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FABRICATION, TREATMENT, AND TESTING OF MATERIALS AND STRUCTURES

On the Laser Detachment of *n*-GaN Films from Substrates, Based on the Strong Absorption of IR Light by Free Charge Carriers in n^+-GaN Substrates

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Abstract—The physical and technological basics of the method used to lift off lightly and moderately doped *n*-GaN films from heavily doped n^+-GaN substrates are considered. The detachment method is based on the free-charge-carrier absorption of IR laser light, which is substantially higher in n^+-GaN films.

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1. INTRODUCTION

Over the last decade, gallium nitride has found wide use in the manufacturing of light-emitting diodes (LEDs) for the blue-green and near-ultraviolet (UV) spectral ranges, laser diodes, and devices for high-power and microwave electronics. One of the main problems hindering the further development of nitride optoelectronics and power electronics is the lack of bulk GaN substrates. Existing bulk GaN substrates are expensive, which restricts their use in mass production despite the known advantages of homoepitaxy. Manufacturers of semiconductor devices based on InGaN/GaN and AlGaN/GaN structures use sapphire, silicon, and silicon carbide growth substrates. Device structures grown on these substrates contain a large number of dislocations, which is due to the lattice mismatch between GaN and the substrate material.

A possible way to solve this problem is by separating the GaN films and GaN-based device structures from the bulk GaN substrate. The detached film is transferred to a carrier substrate, with the growth substrate repolished and reused [1, 2]. This approach will make it possible to reduce the production cost of devices through the repeated use of expensive GaN substrates and to raise the power of devices [3] by using carrier substrates with a high heat conductivity.

Presently known methods for the detachment of GaN films from growth substrates, namely, Smart-Cut [4], Laser Lift-off [5, 6], chemical detachment with various sacrificial layers (Chemical Lift-off) [7–11], and electrochemical etching [12] cannot solve this problem. The Smart-Cut process based on irradiation of the film being detached with helium or hydrogen ions enables the repeated use of growth substrates after the detachment process. However, it results in the appearance of defects in the film being detached during processing. Being comparatively simple and inexpensive, the Laser Lift-off method is widely used in manufacturing LEDs, but it is only applicable to the detachment of device structures from sapphire growth substrates. The main advantage of the Chemical Lift-off method over laser-detachment techniques consists in that there is no mechanical damage to the films being detached, but it requires that intermediate sacrificial layers be created in the structure being grown, which adversely affects the quality of the device structure.

In this work, we consider the fundamental physical and technological aspects of the process by which *n*-GaN films are detached from heavily doped n^+-GaN substrates due to the absorption of IR light by free charge carriers. It is shown that, at a wavelength of $\lambda = 10.6$ μm, the absorption coefficient in heavily doped regions of a GaN film with an electron concentration of $n \sim 10^{19}$ cm^{-3} exceeds by more than an order of magnitude that in regions with $n \leqslant 10^{17}$–10^{18} cm^{-3}. This makes it possible to detach the substrate in device structures of LEDs, laser diodes, and Schottky diodes for which thin lightly and moderately doped layers of a semiconductor structure are frequently grown on n^+-GaN substrates. When a film or a structure grown on the substrate is illuminated on the lightly doped side with a CO_2 laser, it is possible to create voids filled with gaseous nitrogen or liquid gallium at the interface

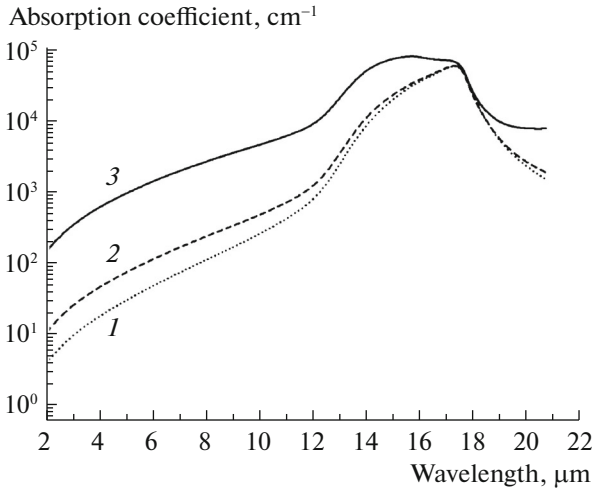

Fig. 1. Spectral dependence of the absorption coefficient for *n*-type GaN with various doping levels, calculated by formula (1). Electron concentration: (*1*) 10^{17}, (*2*) 10^{18}, and (*3*) 10^{19} cm^{-3}.

with the heavily doped substrate as a result of the local overheating and dissociation of GaN due to the strong absorption of IR light. Theoretical estimates show that the dissociation of GaN may begin at $T = 1300$ K [13, 14].

