Laser-induced damage threshold and laser processing of GaN

Hong-Bo Sun*a, Saulius Juodkazis†, P. G. Eliseev‡, T. Sugahara§, Tao Wang¶, Shigeki Matsuo∥, Shiro Sakai‖ and Hiroaki Misawa¶

*Nitride Photonics Laboratory, S-VBL, The University of Tokushima, 2-1 Minamijyosanjima, Tokushima 770-8506, Japan
†Department of Electronic and Electric Engineering, The University of Tokushima, 2-1 Minamijyosanjima, Tokushima 770-8506, Japan
‡Department of Ecosystem Engineering, Graduate School of Engineering, The University of Tokushima, 2-1 Minamijyosanjima, Tokushima 770-8506, Japan

ABSTRACT

The single-shot pulse laser-induced damaging thresholds (LIDTs), an important laser-optical constant of GaN material, were determined to approximately 34 and 65 nJ upon the irradiation of 400 and 800 nm wavelengths, 150 fs duration laser pulse focused by 40x magnification of dry objective lens (a lateral size of focal spot roughly at 1.22λ/NA, where NA=0.65). The critical energy of sub-threshold pulses was determined for multi-shot optical damaging. The factors that influenced the LIDTs, optical properties of damaged GaN material and the possibility of laser processing of nitride devices were also discussed.

Keywords: Gallium Nitride (GaN), Femtosecond laser pulse, Femtosecond laser ablation, Laser processing, Laser-induced damage threshold (LIDT), Laser Microfabrication, Photonic crystal

1. INTRODUCTION

The demonstration1 of high-brightness light-emitting diodes (LEDs) and laser diodes (LDs) and the commercial availability2 of LDs under room temperature continuous-wave operation have established III-V nitrides as an important material system for optoelectronics operating in the green-UV spectra range3. On the other hand, femtosecond laser, which emits pulse trains with high transient power (~10⁴ W/pulse), is a powerful tool for the investigation of light-matter interactions4 and laser fabrications5. We are interested in the issue of laser processing of nitrides from two aspects: (i) Materials properties of laser-damaged nitrides. III-V nitrides have proved to be laser and optical related material system with huge application potential. However, a lot of properties of materials are still undetermined since the high-quality bulk material isn’t available until recently. Also the fabrication of nitride devices attracted much more research attention due to

* Correspondence: misawa@eco.tokushima-u.ac.jp, or hbsun@ieee.org
its exciting progresses than the characterizations of material properties. For example, the InGaN-based lasers emit the wavelength of near 400 nm, however, the optical power limit in nitrides, to our knowledge, has not been investigated from the point of view of optical damage. Recent data on power performance of CW LDs suggest that there is no optical damage at the emitted power of more than 100 mW per micrometer of the laser stripe width. Rapid degradation phenomenon in InGaN-based MQW was reported. The damage sites were observed, which were associated with optically assisted internal processes but not at the facet mirrors. (ii) Prospects of laser processing of nitride optoelectronic and photonic devices. Crystalline III-group nitrides are known as inert and robust materials which are not easily treated by a wet etching although a UV irradiation-assisted alkali etching method has been employed. Laser processing may be prospective for material treatment and the fabrication of nitride devices. Actually a Q-switched Nd:YAG laser with 355 nm wavelength and 5 ns pulsewidth has been used to liftoff the epitaxial film from the sapphire substrate.

In this paper, we make a research on the laser-induced damage threshold (LIDT) of GaN at wavelengths of 400 and 800 nm. The properties of damaged materials and the possibility of laser processing are also discussed.

2. LASER-INDUCED DAMAGE THRESHOLD AT 400- AND 800-NM WAVELENGTH

2.1 GaN Sample Preparation and Laser-Processing System

The GaN samples were grown on the sapphire (0001)-oriented (C plane) substrate by a horizontal atmosphere metal organic vapor phase epitaxy (MOVPE) system with three layered laminar flow gas injection. Flow rate of trimethyl-gallium (TMG) and NH₃ used as source gases in GaN growth were 88 µmol/min and 10 SLM (standard liters/minute). The growth temperature for a nominal GaN buffer layer (25 nm) and an epitaxial layer (7.0 µm unless specially specified, and undoped) were 450 and 1075°C, respectively. The full width at half maximum (FWHM) of θ-2θ curve of x-ray diffraction from (0002) plane was 290 arcsec. All the samples exhibited less than 20 nm rms of surface roughness.

