

Development of periodically oriented gallium nitride for non-linear optics [Invited]

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Abstract: Methods for growing periodically alternating polarities of GaN on GaN substrates have been developed. The resulting periodically oriented samples demonstrate feasibility of using this method to produce structures of utility in optical parametric generation.

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1. Introduction

Materials with second order non-linear susceptibility (χ^2) are widely used for frequency conversion applications, from second harmonic generation (SHG) to optical parametric oscillation (OPO). This is commonly achieved by periodically alternating the material structure, either in ferroelectric domains or in crystal orientation, to maintain quasi-phase matching (QPM) [1]. The first option has shown the most commercial success in the form of periodically poled lithium niobate (PPLN), but has also been extended to other ferromagnetic oxides like periodically poled potassium titanyl phosphate (PPKTP) [1,2]. However, the performance of such oxides drops off dramatically beyond 4 μm due to multi-phonon absorption [1]. In addition, PPLN has a low threshold for laser damage and its operation is temperature sensitive [1,2]. This has led to interest in the second option of achieving QPM by alternating the crystal orientation of the semiconducting materials. Semiconductors with non-linearity coefficients close to or higher than the ferromagnetic oxides allow a choice of materials with high thermal conductivity, large band gaps, and higher laser damage thresholds, and offer a path toward mid-IR wavelengths. The most mature of the periodically oriented (PO) semiconductors is GaAs, which has shown OPO with watt-level output in the mid-IR range [3]. With this success, other semiconductors are being studied such as GaP [4]. This paper will focus on developing GaN as a periodically oriented structure for use in non-linear optics (NLO).

2. Gallium nitride as a NLO candidate

GaN possesses a wurtzite crystal structure and can be grown in the c-direction of its lattice with two different polar faces, nitrogen- (N-) or gallium- (Ga-) polar. The face, or polar orientation, establishes such material properties as chemical reactivity, dopant incorporation, and spontaneous and piezoelectric-induced electric field directions in the crystal [5]. Alternating the c-face polarity should allow quasi-phase matching to be achieved in GaN by analogous methods used to develop orientation patterned GaAs.

GaN has been widely used in both electronics and optoelectronics. With a wide band gap (3.4 eV) and high thermal conductivity (220 W/m $^{\circ}\text{C}$ at room temperature [6]) that is greater than those of both PPLN and GaAs, GaN is well-suited for the power electronics arena, and, similarly, to enable higher power applications in the NLO field. Table 1 contains characteristic data for the two most mature NLO materials, PPLN and GaAs, as well as GaN. The table includes comparisons of the band gap, thermal conductivity, substrate material, and transparency window. These last two categories will be discussed in detail later. Further advantages of GaN include a high laser damage threshold and the ability to use standard 1 μm pump lasers (OP GaAs has been restricted to 2 μm sources [1]). In addition to these properties, GaN possesses a second order non-linear susceptibility which, although differing values have been reported in the literature, is generally thought to have a similar magnitude to that of PPLN [7–10].

Table 1. Properties of NLO Materials

Material	Periodicity	Band Gap (eV)	Thermal Conductivity (W/m°C)	Substrate	Transparent Window
LiNbO ₃	Periodically Poled	4	5.6	CZ-grown LiNbO ₃	0.35-5 μm
GaAs	Periodically Oriented	1.4	55	GaAs	0.8-17 μm [11]
GaN	Periodically Oriented	3.4	220 [6]	Sapphire or GaN	0.36-7 μm [12]

2.1 Quasi phase matching in gallium nitride

SHG in GaN has been observed in several different forms. In bulk, the SHG efficiency is too small to be practical [7]. However, SHG spectroscopy has been used to investigate the surface of GaN thin films grown on both Ga- and N-polar surfaces [13]. To achieve QPM conditions, one approach has employed photonic crystals of GaN [10,14]. In the case of a 1D photonic crystal, the SHG response was 5000 times greater than for unpatterned epilayers [14]. Additionally, SHG has been observed in GaN nanowires, whose crystallographic orientation can be determined by SHG measurements [15].

Following the highly successful method of using periodic orientation to induce QPM in both ferroelectrics and semiconductors, several groups have demonstrated periodic polarity orientation of GaN on sapphire substrates [9,16,17]. However, only one of these efforts produced SHG [9]. Although the conversion efficiency was only 12.8%, that work demonstrated the feasibility of achieving SHG through periodic patterning of the GaN polarity.

2.2 Roadblocks

With evidence of SHG, why has GaN not been more rigorously studied for NLO? Two main roadblocks have hindered the development of GaN for NLO. The first has been a lack of high quality native substrates. Unlike the other NLO materials listed in Table 1, for which large scale, native substrates are commercially available, until recently the main substrate used for growing GaN has been sapphire (Al₂O₃). The examples of periodically oriented GaN in the prior section all employed this method to create the structures. However, the significant lattice mismatch between GaN and sapphire (~14%) poses a problem in two ways. First, the mismatch causes high dislocation densities in the GaN (on the order of 10^9 - 10^{10} cm⁻² [18]), and it also limits the GaN thickness to less than 20 μm [19]. For NLO devices utilizing the high power capacity of GaN, thicknesses greater than 100 μm will be required.