2. THEORETICAL SUBSTANTIATION OF THE METHOD

The basic concept of the method suggested for the detachment of thin semiconductor layers (5–100 μm) and active layers of devices from thick (0.1–2 mm) GaN crystals consists in that the IR absorption coefficients α are not the same in layers with different doping levels.

The free-charge-carrier absorption coefficient $\alpha(\omega)$ is related to the imaginary part $\varepsilon''(\omega)$ of the high-frequency dielectric constant $\varepsilon(\omega)$ by

$$\alpha(\omega) = \frac{2\pi\varepsilon''(\omega)}{r\lambda}, \quad (1)$$

where r is the refractive index [15]. With the plasmon-phonon interaction taken into account, the high-frequency dielectric constant $\varepsilon(\omega)$ has in the isotropic approximation the form

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 - \dfrac{\omega^2 + i\omega\Gamma}{\omega_{TO}^2}} - \frac{4\pi mne^2}{m\omega^2 - \dfrac{i\omega e}{\mu}}. \quad (2)$$

Here, we have for gallium nitride $\varepsilon_\infty = 5.3$ and $\varepsilon_0 = 8.9$ are the optical and static dielectric constants; $\omega_{TO} = 555$ cm^{-1} and $\Gamma = 0.05\omega_{TO}$ cm^{-1} are the frequency and the decay rate of transverse optical phonons [16]; m, e, μ, and n are the effective mass, charge, mobility, and concentration of electrons, respectively. The second and third terms in formula (2) describe the contributions from optical phonons and free charge carriers, respectively.

Figure 1 shows the spectral dependences of the absorption coefficient for *n*-GaN with different doping levels at room temperature, calculated by formula (1). Estimate calculations were made for the electron concentrations $n = 10^{17}$, 10^{18}, and 10^{19} cm^{-3} and $\mu = 450$, 300, and 150 cm^2/(V s), respectively [17, 18].

It can be seen in Fig. 1 that the increase in the absorption coefficient with growing electron concentration is the most pronounced at wavelengths in the range from 6 to 11 μm. The absorption depth z of IR light, along which the light intensity I becomes e times lower than the intensity I_0 of incident light, can be found from the Bouguer law:

$$I(\alpha) = I_0 e^{-\alpha z}. \quad (3)$$

For a CO_2 laser with an emission wavelength of 10.6 μm, the absorption depth of light in GaN, $z < 1$ μm at $n = 10^{19}$ cm^{-3} and $z > 100$ μm at $n = 10^{17}$ cm^{-3} (Fig. 1). Thus, the emission of a CO_2 laser can easily pass through a lightly doped GaN film and be fully absorbed in a gallium-nitride layer with a high carrier concentration. It is believed that the absorbed light will cause heating and the subsequent decomposition of GaN, with a void formed between the lightly doped GaN layer and n^+-GaN layer [4]. This void will be partly filled with liquid Ga and gaseous N_2 under high pressure (Fig. 2).

On the assumption that GaN is fully dissociated within the volume in which light is absorbed, the free volume made available for gaseous nitrogen N_2 can be calculated as $V_{N_2} = V_{GaN} - V_{Ga}$, where V_{GaN} and V_{Ga} are the volumes of GaN and liquid Ga, respectively: $V_{GaN} = k\mu_{GaN}/\rho_{GaN}$ and $V_{Ga} = k\mu_{Ga}/\rho_{Ga}$, where k is the number of GaN moles dissociating to give k moles of liquid Ga and $k/2$ moles of gaseous nitrogen N_2. Taking into account that the densities of GaN, liquid Ga, and gaseous nitrogen N_2 are $\rho_{GaN} = 6.15$ g/cm^3, $\rho_{Ga} = 6.03$ g/cm^3, and $\rho_{N_2} = 0.001251$ g/cm^3 and the molar masses are $\mu_{GaN} = 84$ g/mol, $\mu_{Ga} = 70$ g/mol, and $\mu_{N_2} = 14$ g/mol, respectively, we obtain for $k = 1$ $V_{GaN} = 13.6$ cm^3, $V_{Ga} = 11.6$ cm^3, and $V_{N_2} = 2$ cm^3. The volume occupied by gaseous N_2 under standard conditions ($T_0 = 273$ K) is $V^0_{N_2} = 22400/2 = 11200$ cm^3. Assuming that the Mendeleev-Clapeyron equation is valid both for the initial state of the gas and for its final state, we obtain $PV_{N_2}/P^0V^0_{N_2} = T/T^0$, where $P^0 = 1$ bar is the N pressure at $T^0 = 273$ K. Consequently, the maximum equilibrium pressure of N_2 at a gas temperature T in the resulting void can be estimated by the formula $P(T) = 5600T/273$.