Laser irradiation was carried out with a femtosecond laser generation and amplification system. A mode-locked Ti:sapphire laser (Tsunami) pumped by Argon ion laser (Beamlok 2080) operated at the fundamental wavelength of 800 nm. After a chirped pulse amplification by a multikilohertz pulsed Ti:sapphire regenerative amplifier (Spitfire), the pulse energy was lifted by 10⁶ factor up to 1 mJ. The second harmonic of 400 nm was accomplished by a frequency-doubling unit (HGS-T, this and the entire laser system are from Spectra Physics). The pulse energy stability was ±3% and FWHM of the laser pulse was approximately 150 fs. The repetition rate was adjustable in progressional steps from 1 till 1000 Hz. A computer-controlled piezoelectric ceramic stage and a beam shutter were used to fulfill a single-shot irradiation. The laser pulse energy was changed by calibrated neutral density (ND) filters and an aluminum-evaporated disk filter whose transmission was rotation-dependent and therefore continuously adjustable. The laser was focused into a diffraction-limited spot on the GaN layer surface using an inverted microscope (Olympus IX 70). The laser diffraction limitation for the round aperture is defined as \( d = 1.22\lambda/NA = 1.5 \mu m \), where \( NA = 0.65 \) is the numerical aperture of the dry 40× magnification objective lense, which was employed for the focusing of \( \lambda = 800 \text{ nm} \) wavelength. This condition, unless specified, was used for all irradiation experiments. The judgement of focusing the laser on the sample surface was technically important, and was determined as a position where the smallest energy is necessary for introducing the damage. Any deviations from this
focusing level (to the air side or to the crystal) inevitably demanded a higher energy for damage since LIDT inside bulk is much larger than that at the surface (see later in § 2.2).

2.2 Laser-Induced Damage Threshold of GaN and Several Transparent Materials at 400- and 800-nm Wavelengths

For longer pulses, for example, hundreds of picoseconds, the generally accepted picture of the surface damage involved the heating of conduction band electrons by the incident laser and transfer of this energy to the lattice. The damage was caused by the heat deposition resulting in a melting and boiling of the dielectric material. The fractured damaged domain occurred over the entire irradiated area. However, in the case of fs pulses, the laser damage was ablative in nature, dominated by an impact ionization and plasma formation. The modification was confined to a small region at the peak of the Gaussian beam profile, where the intensity was sufficient to ignite multiphoton absorption. With insufficient time for electron-lattice coupling, there was no collateral damage. As a result, the damaged region was highly confined and well shaped within a certain pulse energy range.

When the laser was focused just on the surface of GaN samples, a damaged pit was induced by single-shot pulse irradiation and presented as a dark spot under the transmission image of an optical microscope. The LIDT was determined, as usually done, by in-situ observation of the occurrence of transparency change. The LIDT here was defined as the energy level at which an observable surface modification of the material just appeared at the irradiated spot. The divergence of LIDT from the average in multi-measurement was approximately 10%, which was very possibly from a comprehensive effects of many factors such as the shot-by-shot stability of laser pulse energy, the material uniformity of the epitaxial surface and a fluctuation of the focusing point. According to this definition, the LIDTs for 400 and 800 nm wavelengths with 150 fs of FWHM (focused by an objective lens of 40 X and 0.65 of NA, dry optics) were determined to 34±4, and 65±7 nJ, which corresponded to transient laser fluence of 35 and 16 TW/cm².

Under a focusing condition different from that mentioned above, i.e. by an oil-immersion objective lens (100 X, NA = 1.35), different LIDTs were obtained. For a comparison, LIDTs of several transparent materials determined at this condition are listed in Tab. 1. All data have been normalized to the LIDT value of GaN.

Tab. 1 Laser-induced damage threshold of several transparent materials. The LIDTs were determined under an irradiation of 150 fs laser pulse focused by 100 X, 1.35 of NA and oil-immersed objective lens. The samples were directly contacted the oil.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Wavelength (nm)</th>
<th>Surface LIDT</th>
<th>Materials</th>
<th>Wavelength (nm)</th>
<th>Surface LIDT</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>400</td>
<td>1</td>
<td>V-Silica (SiO₂)</td>
<td>400</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1</td>
<td></td>
<td>800</td>
<td>7.6</td>
</tr>
<tr>
<td>10 GeO₂/90 SiO₂</td>
<td>400</td>
<td>19</td>
<td>Diamond (C)</td>
<td>400</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>5.2</td>
<td></td>
<td>800</td>
<td>5.7</td>
</tr>
<tr>
<td>Rutile (TiO₂)</td>
<td>400</td>
<td>4.3</td>
<td>PMMA</td>
<td>400</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.0</td>
<td></td>
<td>800</td>
<td>4.2</td>
</tr>
<tr>
<td>Sapphire (Al₂O₃)</td>
<td>400</td>
<td>7.2</td>
<td>As₂S₃ (glass)</td>
<td>400**</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>4.0</td>
<td></td>
<td>800</td>
<td>0.13</td>
</tr>
</tbody>
</table>

*Note LIDT values for each material were normalized to those of GaN at 400 and 800 nm, respectively.
Besides the surface damaging, a thick GaN layer allowed us to determine LIDT in the bulk. When the laser was focused 3.5 μm below the sample surface, a bulk damaging threshold of 400 nJ was obtained.

