form Al$_x$Ga$_{1-x}$N/Al$_y$Ga$_{1-y}$N QWs [4]. Recently, we have also demonstrated the ability of PA MBE to fabricate solar-blind p-i-n photodiodes with polarization-doped $p$- emitters, which exhibit a maximum photoresponse of 35 mA/W at $\lambda = 271$ nm [11].

In this paper, we demonstrate the capabilities of PA MBE in fabrication of sub-300-nm UV-LEDs with SDA AlGaN QWs, as well as initial results on sub-300-nm Schottky PDs.

2. Experiment

The (Al,Ga)N-based heterostructures were grown on $c$-Al$_2$O$_3$ substrates by a PA MBE setup Riber21T equipped with a plasma source offering a flux of activated nitrogen of 0.6 ML/s at 220 W. Firstly, 65-nm-thick AlN nucleation layers were grown by migration enhanced epitaxy on annealed and nitridated substrates at a substrate temperature $T_S = 780^\circ$C, as described earlier [12]. Sketches of the UV-PD and UV-LED structures are shown in figure 1. Both devices have the same 2-µm-thick AlN buffer layer grown at slightly Al-rich growth conditions ($F_{\text{Al}} / F_{\text{N}} = 1.05$ at $T_S = 780^\circ$C) by the metal-modulation epitaxy technique [13]. During the growth of the Al$_{0.75}$Ga$_{0.25}$N:Si (UV-LED) and Al$_{0.55}$Ga$_{0.45}$N:Si (UV-PD) layers with an electron concentration of $10^{18}$ cm$^{-3}$, a periodic change (with a period of about 10 min) of stoichiometric growth conditions from $F_{\text{III}} / F_{\text{N}} = 2$ to 1.6 was used, which led to a corresponding variation of the surface morphology from 2D to 3D. This was done to prevent the Ga-droplets accumulation on the surface and to achieve a relatively smooth and continuous surface morphology [14]. As a result, we could avoid the formation of short-circuiting due to the excess metal accumulated along the extended defects. The results of our previous calculations of the optimal design for AlGaN-based QWs for UV-LEDs were used to determine the nominal parameters of the QWs with an Al$_{0.75}$Ga$_{0.25}$N barrier layer and three QWs having a thickness of 1.5 nm [15]. The QWs were fabricated by the SDA technique using ten 0.25-ML-thick GaN insertions spaced by 0.32-ML-thick AlGaN barriers (figure 1(b)). An electron blocking Al$_{x}$Ga$_{1-x}$N and $p$-doped AlGaN:Mg ([Mg]$-10^{18}$ cm$^{-3}$) layers were grown with a gradient $x = 0.90$-0.85 and $x = 0.85$-0.30, respectively, to obtain polarization-enhanced $p$-doping therein [11]. The UV-LED structure was capped by a 20-nm-thick GaN:Mg layer. Figure 2 shows a cross-section SEM image of the UV-LED heterostructure.
The 100 × 100 µm² mesa type devices were fabricated by accessing the bottom n- AlGaN layers using CCl₄ plasma reactive ion etching. The Ti/Al/Ti/Au and Ni/Au metallizations annealed at 850°C and 450°C were used for n- and p- ohmic contacts for UV-LEDs, respectively. The former was also used for an n- type ohmic contact in UV-PDs, whereas the latter provided a Schottky contact. UV-PD possesses single Schottky and ohmic n- contact pads with areas of 100 × 100 µm² and 200 × 200 µm², respectively. Each UV-LED had a single 200 × 200 µm² n- type contact and a varied number of p- contact pads (1 × 1, 2 × 2, or 3 × 3) which were merged.

Scanning electron (SEM) and optical (OM) microscopies were used for post growth control of UV-LED and UV-PD devices. Current-voltage (I-V) characteristics were measured at room temperature by point contacts by using a Keysight B1505A setup. Electroluminescence (EL) spectra of the UV-LEDs were measured from the substrate side at a cw drive current up to 60 mA. The spectral photoresponse of UV-PDs was measured for the back-illuminated geometry.

