Erbium doped GaN synthesized by hydride vapor-phase epitaxy

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Abstract: New and improved gain materials for solid-state high power and high energy lasers are highly sought. GaN satisfies many of the criteria of an excellent lasing gain medium including its higher thermal conductivity and lower thermal expansion coefficient than traditional gain materials such as yttrium aluminum garnet (YAG) crystals doped with neodymium emitting 1.06 µm wavelength. Single crystals of erbium doped GaN (Er:GaN) thick layers have been successfully synthesized by hydride vapor-phase epitaxy. By utilizing a thin GaN epilayer grown on c-plane sapphire using metal organic chemical vapor deposition as a template and varying growth parameters including the NH_3 flow rate, thick layers of Er:GaN which exhibit the desired Er^{3+} related emission at 1.54 µm window at room temperature have been realized for the first time. The work opens up the feasibility to utilize Er:GaN bulk crystals as a gain medium for next generation solid-state high power and high energy lasers operating in the eye-safer 1.5 µm window.

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OCIS codes: (140.3500) Laser erbium; (160.5690) Rare-earth-doped materials.

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1. Introduction

The development of high power and high energy solid-state lasers has progressed at a steady pace and opened up a wide range of technologically important applications, including laser projectors, laser surgery, laser spectroscopy and microscopy, laser fusion, laser welding and cutting, laser radar, remote sensing, range finding, target tagging, and military countermeasures. Yttrium aluminum garnet (YAG) crystals doped with neodymium (Nd^{3+}:YAG) emitting 1.06 μm wavelength have attained a dominant position in the field and are being used in low-power continuous-wave (CW) lasers to high energy lasers [1–3]. However, 1.06 μm Nd^{3+} emission line is non-eye-safe. Moreover, the thermal conductivity of YAG is relatively low (κ = 14 W/m·K), which limits its ability to rapidly remove the waste thermal energy and hence the power output and the duty cycle of the laser performance. Finding improved gain media to provide higher lasing power, power density and beam quality is highly desirable. Furthermore, in many applications where laser beams must be transmitted through the open air, the use of eye-safer lasers is preferred.

Due to their outstanding physical properties, III-nitride wide bandgap semiconductors have demonstrated excellent performance for high power/temperature electronic devices and UV/blue/green optoelectronic devices over the last 2 decades [4–8]. Recent studies on erbium (Er) doped GaN thin films produced by metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) have also indicated that GaN is an excellent host material for Er ions [9–19]. The 1.54 μm emission line from Er^{3+} originates from the atomic-like intra-4f transitions between the 1st excited manifold ($^4I_{13/2}$) and the ground state ($^4I_{15/2}$), which coincides with the wavelength of minimum optical loss in optic fibers and hence is highly

desired and widely utilized in optical communication applications. It is now well established that the thermal quenching of Er related emissions in GaN is much less severe than that in other semiconductor hosts due to its wide band gap [9–19]. Moreover, the maximum permissible laser exposure limit for eye safety at 1.5 µm is more than 4 orders of magnitude higher than that near or below 1.06 µm [20,21]. Thus laser sources emitting in the 1.5 µm region offer superior eye-safety over the 1.06 µm Nd^{3+} line. Though Er can also be doped into YAG, comparing with Nd:YAG for solid-state lasers, one of the most outstanding properties of Er doped GaN (Er:GaN) as a gain medium for solid-state lasers is its outstanding thermal properties. GaN has a high thermal conductivity (κ = 230 W/m·K) [22] which is more than one order of magnitude higher than YAG (κ = 14 W/m·K), while its thermal expansion coefficient ($\alpha \approx 4 \times 10^{-6}$ °C^{-1}) is about 2 times smaller than those of YAG ($\alpha \approx 8 \times 10^{-6}$ °C^{-1}). The thermal conductivity may not be the only parameter for determining the properties of a high energy laser gain medium, but it is one of the most important parameters. In a typical solid-state laser material placed at a heat sink, the maximal attainable lasing power is roughly proportional to the thermal shock parameter, κ/α^2, where κ is the thermal conductivity and α is the thermal expansion coefficient [23,24]. Therefore, Er:GaN lasers have the potential to outperform Nd:YAG lasers by a factor of about 65.

To realize the full potential of Er:GaN as a gain medium for high power and high energy solid state lasers, however, it is necessary to develop crystal growth and in situ doping processes to produce Er:GaN bulk crystals in wafer scale to allow laser bar or laser disk design. An earlier work has indicated that it is possible to obtain Er:GaN thick films (~20 µm in thickness) via hydride vapor phase epitaxy (HVPE) growth technique [25]. However, the Er related emissions were not detectable at room temperature. Here, we report the successful synthesis by HVPE Er:GaN crystals exhibiting 1.54 µm emission at room temperature. The work paves the way for using Er:GaN bulk crystals as a gain medium for next generation high power and high energy solid-state lasers operating in the eye-safer 1.5 µm window.