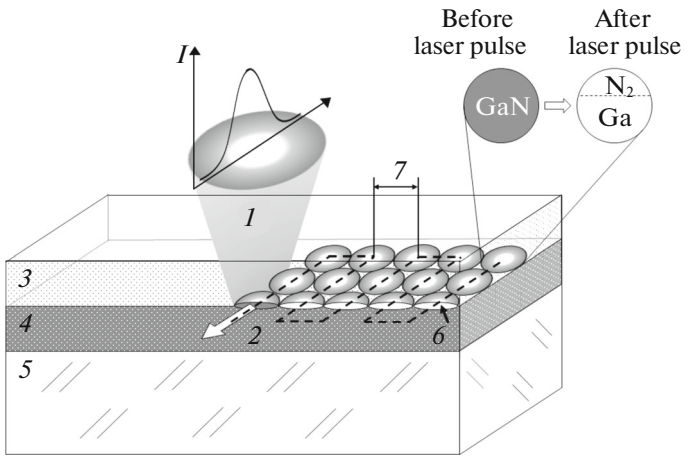

Fig. 2. Schematic of the detachment of GaN films. (*1*) Emission of the pulsed CO_2 laser, (*2*) trajectory and propagation direction of the laser beam, (*3*) lightly doped *n*-GaN layer, (*4*) heavily doped n^+-GaN layer, (*5*) sapphire substrate, (*6*) void formed as a result of GaN dissociation, and (*7*) distance between void centers.

However, the above estimates of the N_2 pressure in the void disregard the expansion of liquid Ga with increasing temperature. Depending on the temperature, liquid gallium can occupy a volume of $V_{Ga}(T) = V^0_{Ga}(1 + uT)$, where $u = 0.85 \times 10^{-4}$ K^{-1} is the volume expansion coefficient of liquid Ga, $V^0_{GaN} = 11.6$ cm^3.

To estimate the N_2 vapor pressure with consideration for the temperature dependence of the volume of Ga, we assume that the volume occupied by gaseous nitrogen can be calculated from the formula $V_{N_2}(T) = V_{GaN} - V_{Ga}(T)$. Hence, the N_2 vapor pressure in the void at a temperature T can be estimated using the formula

$$P^*(T) = \frac{0.5RT}{V_{N_2}(T)}, \qquad (4)$$

where $R = 8.3$ J/(mol K) is the gas constant.

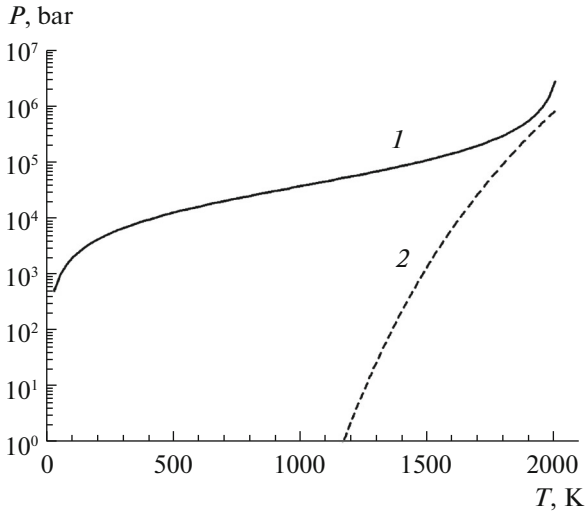

Fig. 3. Temperature dependences of the N_2 pressure in a void, calculated by formulas (*1*) (4) and (*2*) (8) in [13].

