

Toward the realization of erbium-doped GaN bulk crystals as a gain medium for high energy lasers

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Er-doped GaN (Er:GaN) is a promising candidate as a gain medium for solid-state high energy lasers (HELs) at the technologically important and eye-safe 1.54 μm wavelength window, as GaN has superior thermal properties over traditional laser gain materials such as Nd:YAG. However, the attainment of wafer-scale Er:GaN bulk or quasi-bulk crystals is a prerequisite to realize the full potential of Er:GaN as a gain medium for HELs. We report the realization of freestanding Er:GaN wafers of 2-in. in diameter with a thickness on the millimeter scale. These freestanding wafers were obtained via growth by hydride vapor phase epitaxy in conjunction with a laser-lift-off process. An Er doping level of 1.4×10^{20} atoms/cm³ has been confirmed by secondary ion mass spectrometry measurements. The freestanding Er:GaN wafers exhibit strong photoluminescent emission at 1.54 μm with its emission intensity increasing dramatically with wafer thickness under 980 nm resonant excitation. A low thermal quenching of 10% was measured for the 1.54 μm emission intensity between 10 K and 300 K. This work represents a significant step in providing a practical approach for producing Er:GaN materials with sufficient thicknesses and dimensions to enable the design of gain media in various geometries, allowing for the production of HELs with improved lasing efficiency, atmosphere transmission, and eye-safety. *Published by AIP Publishing.*

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The steady and fast progress of high energy and high power solid-state lasers has enabled a variety of applications which have had and will continue to have profound and far-reaching impacts on emerging technologies. The optical gain medium is the heart of a high energy laser system. Presently, the dominant gain material for solid-state high energy lasers (HELs) is synthetic garnet such as YAG doped with neodymium (Nd:YAG) emitting at 1.06 μm . The gain medium is generally fabricated with disk, rod, or slab geometry to provide high lasing efficiency and power. This requires large crystals with thickness on the millimeter (mm) scale. One key challenge involved in solid-state HELs is the handling of the heat dissipation in the gain medium. It is presently recognized that the damage on the optical gain medium caused by the laser beam flux itself is a principal limitation on further improvement of lasing efficiency.^{1,2} Therefore, finding gain materials with improved heat dissipation capability is highly desirable.

Of the wide bandgap III-nitride semiconductor materials which have demonstrated excellent performances in high power, high temperature electronics and optoelectronics applications, GaN is one of the more promising as a potential gain medium of HELs. The maximum achievable lasing power for a solid-state laser with a heat sink can be characterized roughly by the thermal shock parameter, κ/α^2 , in which κ is the thermal conductivity and α is the thermal expansion coefficient of the gain material.^{3,4} GaN has a much larger thermal conductivity ($\kappa = 230$ W/m K)⁵ and lower thermal expansion coefficient ($\alpha \approx 4 \times 10^{-6}$ °C⁻¹) than YAG ($\kappa = 14$ W/m K, $\alpha \approx 8 \times 10^{-6}$ °C⁻¹). Thus, in principle, HELs based on GaN can significantly surpass

those based on YAG in terms of maximum lasing power. Owing to its wide band gap, GaN doped with erbium (Er) has a significantly reduced thermal quenching of the Er related emission intensity from cryogenic to elevated temperatures as compared to other semiconductor host materials such as Si and GaAs.⁶ A low thermal quenching of 20% from 10 to 300 K of the 1.54 μm emission resulting from the intra-4f transition from the first excited manifold (⁴I_{13/2}) to the ground state (⁴I_{15/2}) in Er³⁺ ions has been previously demonstrated in Er doped GaN (Er:GaN) epilayers grown by metal organic chemical vapor deposition (MOCVD).⁷ This 1.54 μm emission not only perfectly matches the technologically important wavelength window of minimum propagation loss in optical fibers, but also has a good transmittance in atmosphere, which enables a wide range of applications in the open air.⁸ Additionally, the 1.54 μm is a relatively eye-safe wavelength, in that the upper limit of eye-safe laser exposure at 1.5 μm is more than 4 orders of magnitude higher than that of the wavelength range below or close to 1 μm .^{9,10}

