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Wavelength dependent photochemical etching of GaN films reveals strong dependence of the photocurrent on the excitation wavelength. Sharp increase in the photocurrent with increasing photon energy is attributed to the onset of absorption above the GaN bandgap. The etching rate of GaN films strongly correlates with the measured photocurrent. No photocurrent and etching is observed for AlGaN films under same conditions. The method could pave the way to the development of truly selective self-stop etching of GaN on AlGaN yielding smooth surfaces for the fabrication of GaN based microcavities.

1 Introduction

Recent reports highlight the potential of GaN based microcavities in which many fascinating phenomena such as polariton amplification [1], stimulated scattering [2], oscillation [3] and lasing [4] demonstrated recently can be realized at room temperature owing to the large exciton binding energy and oscillator strength in this material system [5]. However the development of such devices has been hindered by technological difficulties related to the MBE growth and processing of GaN material.

An important requirement in the microcavity fabrication is the use of high reflectance mirrors, usually in the form of distributed Bragg reflectors DBRs. The main difficulty in fabricating monolithic nitride DBRs with high reflectivity and large bandwidth is the small index of refraction contrast that can be obtained within the entire InAlGaN alloy composition [6]. In addition, thermal and lattice mismatch between AlN and GaN usually leads to highly strained structures and eventually to generation of cracks, all which adversely affect the quality of QWs of the active region [7]. Alternatively laser lift-off (LLO) [8, 9] of InGaN QWs from sapphire substrates has been employed, with subsequent evaporation of dielectric mirrors [10] on both sides, for fabrication of optically pumped VCSELs [11] and vertical-structure blue LEDs [12]. The process flow requires etch-back to remove the uppermost low quality GaN nucleation layer, and reduce the thickness of the optical structure. The etched GaN surface must be smooth, without any etch-induced damages during the etch-back until the etch endpoint. However, until now, there is no well established wet or dry chemical etching technique which is selective within the family of III-Nitride materials, to yield smooth surfaces necessary for high quality microcavity fabrication.

In this work, we investigated the possibility of employing wavelength selective wet photoelectrochemical (PEC) etching technique to selectively etch GaN films on AlGaN, when the excitation energy is above the GaN bandgap and below the gap of the underlying AlGaN material. The use of such selective thinning process in combination with laser lift-off technique for the fabrication of GaN based microcavities is discussed.

2 Experiments

For the development of laser lift-off (LLO) technique used for separation of GaN films from their sapphire substrates, a thick 3 μm GaN film has been grown by MBE on sapphire substrate. Two additional samples have been prepared for selective photochemical etching experiments. The first sample consists of 4 µm thick unintentionally doped GaN (8×10^{14} cm^{-3}) film grown on sapphire substrate. The second sample consists of 300 nm of $Al_{0.32}Ga_{0.68}N$ layer on top of 50 nm of GaN grown over high-resistivity 1 µm thick AlN Aixtron substrate.

In the LLO experiment, the sample is mounted on a quartz substrate using epoxy and is back-illuminated, using multiple 400-600-mJ/cm^2 pulses from a KrF laser with its wavelength tuned at 248 nm and directed through the transparent sapphire substrate with its backside polished. Laser beam homogenizer is used to achieve uniform illumination of the sample. Following laser irradiation, a low-temperature annealing at 60 °C completes the separation process, by melting the Ga-rich interface. Figure 1 shows SEM image of the 3 µm thick GaN film separated from its sapphire substrate by LLO.

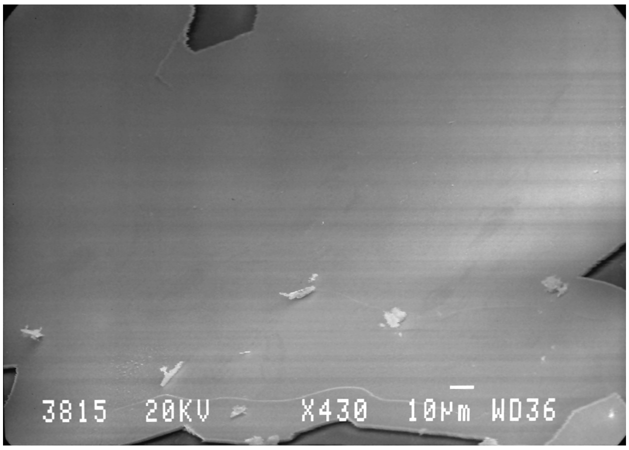

Figure 1 SEM image showing 3 µm thick film following laser lift-off.

Although the proposed GaN microcavity fabrication process involves the use of selective thinning of the above GaN films to the desired thickness following laser lift-off, at this development stage, we perform photochemical etching experiments on newly grown samples to avoid unnecessary complexity.