The much difference of LIDTs between surface and bulk can be interpreted by the different mechanism of matter response to the laser excitation. After valence electrons were pumped by a MPA, the ensuing process depended on the excitation site was on (near) the surface or inside the material. In the former case, the damaging was a laser ablation, while the latter featured a microexplosion followed by a material densification (for this, we have clear evidence at least of vitreous silica and sapphire). In the case of inner damage, our observation contradicted with that reported by Mazur group\(^{10}\), who claimed that LIDTs for different materials were quite similar. It seems that LIDTs depends not only on the absorption efficiency of MPA which involves, at least, irradiation photon energy and bandgap width of solids.

2.3 Spot Size and Shape versus Laser Pulse Energy

A damaged spot was observed when the laser pulse energy increased beyond LIDT. Then its size increased monotonously with increased pulse energy. Fig. 1 shows optical microscopic images of pits created with different irradiation intensity. A well-defined spherical shape was achievable until approximately 3 times of LIDT, which set a limitation for the fabrication of microstructures that demanded a regular circle. The laser pulse energy in the figure has been normalized to the value of LIDTs of 800 nm wavelength. For a convenience of comparison, we will use the same strategy in the following paragraphs.

![Fig. 1 Optical microscopic images of pits induced by 150 fs laser pulses at 800 nm of wavelength. The pulse energy have been calibrated by the LIDT (65 nJ) and is A—1.5, B—2.0, C—2.3, D—2.9, E—4.0, F—5.7, G—8.0, H—11.4, I—16 and J—23. The scale bar is 5 μm.](image)

An atomic force microscope (AFM, SPI3700, Seiko) was employed to recognize the details of the damaged region. Since the resolution was at a level of several nanometers, any tiny variation on the surface could be resolved. Fig. 2 shows AFM images of the pits induced by the laser of wavelengths of 400 nm (a) and 800 nm (b). From series of measurements, we found that the LIDTs determined by microscope were consistent with those by an AFM. The dark site under optical microscope was reflected with pits under an AFM. The profile of damaged bits, abstracted from (a), was shown in Fig. 4 (c).
Fig. 2 AFM images of pits induced by single-shot laser pulses with wavelengths of 400 nm (a) and 800 nm (b), and the bit profiles (c) abstracted from (a). In (a) the pulse energy levels are A—0.9, B—1.4, C—1.8, D—2.5, E—3.6 and F—5.2 times of (LIDT)_{nm}, where (LIDT)_{nm} is about 34 nJ. In (b) the energy levels are A—2.0, B—3.0 and C—24 (LIDT)_{nm}, and the value of (LIDT)_{nm} was approximately 65 nJ. Note the difference of scales in different images.

Depending on the incident pulse energy, the depth of pit ranged from 20 nm to 240 nm, which would be less than the real value due to the limitation of the pyramid AFM tip geometry.

Different from the depth measurement, the lateral size was obtained more accurately. Shown in Fig. 3 are the laser pulse energy-dependent diameters of hole. The irregular area from higher energy irradiation has been calibrated to equivalent circles.
The size of holes was related with the light field distribution, but not solely determined by it. Medium properties (absorption constant, bandgap width, elastic coefficient, etc) must be involved. This was manifested by the fact that the laser diffraction limitation was constant for a specified wavelength, while the size of ablated holes depended significantly on the laser pulse energy. The ablated hole can be generated from very small (e.g. hundreds of nanometers) to several tens of micrometers. A significant difference between the two wavelengths was that 800 nm seemed give much larger pits. This perhaps arose from a larger diffraction limitation for a wavelength of 800 nm.

### 2.4 Sub-Threshold Effects and Multi-Shot Irradiation

We have obtained single-shot thresholds for both 400 and 800 nm wavelengths. If the laser energy was continuously decreased from the threshold level, still we have the possibility to ablate material by multishot irradiation. However, the shot number necessary for introducing the ablation rapidly increased, till a critical value, below which no any visible damage can be achieved no matter how many shots were exerted as shown in Fig. 4.

