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Photo-assisted field emission and electro-reflectance modulation investigations of GaN nanorod arrays

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ABSTRACT

GaN cathodes with nanometer-scale diameters were produced by plasma and photoelectrochemical etching of the structure formed on the n^+-GaN substrate with n^+-GaN top active layer. The values of band gap energy for GaN nanorods were determined by electro-reflectance modulation spectroscopy and are 3.374 eV, 3.424 eV, and 3.509 eV for the light and heavy holes, respectively. The energy separation between main (Γ) and satellite (X) valleys was estimated using the field and photo-assisted field emission data and is equal to $\Delta E_{\Gamma-X} = 1.258$ eV.

1. Introduction

Gallium nitride (GaN) is a promising material for high frequency, high power and high temperature electrical and optical devices due to its unique parameters such as high electron saturation velocity, high breakdown voltage, and direct energy band gap [1,2]. Among the possible GaN-based applications, Gunn diodes attracted special attention as powerful generators of electromagnetic radiation in a THz range of frequencies [3]. A key characteristic making GaN suitable for this purpose is its energy band structure with several subbands in the conduction band, similar to those in GaAs. The band structure of GaN was theoretically calculated in Ref. [4] and some of its characteristic values were measured [5,6]. However, while properties of the bulk GaN are well-defined, the properties of nanometer scale multilayered structures which are used in modern devices still remain underinvestigated. Therefore, the characterization of the electronic band structure of nanostructured GaN is an important task required for a controlled design of a multilayered structure. Electro-reflectance modulation (ERM) spectroscopy is one of non-destructive methods usually applied for a determination of direct band gap due to its high resolution and sensitivity to small changes in the band structure [7]. The analysis of electroabsorption spectrum converted by Kramers–Kronig integrals gives the possibility to estimate concentration of electrons in the conduction band, energies of direct optical transitions corresponding to the critical points of the Brillouin zone as well as values of effective masses of electrons. Moreover, assuming that ERM spectrum can be reconstructed by Lorentzian functions, absorption and reflection coefficients can be easily estimated. On the other hand, the possibility of a determination of electron states between the Fermi and the vacuum level by studying the field emission (FE) and the photo-assisted field emission (PA-FE) of electrons has also been reported [8,9]. These methods rely on the change of the work function of electrons under light illumination of the sample surface during electron tunneling according to the Fowler–Nordheim (F-N) law. In this article we combine both methods to get additional information about the band structure of the nanostructured material playing the role of cathode arrays.

2. Experiments and details

GaN nanorods were fabricated on the multi-layered structure consisting of the 5 μm thick n-GaN active layer sandwiched between the n^+-GaN cap layer (100 nm thick, doping element is Si = $5\cdot10^{18}$ cm^{-3}, with the activation energy being 0.12 eV) and the n^+-GaN substrate. The active and the top layers were grown by metalorganic chemical vapor deposition. A photoresist mask was used for the 20 min argon plasma etching of circular mesas with 25 μm diameter and 400 nm height. The n^+-GaN layer was etched

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in the area surrounding the mesa. The samples were then cleaned and etched by photoelectrochemical (PEC) etching in a KOH water solution for 12 min in the presence of Hg lamp illumination, as proposed in Ref. [10]. Process-specific conditions allowed obtaining high PEC etching selectivity between the n^+- and opened n-GaN layers, where n-GaN layer was not affected at all. The GaN field emitter rods resulting by processing are shown in Fig. 1.

We measured the FE and PA-FE current–voltage characteristics of circular mesas on the GaN tip with and without GaN nanorod arrays. An ohmic contact was formed on the back side of substrate, while an indium tin oxide coated quartz window was used as the anode electrode. The distance between the cathode and the anode was controlled by 7.5 μm thick Kapton spacer with 1 mm diameter of the emitting area. The cross section of GaN emitters before and after treatments is presented in Fig. 1c. The UV laser diode ($\lambda = 365$ nm, $\Delta\lambda = 7$ nm, $P_{opt} = 110$ mW) was connected to the anode side outside the vacuum chamber for illuminating the sample during PA-FE measurements. Measurements of the FE and PA-FE were done by Keithley-2410H in the Kelvin mode setup. The voltage sweep step was set to 1 μV with 5000 points per range were measured with collection of error bars, and without any filters applied. To avoid a quick damaging of the samples forward and reverse bias directions were used until the reproducibility in current–voltage curves was observed with the small FE current flow. Additionally, to avoid a short circuit in the equipment with connected samples, a series resistor (11 MΩ with accuracy of 0.1%) was connected to the circuit. More details about the cathode preparation and design features of the vacuum cell used for FE measurements were described in our earlier publications [9,10].

An electrolyte method was used in the measurements of the ERM spectra of GaN [7]. A sample was fixed onto the holder and isolated. A negative biased Pt electrode was placed facing the top surface of the sample dipped in the 0.1 M KCl water solution. The back side of the sample was connected to a positive electrode, and GaIn eutectic alloy was used for obtaining ohmic contacts. A modulating signal of 1500 Hz frequency and 0.3 V amplitude was used with a simultaneous application of a fixed bias voltage in the 0.1 to 0.3 V range. The reflected light beam from the sample was focused on a photo-amplifier combined with a lock-in-amplifier and the detected signal was recorded as a function of frequency.