In [13], a formula for calculating the N_2 pressure (P^{**}) was derived from the equation for the change in the Gibbs free energy, ΔG, for the case of thermodynamic equilibrium:

$$\Delta G = -RT \ln\left(\frac{(P^{**})^{0.5} a_{Ga}}{a_{GaN}}\right), \qquad (5)$$

where a_{GaN} and a_{Ga} are, respectively, the activities of GaN and Ga in the reaction GaN $\rightarrow$ Ga + 0.5N_2.

Figure 3 shows the temperature dependences of the N_2 pressure within the void, calculated by formulas (4) and (5). At low temperatures, the pressure values differ because of the threshold nature of GaN decomposition, which occurs at $T = 1162.5$ K when $\Delta G > 0$ [13]. At high temperatures, the graphical dependences converge. To obtain a qualitative upper estimate at high temperatures, any of these equations can be used. Thus, the pressure may reach values of ~10^5 bar at a temperature of $T = 1800$ K. Then, the force acting on the film in a round void with a diameter of 10 μm is 6.28 N or 0.64 kg. To avoid cracking of the film as a result of a single shot, it is necessary to focus the laser beam into a spot with the minimum possible diameter. To detach large-area films (2 × 2 mm and more), it is necessary to provide N_2 removal.

3. SAMPLES AND EXPERIMENTAL

3.1. Samples

Samples for study were grown by hydrogen vapor-phase epitaxy (HVPE) on sapphire (0001) substrates with a diameter of 2 in. Preliminarily, the growth surface of the substrate was subjected to nitridation in an atmosphere of ammonia at $T = 1403$ K for 3 min. A 1-μm-thick low-temperature GaN buffer layer was grown at $T = 1123$ K under a pressure of

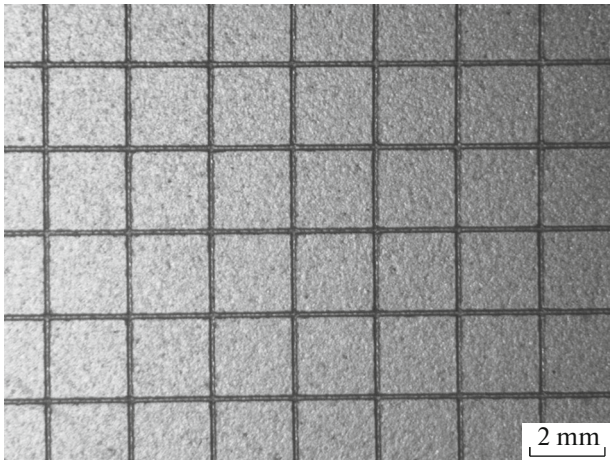

Fig. 4. Optical photograph of a sample upon cutting the GaN film into separate 2 × 2 mm square chips. The backside of a ground sapphire substrate is seen through the thin transparent GaN film.

250 Torr over the course of 3 min. The main growth stage occurred in an atmosphere of nitrogen under a pressure of 800 Torr in two stages. First, an n^+-GaN layer with a thickness of 15–30 μm was grown at $T =$ 1353 K over 7 min. After that the temperature was raised to 1423 K and lightly doped GaN with a thickness of 15–30 μm was deposited over 6 min. The deposition rates for both stages of the growth process were 130 μm/h. A more detailed description of the growth process can be found in [19].

3.2. Sample Preparation before Laser Detachment

Prior to laser detachment, the lightly doped GaN layer was cut through with a CO_2 laser operating in the continuous-wave (CW) mode down to the heavily doped layer as shown in Fig. 4. The chip size was 2 × 2 mm. The working power of the CW laser was 7 W.

3.3. Laser Processing

Sample separation was performed with a pulsed CO_2 laser with a working wavelength of 10.6 μm. The laser-pulse width was ~60 ns at a maximum power of 60 mJ. The energy of the laser pulse incident on the sample surface was varied with a polarization attenuator within the range from 0 to 20 mJ. Laser light was focused with an aspheric zinc-selenide meniscus with a diameter of 27.94 mm and focal distance of 38.1 mm. The sample was moved during processing by a 3D motorized stage with a positioning accuracy of 2.5 μm.

The irradiation process is shown schematically in Fig. 2. The samples were irradiated from the side of the lightly doped GaN layer. Each laser pulse yielded a void at the interface between the lightly and heavily doped GaN layers. During processing, the samples were moved in such a way that the voids came into contact with each other to form close packing. At sufficient proximity of the voids, the film was detached.