This critical value meant a new threshold, which was intuitively termed as multi-shot laser induced damaging threshold, \((\text{LIDT})_M\), while the values in Tab. 1 were single-shot ones, \((\text{LIDT})_S\). In the current fabrication condition, \((\text{LIDT})_M\) was half of \((\text{LIDT})_S\). The initial damage at \((\text{LIDT})_M\) may have many forms: ablation of a few atomic layers, formation of a color center, shallow traps, or lattice defects. These weak effects were very difficult to detect. From a multi-shot irradiation, the damage was “amplified” to an easily observable size. No any trace of damage were observed even after irradiation of more than \(10^3\) shots at one location if the average energy delivered to the sample was reduced by 3%. This showed an extremely sharp threshold resulting from the multiphoton ionization.

In the case of single-shot irradiation, when the laser pulse energy was higher than approximately 3 times of \((\text{LIDT})_S\),
the shape of pit became irregular. It was natural to ask whether there were some means to get larger round holes in the sample surface. An alternative way was multi-shot irradiation to the same site. Fig. 5 shows an image of pits introduced by different shot number under a fixed energy of 1.1(LIDT). With the pulse number increased, the hole size also increased, while the shape wasn’t distorted, which implied that multi-shot fabrication could be an effective way to enlarge the hole size, instead of using higher power.

2.5 Thermal Effects, Focusing and Interface States

In current fabrication, the light absorption was from MPA process of valence electrons. When pumped electron density wasn’t high enough to destroy the covalent bond, the energy would be dissipated by the light-emission and Auger recombination. The latter process would ultimately transfer the energy to heat the lattice. When the laser energy was sufficiently high, such a process would take place following the surface ablation. The problem is, at how much degree the thermal effect influences the threshold. We recorded the shot number necessary to induce visible damage in GaN surface at different repetition rate as shown in Fig. 6. The laser pulse energy was about 1.1(LIDT). The data features scattering around a constant, which means, even at the repetition rate of 1 kHz, the thermal dissipation is fast enough so as that thermal effect can be neglected.
Under a tight focusing with high NA, the laser was not delivered as a parallel beam. The distribution of the intensity and the wave vectors in a light electric field in the focal point were determined by focusing conditions (magnification and NA of objective lens). In addition, the surface LIDT was also found to be strongly related with the surface state of the dielectric. In almost all the ablation experiments of this work, dry optics was used, which offered a dielectric/air interface. Absorption and thermal conductivity of some liquids on the sample surface facilitated the ablation, or vice versa. The ablation thresholds were found changed accordingly. Also the shape of ablated regions varied very much under different solid/liquid interfaces. Shown in the figure is an optical microscopic image of irradiated GaN surface pasted with a red oil ink. Even the laser pulse energy was 5 times lower than previously-obtained (LIDT)$_5$, still the surface was damaged. The site of GaN damaging was represented by the central spot as shown in Fig. 7 and the large circle was the region where ink was evaporated.

It is noteworthy to emphasize that different from (LIDT)$_5$, the value of (LIDT)$_m$ wasn't sensitive to the condition of imaging system. For example, a low-resolution CCD camera would overestimate the (LIDT)$_5$, however, (LIDT)$_m$ repeated itself very well. Only if the laser energy reaches (LIDT)$_m$ level, a pronounced damaging can be ultimately achieved with an increasing of the shot number of laser pulse.

Fig. 6 Shot number necessary for inducing a visible optical damage at different repetition rate. The wavelength of laser is 800 nm.

Fig. 7 Laser-irradiated oil-ink pasted GaN surface. The large circle was from the evaporation of ink and the central dot was from the ablation of GaN. The laser wavelength was 800 nm and laser pulse energy was approximately 15 nJ. The four arrow bars point the center of damage.
3. OPTICAL PROPERTIES AND APPLICATIONS OF LASER-DAMAGED GALLIUM NITRIDE

Surface machining was characterized by the fabrication of micromechanical structures from the deposited thin film. Originally employed for integrated circuits, film composed of materials such as polycrystalline silicon, silicon nitride and silicon dioxides were deposited and selectively removed to build or "machined" three-dimensional structures whose function typically required that they be freed from the planar substrate\(^1\). For achieving this, conventional techniques included the wet and dry etching were extensively employed. Here, we are investigating another possibility, i.e. using a femtosecond laser ablation for creating some microstructures, which is especially important for III-V group nitride since they are not easily processed by general etching methods. Several central issues to this technique are the spatial resolution, the aspect ratio and the material selectivity. The spatial resolution in laser microfabrication reaches down to several hundreds nanometer (see, Fig 2) and different material layer can be in part discriminated by their different laser damaging thresholds. However, the aspect ratio of the structures isn’t adjustable. Another important problem is whether the neighborhood of the damaged sites were degraded since the light field distribution in the focal plane was not demarcated by a sharp border, but with a gradually changed profile, e.g. a Gaussian distribution. In this section, we will deal with this issue and demonstrate a fabrication example.