2. Experimental methods

HVPE is an established method for growing high quality GaN bulk crystals with advantages of high growth rate (up to 0.2 mm/hour) and ability to produce GaN semi-bulk crystals with large thickness (up to 10 mm) and wafer size [26,27]. In the present work, Er:GaN crystals were grown by HVPE technique. Our HVPE system is designed to allow *in situ* doping with the ability to separate the optimization process of host crystal growth from doping. GaCl and $ErCl_3$ were formed by reacting Cl from HCl gas with metallic Ga and Er, serving as the group III and in situ Er dopant source, respectively. Ga and Er metal sources were held in quartz boats at 900 °C. The GaCl and $ErCl_3$ in the vapor phase were transported to the deposition zone by H_2 carrier gas. Er:GaN was then formed by reacting hot gaseous metal chlorides (GaCl and $ErCl_3$) with ammonia gas (NH_3). Er:GaN layers were grown at a substrate temperature of 1030 °C. The substrates used were c-plane sapphire. The growth rate was varied from 5 to 100 µm/hour. X-ray diffraction (XRD) measurements were used to assess the crystalline quality. Photoluminescence spectroscopy was utilized to characterize the optical emission properties of Er:GaN crystals.

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3. Results and discussion

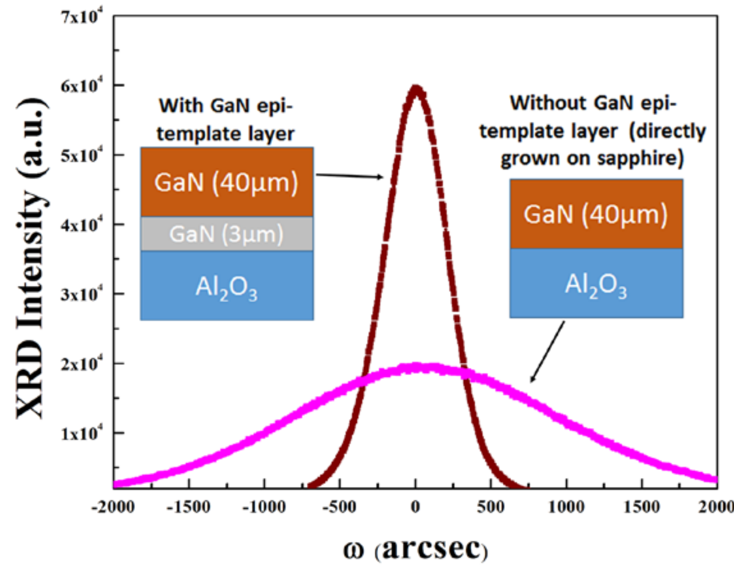

Fig. 1. Comparison of GaN (0002) reflection XRD rocking curves (ω-scans) between two HVPE Er:GaN samples grown on sapphire with and without the use of MOCVD GaN epi-template.

In growing GaN materials by HVPE, the benefits of using a thin GaN epilayer (2-3 μm) grown by MOCVD to serve as a nucleation template have been established previously by many groups [28,29]. We also observed that the use of MOCVD GaN epi-template is crucial for obtaining HVPE Er:GaN with improved crystalline quality. This is illustrated in Fig. 1, where comparison results between the rocking curves of the symmetric GaN (0002) reflection (XRD ω-scans) of two HVPE samples (with and without the use of an MOCVD GaN epi-template) are shown. It is clear that the use of MOCVD GaN epi-template of 3 μm in thickness significantly improves the crystalline quality of the subsequently deposited HVPE layer, as reflected in higher XRD intensity and narrower XRD rocking curve full width at half maximum (FWHM) for the sample deposited on MOCVD GaN epi-template.