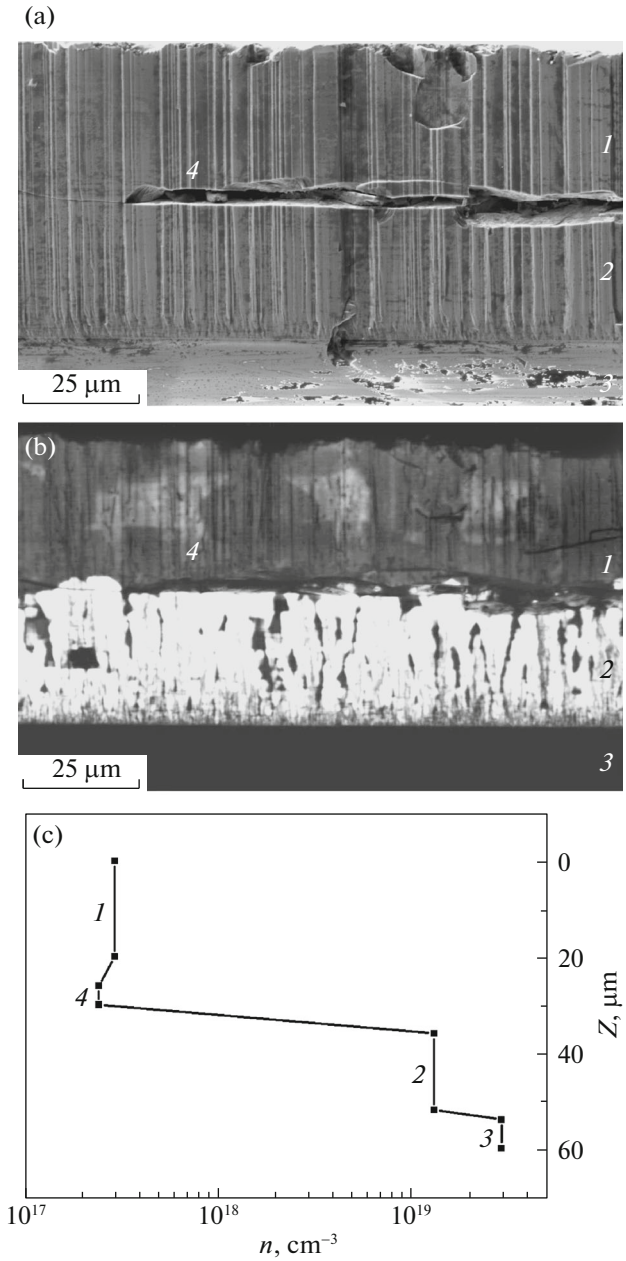

Fig. 5. Cross-sectional (a) SEM and (b) cathodoluminescence images of a film and (c) concentration distribution profile. A void (*4*) and a crack formed as a result of GaN dissociation under the action of pulsed laser light can be seen in a and b: (*1*) lightly doped *n*-GaN layer, (*2*) n^+-GaN layer, (*3*) sapphire, and (*4*) detachment boundary. (c) Electron concentration distribution profile. The numbers correspond to the regions marked in the cathodoluminescence image.

3.4. Detachment of the Processed Parts of the Films

After laser processing, the surface of the treated part of the film was glued to a glass carrier-substrate

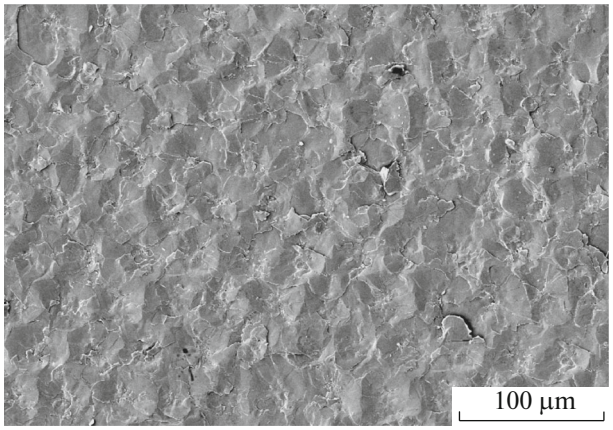

Fig. 6. SEM image of the sample surface upon detachment of a GaN film.

with an adhesive based on cyanoacrylate. Then, the film on the carrier-substrate was detached from the sapphire substrate upon the application of moderate force.