To realize the full potential of Er:GaN as a gain medium for HELs, however, Er:GaN bulk crystals in large wafer sizes are required to enable the fabrication of gain media in disk, rod, or slab geometry to provide high energy and high power operation. Furthermore, a resonant excitation (e.g., at a wavelength of 809 nm, 980 nm or 1480 nm, etc.) is more desirable than a non-resonant excitation as resonant excitation involves direct transition between the ground state to a higher-lying inner 4f manifold in Er³⁺ ions without invoking a non-radiative energy transfer, hence generating a much smaller amount of heat than a non-resonant excitation. Nevertheless, the excitation cross section of Er³⁺ ions is typically very small ($\sim 10^{-19}$ – 10^{-21} cm²) for a resonant

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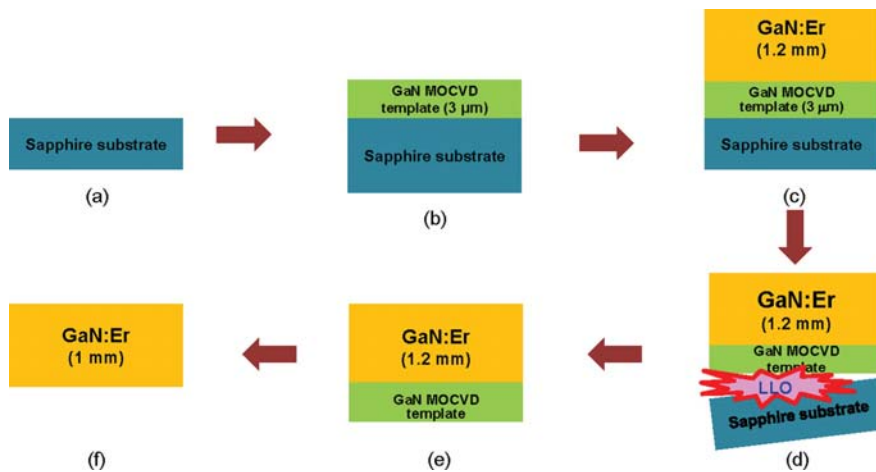
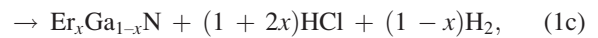
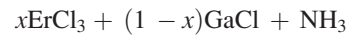
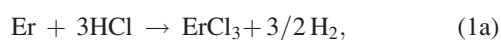


FIG. 1. Processing flow employed in the present work for obtaining free-standing Er:GaN quasi-bulk crystals: (a) Starting with c-plane sapphire substrate. (b) Growth of a $\sim 3 \mu\text{m}$ GaN epilayer template by MOCVD. (c) Growth of a layer of $\sim 1.2 \text{ mm}$ Er:GaN by HVPE. (d) Remove sapphire substrate by laser lift-off (LLO) (using Mallo5000A Equipment from Sino Nitride Co.) (e) Polish both surfaces by mechanical and chemical-mechanical polishing. (f) Final realization of free-standing Er:GaN wafers.

excitation.^{11–15} This makes the optical absorption length for a resonant excitation relatively large (on the centimeter - millimeter scale) for an Er doping concentration ranging from 10^{20} to 10^{21} atoms/cm³. Until now, Er:GaN epilayers grown by MOCVD have had a typical thickness of only a few micrometers, absorbing only a negligible portion of the resonant pumping power, making them unsuitable for HEL applications under resonant pump. Thus, establishing capabilities for producing thick and large Er:GaN crystals (in the mm scale) is necessary to enable the ability to absorb and utilize most of the pumping lasers' energy (with appropriate multi-path configurations) and to allow the optimization of heat removal mechanisms. Hydride vapor phase epitaxy (HVPE) is an established material growth method that is capable of synthesizing single crystals of GaN bulk materials with large wafer sizes at high growth rates.^{16,17} In an earlier work,¹⁸ Er doped GaN epilayers of a few microns in thickness have been synthesized on sapphire using HVPE, but no $1.5 \mu\text{m}$ emission was observed at room temperature. In a more recent work,¹⁹ Er:GaN epilayers have been grown by HVPE on sapphire with a strong emission at $1.54 \mu\text{m}$, but the thickness was still limited to $40 \mu\text{m}$.