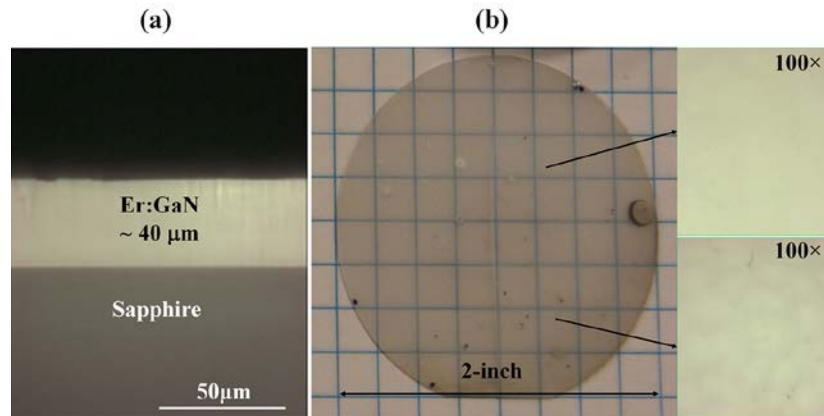

Fig. 2. Micrographs of an Er:GaN wafer grown by HVPE. (a) Cross-section view indicating a 40 μm thickness; (b) Top view. The insets show the surface morphologies of two different regions on the wafer surface.

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Figure 2 shows the optical micrographs of an as-grown Er:GaN wafer on a 3 μm thick MOCVD-grown GaN template layer. The cross section view shown in Fig. 2(a) provides a measure of the thickness of the HVPE grown layer of about 40 μm. On the wafer scale seen with the unaided eye, the morphology of HVPE grown Er:GaN appears to be relatively smooth, as shown from Figs. 2(b). However, the surface morphology varies across the wafer surface, as illustrated in the two insets. In certain areas (e.g., bottom inset), the sample surface exhibits hexagonal pyramid-shaped hillocks. The formation mechanism of hillock features has been attributed to threading dislocations penetrating the growth (0001) surface which caused a localized region of higher growth rate [30]. The use of off-axis templates so far yields similar results. This may be due to the fact that many other important growth parameters remain to be optimized.

Figure 3 compares the XRD characterization results of the symmetric GaN (0002) reflection in both θ/2θ and ω-scans of the underneath MOCVD GaN epi-template and a subsequently HVPE grown Er:GaN layer of about 40 μm thick. As indicated in Fig. 3(a), the peak position of GaN (0002) θ-2θ scan of HVPE GaN sample shifts slightly to lower diffraction angle with respect to that of the MOCVD grown GaN epilayer, indicating the presence of a compressive strain in the HVPE grown layer. Figure 3(b) indicates that the FWHM of the (0002) XRD rocking curve of the HVPE GaN (~390 arcsec) is smaller than that of the MOCVD GaN epi-template (410 arcsec), which points to the fact that the crystalline quality of GaN enhances with an increase of the GaN layer thickness. The XRD rocking curve FWHM reduction is statistically significant and a similar behavior has been observed in undoped HVPE GaN layers. The results shown in Fig. 3 indicate that the crystalline quality of HVPE Er:GaN layer is still limited by that of the GaN epi-template for layer thickness as large as 40 μm.

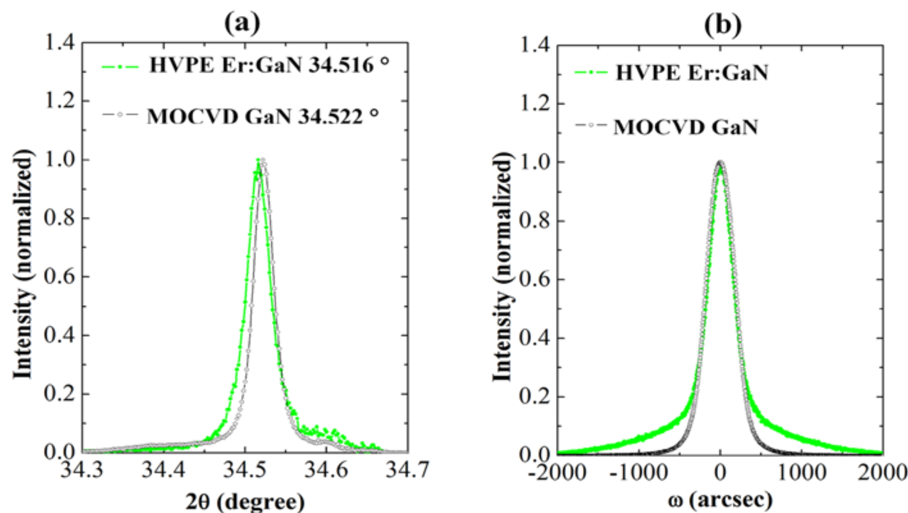

Fig. 3. Comparison of GaN (0002) XRD results between the MOCVD GaN epi-template and the subsequent HVEP Er:GaN layer grown on sapphire. (a) θ-2θ scans and (b) rocking curves (ω-scans).