![Fig. 8 Spatially-resolved mapping of a damaged GaN film surface. (a) PL mapping. The upper is an optical microscopic image and the lower is 8 linear-level gray-scaled PL map. (b) CL mapping. The upper is a SEM image and the lower is from the CL measurement. The bits were fabricated at 800 nm wavelength and energy level of 12 (LIDT)\(_h\), for (a) and 6 (LIDT)\(_h\), for (b). In the both cases of mapping, no monochrometer was used for luminescence measurements.](http://spiedl.org/terms)
3.1 Photoluminescence Properties

AFM image indicated a little material accumulation at the rim of the damaged spots. This inspired us to investigate whether properties of material near the damaged pits were modified by the laser ablation. Optical characteristics are one of important indexes for assessing materials quality. A spatial photoluminescence (PL) mapping was done with the far-field operation mode of a near-field scanning optical microscope (NSOM, Lumina Topometrix). A water-cooled micro-channel photomultiplier tube (PMT, R3809-50U, Hamamatsu Photonics) was used as a detector. To avoid spectral overlapping of the excitation and the PL wavelengths, and to improve the lateral spatial resolution, a two-photon absorption strategy was adopted. Fs laser pulses with 150 fs of duration, 730 nm of the wavelength at 82 MHz of the repetition rate were used for excitation. The laser fluence was lowered more than 20 times as compared to that necessary to launch the surface ablation. Shown in Fig. 8 (a) is the image of the PL mapping (lower inset) and corresponding transmission image (top). Depending on the level of the focal point, the pit region in the mapping presented either as a dark (just on the surface) or as bright (near the bottom of pits) regions. Fig. 8 (a) is the latter case, where the strong emission is perhaps ascribed to a strengthened carrier recombination due to the increased interface state. A monochrometer will be used in the future experiment to acquire the information of PL wavelength responsible for the light emission in defect region.

A quite similar phenomenon was obtained in cathodoluminescence (CL) measurement [Fig. 8(b)]. From both CL and PL mapping, it was found that the luminescence region was almost fitted the damaged area. Therefore, material properties seem not be severely modified at the rim of damaged bits.

3.2 Preliminary Fabrication of Some Microstructures

When the laser pulse was sufficiently high, e.g. >10 (LIDT)$_3$, some splashed fillings were accumulated around the ablated sites. The particle size ranged from less than 10 nm to micrometers. If the ablation occurred on an epilayer consisted of quantum well structures, the particles would have strong 3D quantum confinement effects, i.e., as quantum dots. Size of several nanometers is never accessible by conventional etching techniques. This quantum dot can be useful for the characterizations of the optoelectronic characteristic of nitride devices. A line structure is also achievable by scanning sample surface at a high repetition rate of laser pulse with the adjusted pulse energy and stage velocity.

![Surface Ablation Holes](image)

![GaN epilayer](image)

![Silver film](image)

![Light](image)

![Sapphire Substrate](image)

Fig. 9 A quasi-2D triangular photonic crystal structures that supports a surface mode propagation. (a) The cross section of the designed structure, and (b) AFM images of an array of surface ablated pits. The fabrication wavelength was 400 nm and laser pulse energy was 2(LIDT)$_3$. 

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A most direct application of the ablated pits is arranging them into a periodic array, which acts as quasi-2D photonic crystal structure. A quasi-2D triangular photonic lattice is shown in Fig. 9. When the surface was evaporated with a thin layer of metal, e.g., silver [Fig. 9 (a)], the structure of metal/dielectric will support a surface mode. Since such modes are bound to an interface, mode propagation can be completely blocked by photonic band gap that operates in just the remaining two dimensions. A fine structure has been achieved now and device characteristics are under characterization.

CONCLUSION

The LIDT, an important optical constant, has been determined for GaN at two wavelengths. The multishot damage threshold was obtained, which is considered directly related with an accumulation of irreversible structural damage. Although the absolute value of LIDT varies from material to material, a lot of pure transparent dielectrics should show a similar behavior since they share the same general properties such as fast electron-scattering, rapid Joule heating, and slow thermal diffusion. Therefore the observation here should apply to more transparent solid materials. For the laser ablation fabrication of nitride microstructures, great effort is needed to address the issue of practical applications, the results of the quasi-2D photonic crystal represented a proof-of-principle demonstration of fabrication of periodic array structures.

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