The photochemical etching of GaN samples was carried out in an electrochemical cell at room temperature using stirred 0.01M KOH solution. Although a number of different electrolyte solutions such as KOH, HCl, H_3PO_4 have been used in the literature for PEC, we have chosen KOH because previous results show that it yields smoother etched surfaces and sharper vertical sidewalls. The electrochemical cell consists of two working electrodes, the anode (GaN film) and the cathode (platinum electrode) dipped in the electrolyte solution. The electrolyte/GaN interface forms Schottky contact. When the sample is illuminated with photon energies above GaN bandgap at 300 K, electron-hole pairs are generated in the semiconductor. The application of a DC bias to the semiconductor, confines the holes at the electrolyte/semiconductor interface, where they participate in the etching process described by the following equations:

Ga oxidation:

$$2GaN + 6h^{+} + 6OH \rightarrow Ga_2O_3 + 3H_2O + N_2\uparrow \qquad (1)$$

and oxide dissolution:

$$Ga_2O_3 + 6OH \rightarrow 2GaO_3^{-3} + 3H_2O\,. \qquad (2)$$

The selective PEC method requires the use of tuneable excitation source near the bandgap of GaN. Since it is not possible to achieve the required illumination densities by spectrally filtering a standard Xe lamp, we employ a tuneable Ti:Sapphire fs laser for excitation. The fs pulses with tuning range of 670-760 nm are frequency doubled in a nonlinear BBO crystal to yield UV pulses in the range of 335 nm-380 nm (about 20 nm below and 30 nm above GaN bandgap at 300 K). The dependence of the photocurrent on the excitation wavelength is measured by monitoring the photocurrent with a digital multimeter.

3 Results and discussion

To study the dependence of the photogenerated carriers participating in the etching process on the excitation wavelength and power, the GaN sample was biased at 4 V, while continuously stirring the 0.01 M KOH solution. The induced photocurrent was recorded at different wavelengths with increasing power density. In Figure 2 the linear dependence of the measured photocurrent on the excitation density for selected wavelengths around GaN bandgap is clearly seen. Linear dependence of the photocurrent on illumination power density has been previously observed in similar experiments under broadband excitation from a lamp [13–17]. This result is expected since there is direct correspondence between the photon flux and the number of photogenerated holes. However the photocurrent results only from the holes that participate in the etching process according to Eq. (1). This is because OH^- ions are essential for the Ga oxidation, thereby at a given OH^- concentration the photocurrent (detected electrons in an external circuit; equal to the number of holes participating in the etching process) increases linearly with the light intensity [16].

Figure 2 also reveals strong dependence of the photocurrent on the excitation wavelength near GaN bandgap. Notably there is an apparent increase in the photocurrent when illuminating at 361.17 nm. This could be attributed to the onset of absorption at the GaN bandgap. Such enhancement in the photocurrent would not have been possible to observe using broadband excitation of previous reports.

To shed more light on this resonant behaviour we performed several experiments on GaN and $Al_{0.32}Ga_{0.68}N$ samples, keeping same conditions (KOH concentration 0.01 M, dc bias 4 V, and stirring) while tuning the excitation wavelength between 345-375 nm (Fig. 3a), keeping the same power density of 2.7 mW/cm^2.

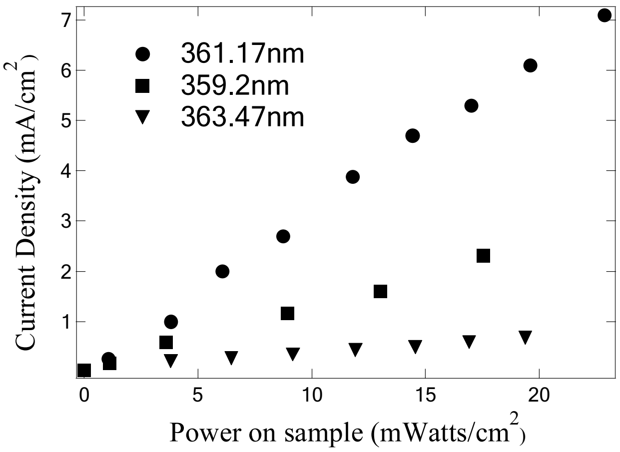

Figure 2 Induced photocurrent vs excitation wavelength. Shows linear dependence of photocurrent on power density and sharp increase when exciting at 361.17 nm.