In this work, we report the realization of free-standing Er:GaN quasi-bulk crystals with a thickness on the mm scale via HVPE growth together with the laser-lift-off (LLO) process. Prior to the deposition of Er:GaN by HVPE, a GaN epilayer of $3 \mu\text{m}$ in thickness was deposited on a (0001) sapphire substrate by MOCVD to serve as a template. Then, the GaN template was transported into an HVPE system for the growth of Er:GaN. In HVPE growth, GaCl and ErCl₃ were formed by reacting Cl from HCl gas with metallic Ga and Er sources, which were held in two different containers at a temperature of about 1000°C , serving as the group III and Er dopant source, respectively. The GaCl and ErCl₃ in the vapor phase are transported to the deposition zone by an H₂ carrier gas. Er:GaN is then formed on the GaN/sapphire template by reacting hot gaseous metal chlorides (GaCl and ErCl₃) with ammonia gas (NH₃). The chemical reactions of HVPE growth of Er:GaN can be described by the following equations:



where x denotes the Er concentration in GaN. The substrate temperature was 1030°C and the growth rate ranged from 10 to $400 \mu\text{m/h}$.

The as-grown wafer of Er:GaN/GaN/sapphire was then processed with LLO (processing flow illustrated in Fig. 1) to remove the sapphire substrate followed by mechanical and chemical-mechanical polishing on both sample surfaces to obtain a free-standing Er:GaN wafer. The inset of Fig. 2(a) shows an optical image of a free-standing 2-in. Er:GaN wafer with a thickness 1.2 mm obtained by HVPE (at a growth rate of about $200 \mu\text{m/h}$, for 6 h) before polishing. After polishing, this freestanding Er:GaN wafer had a thickness of 1.0 mm.

Figure 2(a) compares the X-ray diffraction (XRD) θ - 2θ scans of the GaN (0002) diffraction peak of a freestanding Er:GaN sample (shown in the inset) before and after polishing. Comparison of the peak positions at 34.466° and 34.545° , respectively, for the wafer before and after chemical-mechanical

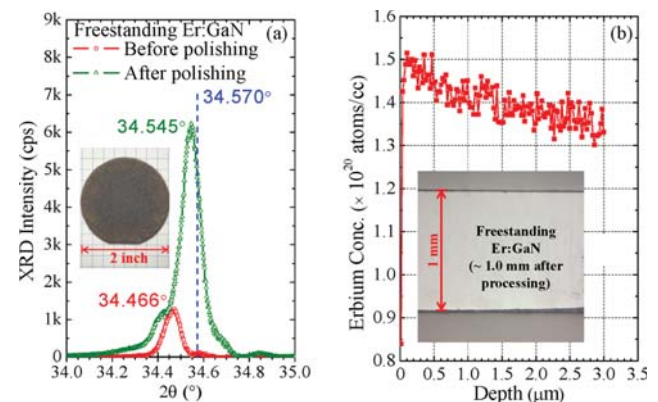


FIG. 2. (a) XRD θ - 2θ scans of the GaN (0002) diffraction peak of a free-standing Er:GaN sample before polishing (1.2 mm in thickness) and after double-side polishing (1 mm in thickness). Dashed line at 34.570° indicates the position of the 2θ diffraction angle of the GaN (0002) peak in strain-free undoped GaN. The inset shows an optical image of a 2-inch freestanding Er:GaN wafer (1.2 mm in thickness) before polishing. (b) Er concentration profile in a freestanding Er:GaN measured by SIMS probed up to $3 \mu\text{m}$ in depth. The inset shows an optical image of a cross-sectional view of a piece of double side polished Er:GaN sample processed according to the procedures illustrated in Fig. 1 having a thickness of 1.0 mm after polishing.