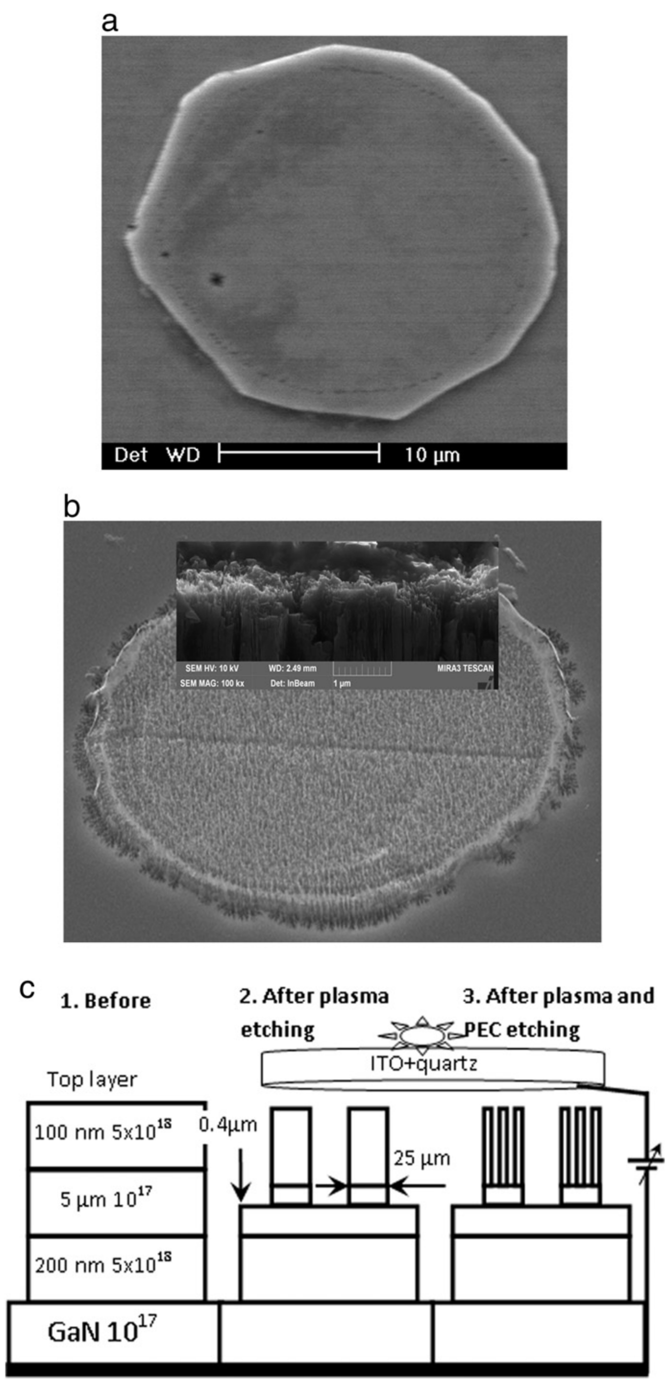

Fig. 1. SEM images of the GaN samples with: a) mesa structure processed by argon plasma treatment (20 min); b) mesa structure with additional photoelectrochemical surface etching (12 min); c) the cross sections of GaN emitters before and after treatments.

3. Results and discussion

3.1. Electro-reflectance modulation spectroscopy

The ERM spectrum of GaN nanorods is plotted in Fig. 2. It shows three features commonly labeled as *A*, *B*, and *C* that can be explained by three interband excitonic transitions $\Gamma^V{}_A - \Gamma^C$, $\Gamma^V{}_B - \Gamma^C$, and $\Gamma^V{}_C - \Gamma^C$, respectively [11–16]. In order to determine the energy values of interband transitions from this spectrum, a standard fitting procedure has been applied solving the equation [10,12]:

$$\frac{\Delta R}{R} = \mathrm{Re}\left[\sum_{j=1}^{3} C_j e^{i\theta_j}\left(E - E_j + i\Gamma_j\right)^{-m}\right], \quad (1)$$

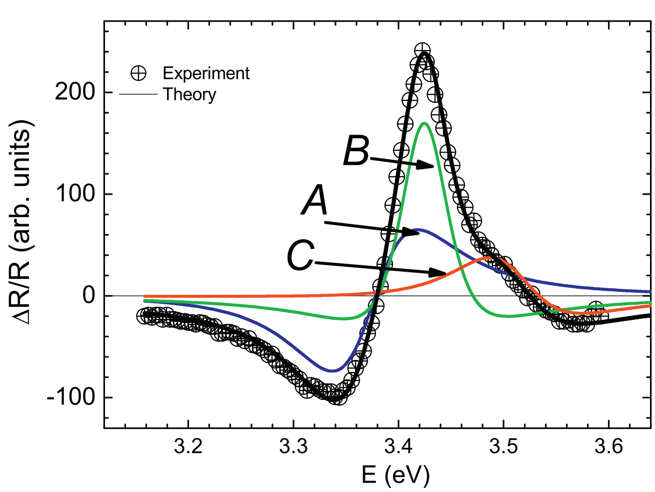

Fig. 2. Electro-reflectance spectra of nanostructured GaN. Decomposition into three peaks (*A*, *B* and *C*) describes three possible interband transitions from light and heavy hole valence bands.