3. Results

All devices grown on 2-µm-thick AlN/c-Al₂O₃ buffer layers and ~1-µm-thick AlGaN:Si layers demonstrate the relatively smooth and crack-free surface morphology. Nevertheless, on the ring area located near the edge of a 2-inch-diameter wafer, rare metallic microdroplets with a density of 10⁴ - 10⁵ cm⁻² are formed due to a lower substrate temperature there as compared to the wafer center. The precise control of excessive metal across the whole wafer surface grown at varied stoichiometric conditions should be developed to provide droplet-free growth.

Figure 3 shows I-V and spectral responsivity characteristics of the Schottky UV-PD. The reverse breakdown voltage of the diode is of 18 V, and the dark current is as low as 0.4 µA at -5 V. The non-exponential reverse I-V curve is apparently related to leakage currents exceeding the thermionic emission limited by the Schottky barrier. The typical value of the ideality factor for the Schottky PD is around 2. The maximum spectral responsivity of 3 mA/W at U_{bias} = 0 V was measured at a wavelength of 271 nm, as shown in figure 3(b). This relatively low value (by one order of magnitude lower than that demonstrated by us for a p-i-n UV-PD [11]) was presumably caused by the back-illuminated scheme of the measurements and insufficient transparency of the thick Al₀.₅₅Ga₀.₄₅N buffer layer with the same Al-content as in the active area of the device under the Schottky contact. To overcome this issue, we plan to develop the devices with either a semi-transparent Schottky contact or the increased Al-content in the buffer layers.

![Figure 3. I-V characteristic (a) and spectral responsivity at U_{bias} = 0 V (b) of the Schottky UV-PD.](image)

Figure 4(a) exhibits I-V characteristics of the UV-LEDs with different areas of a p- contact. The devices turn on at ~3 V with a series resistance reduction from 1000 to 130 Ohm with an increase in
the number of $p$-contact pads from $1 \times 9$ to $9 \times (100 \times 100 \text{ } \mu\text{m}^2)$, respectively. It is worth noting that the analogous first UV-LEDs grown using the MOCVD technology demonstrated a smaller series resistance of 20-60 Ohm for devices with a smaller contact area [1,2]. The dependence of the series resistance of UV-LEDs on the $p$-contact area allows us to conclude that its relatively high value is more likely related to poor conductivity of the polarization-doped $p$-layer than to a high $n$-contact resistance. Thus, the method of polarization-doping of AlGaN:Mg layers should be optimized for use in UV-LEDs, or another approach to $p$-type doping should be applied in further experiments. One should also stress that UV-LEDs demonstrate a relatively low turn-on voltage of $< 4$ V that indicates sufficient leakage currents. The ideality factor of the UV-LEDs is as high as 6.

Despite the moderate I-V characteristics, the UV-LEDs demonstrate a distinct EL even for the simplest measurement scheme through the substrate backside and with a top GaN:Mg layer and a Ni/Au $p$-contact adsorbing UV-radiation. Figure 4(b) shows the EL spectra measured at different drive currents for the UV-LED with the largest $p$-contact area. These spectra reveal dominant peaks at a wavelength of $270-275$ nm with a FWHM value of around $30$ nm. In addition, a second emission peak of much lower intensity can be recognized in the spectra at $305$ nm. This is apparently related to a leakage of electrons through the EBL, followed by their recombination in $p$- AlGaN:Mg cladding layers with the Al-content lowering towards the top contact. It should be noted that our first UV-LEDs with a non-optimized design of the top layers demonstrated the EL spectra in which these long wavelength peaks prevailed (not shown), while the QW-related emission was negligible.

**Figure 4.** (a) I-V characteristics of the UV-LEDs with a varied number of $p$-contact pads having an area of $100 \times 100 \text{ } \mu\text{m}^2$ each, as shown in the inset with a plan-view OM image of the device. (b) Electroluminescence spectra of the UV-LED with $3 \times 3$ $p$-contact pads measured under cw injection up to $60$ mA.

**4. Summary**

We have demonstrated the possibilities of PA MBE to fabricate both Schottky UV-PDs and UV-LEDs operating within a solar-blind spectral range ($\lambda < 290$ nm). Further development of the design and technologies is necessary for both types of devices in order to improve their output parameters: namely, to increase the photoresponsivity of the Schottky UV-PD above the achieved value of 3 mA/W and to achieve a higher output optical power for UV-LEDs.

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