polishing with the 2θ diffraction peak of strain-free GaN (0002) at 34.570° reveals the presence of compressive strain in Er:GaN wafer. However, the smoothing of the surface and removal of shallow defects by chemical-mechanical polishing seem to reduce the stress in the wafer, as suggested by the observed shift of the 2θ diffraction peak position toward that of strain-free GaN (0002) after wafer polishing. The presence of a slight difference in the peak positions of the 2θ angle between the polished freestanding Er:GaN sample and the strain free GaN is not surprising since the size of Er atom is larger than that of the Ga atom and the majority of Er ions in GaN occupy Ga substitutional sites.^{20,21} To confirm the Er doping concentration (N_{Er}), secondary ion mass spectrometry (SIMS) measurement was performed on a freestanding Er:GaN wafer (such as the one shown in the inset of Fig. 2(b)) by Evans Analytical Group (EAG, Inc.). To eliminate the surface effect, the sample was further polished, reducing the thickness of the top surface by a few tens of microns. Then, the SIMS profile of the top $3\mu\text{m}$ of this polished and smooth surface was measured. In Fig. 2(b), the SIMS results indicate that this sample has an average $N_{\text{Er}} = 1.4 \times 10^{20}$ atoms/cm³.

Figure 3 compares the photoluminescence (PL) emission spectra measured at room temperature for freestanding Er:GaN samples of 1 mm and $11\mu\text{m}$ in thicknesses for (a) band-edge non-resonant excitation at $\lambda_{\text{exc}} = 375\text{ nm}$ and (b) resonant excitation at $\lambda_{\text{exc}} = 980\text{ nm}$. The strong $1.54\mu\text{m}$ peak emission line originating from the intra-4f transition of Er dopants was clearly observed in both cases. The measured PL emission spectral shapes under both 375 nm and 980 nm pump wavelengths are quite similar. The spectrometer used to disperse the PL emission spectra has a spectral resolution of 3 nm and was unable to resolve any difference in the

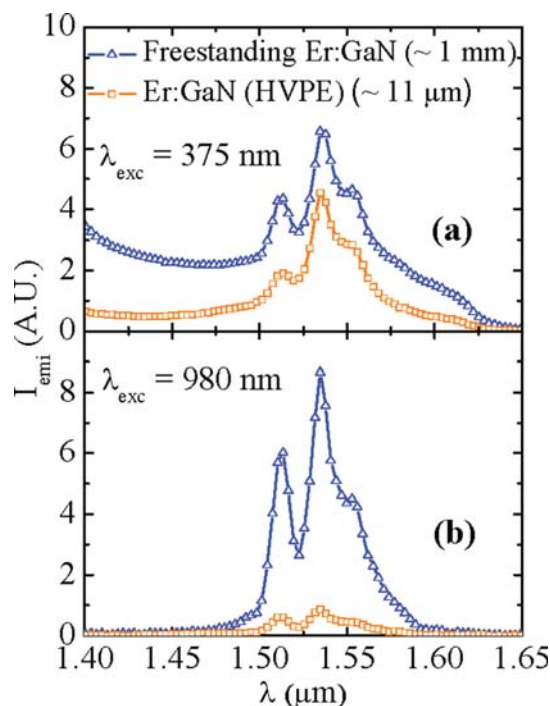


FIG. 3. Comparison of room temperature PL spectra of freestanding Er:GaN samples of two different thicknesses of 1 mm and $11\mu\text{m}$, excited by (a) band-edge excitation at $\lambda_{\text{exc}} = 375\text{ nm}$ and (b) resonant excitation at $\lambda_{\text{exc}} = 980\text{ nm}$.