To confirm that detachment occurs at the interface between the doped and undoped layers, the sample irradiated with the laser was cleaved and the resulting cross-section was examined on an installation which included a scanning electron microscope with a cathodoluminescent attachment.

To determine the free-charge-carrier concentration profile across the sample thickness, the cross-sectional Raman spectra were measured. A YAG:Nd (λ = 532 nm) laser served as the excitation source. Its beam was focused into a spot with a diameter of ~1 μm. Measurements were made at room temperature.

The surface morphology was studied by scanning electron microscopy (SEM).

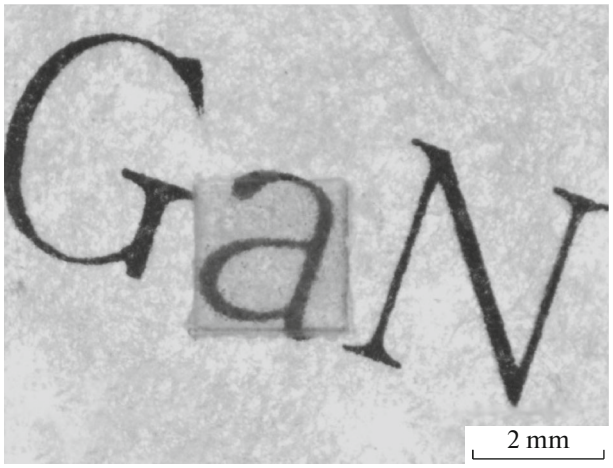

Fig. 7. Optical micrograph of a 15-μm-thick gallium nitride film against a background of printed text.

4. EXPERIMENTAL RESULTS AND DISCUSSION

Figures 5a and 5b show the SEM and cathodoluminescence images of the same part on the edge of a 60-μm-thick film upon its treatment with a pulsed laser. It can be seen in Fig. 5a that detachment occurred at a depth of ~30 μm. Figure 5b shows that the layer above the voids and that below the voids have different contrasts corresponding to high and low doping levels, respectively. The free-charge-carrier concentration distribution across the film thickness, found from the Raman spectra by the procedure described in [20], is shown in Fig. 5c.

A SEM image of the sample surface after detachment of the GaN film is shown in Fig. 6. As a result of exposure to each laser pulse, GaN was decomposed and microcracks appeared, going at a shallow angle into the GaN film being detached [13, 21]. Because of this, the surface of the sample from which the film was detached had irregularities in the form of ordered craters (see Fig. 6). The diameters of the craters vary within the range from 25 to 30 μm, with their depth reaching 1–2 μm.

The micrograph of a free film lying on paper with printed text is shown in Fig. 7. The size of the detached part of the film was 2 × 2 mm, and its thickness, ~15 μm. According to SEM data, the roughness of that side of the film at which the detachment occurred was ~2 μm. It can be seen in the micrograph that the film is transparent to visible light and has no visible cracks. It is noteworthy that the separation of the lightly doped layer into chips (Fig. 4) in the preliminary stage favored successful detachment of all treated parts of the film. Thus, it is desirable to preliminarily separate the films and device structures into chips prior to the detachment process for successful implementation of the procedure under consideration.

In order to determine whether the quality of the film being detached deteriorated after laser processing, the dislocation density of the film surface was examined by the cathodoluminescence method. It was found that the dislocation density in a lightly doped GaN layer [$(7 \pm 2) \times 10^7$ cm^{-2}] remains unchanged within measurement error.

5. CONCLUSIONS

A method was suggested for cutting thin layers of GaN device structures from a heavily doped n^+-GaN substrate with the focused beam of a CO_2 laser. The absorption of laser light in the heavily doped substrate at the interface with the lightly doped layer yields voids filled with liquid Ga and gaseous N_2. At sufficient proximity of the voids, the film is detached.

Films with thicknesses of 15 to 30 μm, dimensions of 2 × 2 mm, and a section plane roughness of ~2 μm were detached. No increase in the dislocation den-

sity in the detached films was observed upon laser processing.

This procedure can be used to detach n-GaN films, device structures of light-emitting diodes, microwave transistors, Schottky diodes, and other lightly and moderately doped n-GaN structures ($n \leqslant 10^{17}$–10^{18} cm^{-3}) grown on heavily doped n^+-GaN substrates ($n \sim 10^{19}$ cm^{-3}) [22].

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