Figure 4 shows the room temperature photoluminescence (PL) spectra of three Er:GaN samples synthesized by HVPE at varying NH_3 flow rates measured at the desired eye-safer 1.5 μm emission window. It can be seen from Fig. 4 that the NH_3 flow rates strongly affect the emission intensity at 1.54 μm. To the first order, the 1.54 μm emission intensity is proportional to the Er doping concentration in GaN crystal host. The results shown in Fig. 4 seem to suggest that the V/III ratio as well as the pre-reaction between $ErCl_3$ and NH_3 in the gas phase could affect the in situ incorporation of Er concentration during HVPE growth.

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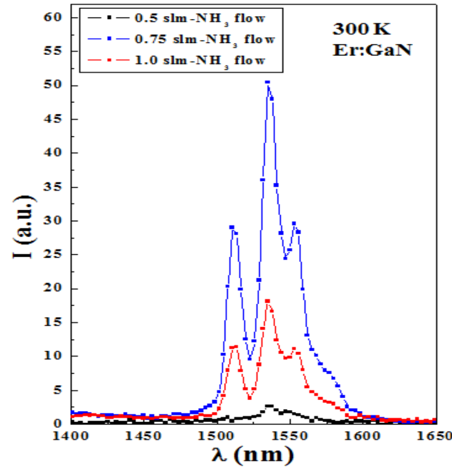

Fig. 4. Room temperature photoluminescence spectra of three HVPE Er:GaN samples grown under different NH_3 flow rates.

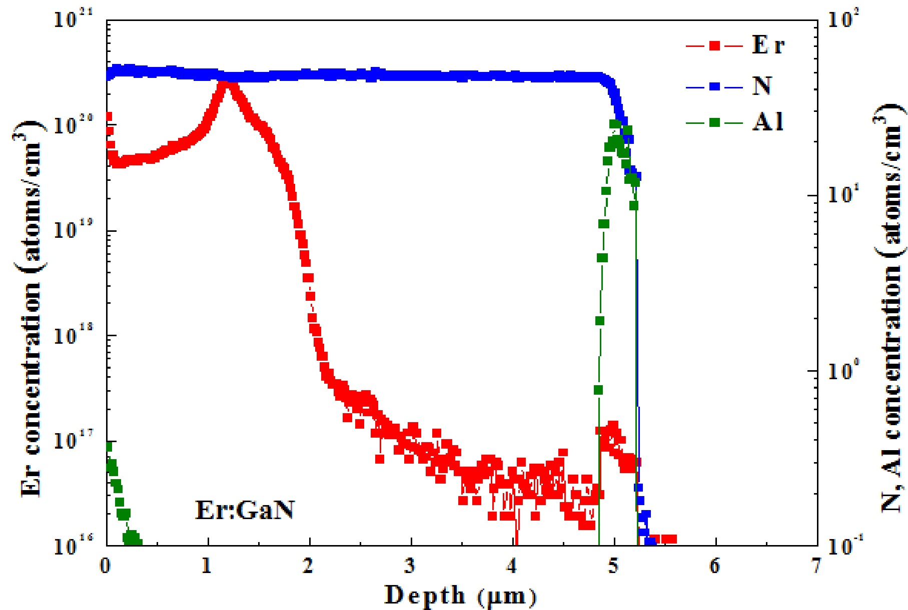

Fig. 5. SIMS measurement results of an Er:GaN sample grown by HVPE. The thickness of the MOCVD GaN epi-template is about 3 μm and the thickness of the subsequent HVPE grown Er:GaN was controlled to about 2 μm in order to reduce the cost of SIMS measurements.

To check the Er doping concentration, secondary ion mass spectrometry (SIMS) measurements were performed by Evans Analytical Group (EAG). For SIMS characterization, an Er:GaN eilayer with a thickness of only 2 μm was grown on the MOCVD GaN epi-template of about 3 μm. The SIMS profile shown in Fig. 5 revealed an average Er concentration in the HVPE grown film of about 5×10^{19} atoms/cm^3. Based on our previous studies on Er:GaN thin films grown by MOCVD, the attainable Er concentration in GaN can be as high as 5×10^{21} atoms/cm^3 [16,31,32].

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4. Conclusion

In summary, we report the synthesis of Er doped GaN thick layers by HVPE. The grown Er:GaN crystals exhibit the desired Er^{3+} related emission in the eye-safer 1.54 μm window at room temperature. An Er doping concentration of 5×10^{19} atoms/cm^3 has been confirmed by SIMS measurements. Further optimization in HVPE growth processes is needed to improve the Er doping concentration and the emission efficiency at 1.5 μm. The availability of Er:GaN thick layers makes it possible to study their basic properties and paves the way to further develop Er:GaN semi-bulk crystals as a gain medium for next generation solid-state high energy and high power lasers with improved eye-safety.

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