spectral fine features due to the two pump wavelengths of band-edge (375 nm) and resonant (980 nm) excitation. However, compared to the thin Er:GaN sample which had a thickness of only $11\mu\text{m}$, the freestanding Er:GaN with a thickness of $\sim 1\text{ mm}$ exhibits a much stronger PL emission intensity under 980 nm resonant excitation, whereas both thin and thick Er:GaN samples have a comparable PL emission intensity under band-edge non-resonant 375 nm excitation. This can be explained by the fact that the band-edge excitation at 375 nm is predominantly exciting the electron and hole pairs in the GaN host, which has a much larger optical excitation cross section ($4.6 \times 10^{-17}\text{ cm}^2$)^{11,12} and consequently a small absorption length ($< 2\mu\text{m}$). This means that the 375 nm photons are completely absorbed within the top surface of $2\mu\text{m}$. Therefore, increasing the sample thickness to 1 mm does not further increase optical absorption at 375 nm and PL emission intensity at $1.54\mu\text{m}$. In sharp contrast, 980 nm resonant excitation has an excitation cross section of about $2.2 \times 10^{-21}\text{ cm}^2$ (Refs. 13) and an optical absorption length $> 1\text{ mm}$. Thus, the 1 mm freestanding Er:GaN wafer takes advantage of large thickness, which allows it to absorb much more of the excitation laser's power at 980 nm than the $11\mu\text{m}$ thick wafer. This in turn leads to a much higher emission intensity at $1.54\mu\text{m}$.

The temperature dependence of the PL emission spectra under the 980 nm resonant excitation was measured from 10 K to 400 K to evaluate the thermal quenching effect of the $1.54\mu\text{m}$ emission line in a free-standing Er:GaN wafer of 1 mm in thickness and the results are presented in Fig. 4(a). Figure 4(b) plots the PL emission intensity integrated from $1.5\mu\text{m}$ to $1.6\mu\text{m}$ as a function of the temperature from 10 K to 400 K. There is only a 10% decrease in Er emission near $1.54\mu\text{m}$ between 10 K and 300 K. The low thermal quenching (10%) of this freestanding Er:GaN material again affirms the promise of Er:GaN for HEL applications.

In summary, freestanding Er:GaN wafers with thicknesses on the millimeter scale have been realized via HVPE growth in conjunction with the laser lift-off process. An Er doping concentration of 1.4×10^{20} atoms/cm³ has been confirmed by SIMS measurements. The freestanding Er:GaN

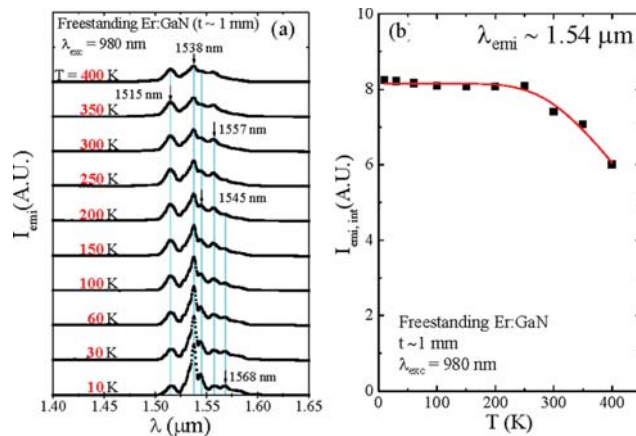


FIG. 4. (a) The temperature dependence of the PL spectra of a freestanding Er:GaN sample (1 mm in thickness) under a resonant excitation at $\lambda_{\text{exc}} = 980\text{ nm}$ measured between 10 K and 400 K. (b) Integrated PL emission intensity of the $1.54\mu\text{m}$ emission of the same freestanding Er:GaN sample as a function of the temperature ($\lambda_{\text{exc}} = 980\text{ nm}$).

wafers emit a strong Er^{3+} ion related emission in the $1.54\ \mu\text{m}$ window under both 375 nm and 980 nm laser excitation. However, the emission intensity increases dramatically with an increase in layer thickness under 980 nm resonant excitation. Furthermore, the thermal quenching of Er emission intensity around $1.54\ \mu\text{m}$ is only 10% for temperatures between 10 K and 300 K, indicating great thermal stability of Er:GaN as a gain medium. The realization of freestanding thick Er:GaN large crystals opens up the possibility of design and fabrication of gain media in different form factors including disk, rod, and slab for high power and high energy lasers operating in the $1.54\ \mu\text{m}$ wavelength window with improved lasing efficiency, atmosphere transmission, and eye-safety.

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