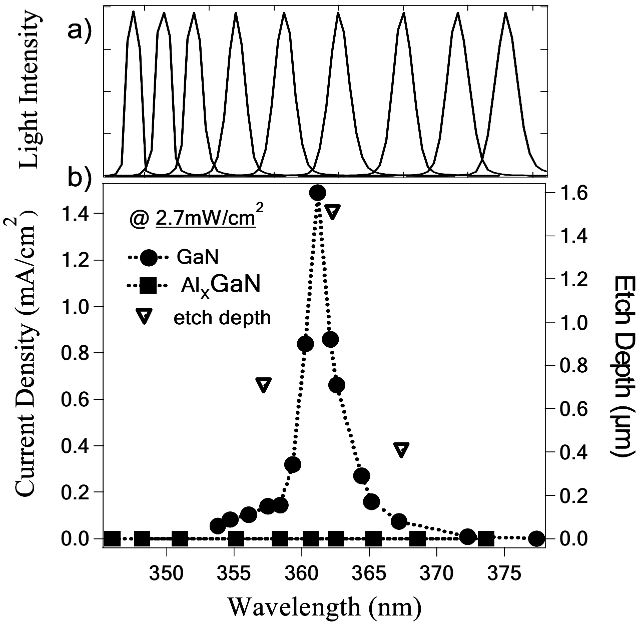

Figure 3 a) Tunable spectra of the frequency doubled fs laser pulses used for excitation in the photochemical etching process. b) Photocurrent vs wavelength dependence for two thin film samples: GaN (circles) and $Al_{0.32}Ga_{0.68}N$ (squares). In the GaN sample, a sharp photocurrent resonance is observed near the GaN bandgap. In triangles, we show the etch depth for three excitation wavelengths on GaN, as measured by profilometer.

Figure 3b reveals sharp resonance in the measured photocurrent which coincides with the onset of absorption at the GaN bandgap. Although an abrupt increase in the photocurrent is expected for photon wavelengths shorter than the bandgap, nevertheless the origin of such sharp resonance can not be understood considering the GaN absorption spectrum. One possibility to account for it is that, when tuning the excitation wavelength, the incident power varied due to the dropping efficiency of the BBO frequency doubling. This could lead to some overestimation of the incident power density at short wavelengths and explain the sharper than expected resonance. More experiments are under way to improve the filtering of the incident laser pulse and clarify this issue.

To independently test that photocurrent is directly related to the etch rate, several tests have been performed on the GaN sample at three selected wavelengths (357.3 nm, 362.4 nm and 367.5 nm) for same etching time and under same etching conditions. The SEM image of the etched sample using 362.4 nm excitation is shown in Fig. 4. As shown in Fig. 3b in triangles, the etch depth correlates well with the measured photocurrent, leading to the conclusion that the etch rate is strongly related to the excitation wavelength.

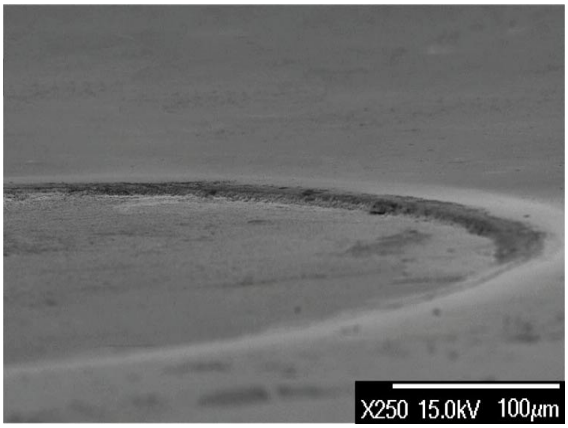

Figure 4 SEM image showing a profile after GaN PEC etching.

Notably, same experiments on $Al_{0.32}Ga_{0.68}N$ sample show no photocurrent at all in this wavelength range. This result is expected, because the excitation used is below the $Al_{0.32}Ga_{0.68}N$ bandgap, resulting in zero absorption and photocurrent. This is remarkable since it suggests that one could exploit GaN photocurrent resonance at 361.17 nm to selectively etch GaN on AlGaN and use it as stop etch layer. Indeed PEC experiments on $Al_{0.32}Ga_{0.68}N$ sample at 361.17 nm reveal no etching at all. Further experiments are under way on structures which incorporate both layers in the same structure with GaN above AlGaN layer to demonstrate a stop etch following the photochemical etching of the GaN layer.

4 Conclusions

We report strong dependence of the photocurrent on the excitation wavelength and show linear dependence of photocurrent on illumination power density. We also find good correlation between measured photocurrent and actual photochemical etch rate. The resonance in the photocurrent is attributed to the onset of absorption above the GaN bandgap. In contrast, zero photocurrents are measured on the $Al_{0.32}Ga_{0.68}N$ sample when exciting at same wavelength and no etching is observed. The above results constitute an important step towards the development of a truly selective self-stop GaN etching which yields smooth surfaces.

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