Addressing this issue, GaN substrates grown by hydride vapor phase epitaxy (HVPE) have recently become commercially available. This now enables thicker, higher quality GaN films to be grown, starting from substrates that typically have dislocation densities on the order of 10^6 - 10^7 cm⁻². These substrates also allow the transparency window of GaN to be probed experimentally. Though cited theoretically as extending to 13.7 μm [9], the observed transparency window has not reached this expectation. Early measurements of this metric relied on growth on sapphire, which means the layers were thin and plagued by dislocations as discussed above, and had considerably reduced transparency. However, with the introduction and optimization of HVPE and ammonothermal substrates, this window has been extended, with some recent reports of ~7 μm for the long wavelength cutoff [12,20]. These reports also point to second-harmonic optical-phonon absorption as the reason for the early cut-off of around 7 μm .

The second historical roadblock relates to how the alternating c-face polarity on native substrates or even GaN epilayers can be controlled. As mentioned, prior efforts to create periodically oriented structures used sapphire substrates, on which it is relatively easy to control the GaN polarity by manipulating the buffer layer [5]. However, on GaN epilayers, the

only reported method for inverting the GaN polarity has relied on Mg-induced inversion, by either using high Mg doping ($>10^{20} \text{ cm}^{-3}$) or adding a Mg_xN_y layer. The former introduces issues like dopant clustering and uncontrolled inversion domain formation, while the latter introduces a faceted interface, both of which would adversely impact device performance. These considerations demonstrate the need for a method of GaN polarity inversion that does not rely on Mg-induced inversion. Recent work has shown the feasibility of using a thin AlN layer to grow Ga-polar GaN on N-polar GaN [21].

3. Periodically oriented gallium nitride

To develop PO GaN on GaN, several approaches can be adopted. The first decision is whether to focus on Ga-polar or N-polar substrates. After that, inversion layers that change the overlying GaN polarity from that of the substrate must be developed. Next, approaches to selectively inverting the polarity must be established, preferably using methods compatible with normal semiconductor processing. It is even more important to employ a method that does not rely on dry etching, so as to minimize damage to the layers prior to regrowth. One additional desired attribute is to allow for simultaneous growth of both polarities over the substrate and inversion layer, which requires similar growth rates of the N- and Ga-polar GaN.

Our efforts have mainly focused on using N-polar substrates and using a thin, selectively grown AlN layer to invert the polarity from N- to Ga-polar over the AlN and simultaneously growing N-polar material over the bare substrate. A schematic of this process is shown in Fig. 1, and details can be found in [22]. Using this process, metal organic chemical vapor deposition (MOCVD)-grown periodically oriented GaN samples have been reproducibly created on the N-polar face of GaN HVPE substrates, as well as $2\mu\text{m}$ thick MOCVD-grown N-polar templates on sapphire substrates. These PO GaN structures have been grown up to $2\mu\text{m}$ thicknesses, with similar growth rates between the polarities as evidenced by the relatively smooth sample surface. These samples have shown a strong inversion domain

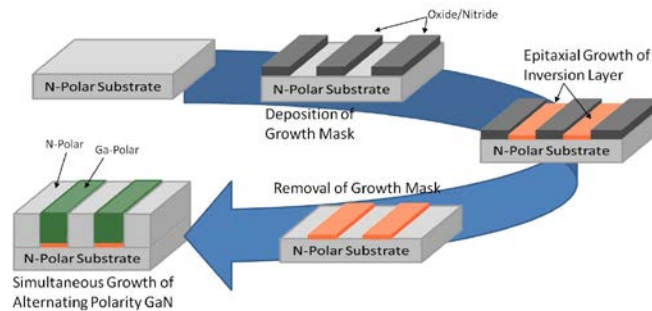


Fig. 1. Schematic of growth method used to produce alternating GaN polarity on GaN substrates.

boundary only at the intersection of the two polarities, as observed in TEM. The scanning electron microscopy (SEM) image in Fig. 2 shows that the surface of the MOCVD-grown sample is relatively smooth. The observed contrast in the image arises from different electrical conductivities in each of the polar materials as accentuated by SEM.

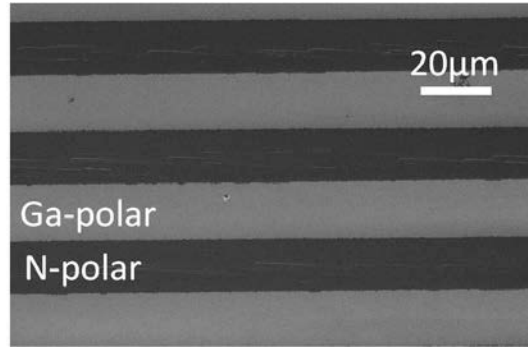


Fig. 2. SEM of the surface of a 2 μm thick MOCVD-grown PO GaN sample. The different polarities are marked.

Currently, dislocation densities in the inverted (Ga-polar) material on HVPE substrates are an order of magnitude greater than in homo-polarity (N-polar) material. However, this can simply be attributed to the distance from the hetero-interfaces, 300 μm (backside of wafer) for N-polar versus a mere 2 μm for the inverted Ga-polar material. High power applications will require much thicker material, which actually presents an advantage in that dislocation densities have repeatedly been reduced in thicker material [23].

To prove the feasibility of extending the PO GaN structure, 2 μm thick MOCVD-grown PO GaN samples, or “templates,” have been exposed to regrowth via HVPE. To date this has been done to thicknesses up to $\sim 80 \mu\text{m}$. The samples with HVPE re-growth demonstrate the ability to maintain the periodically alternating polarity of the MOCVD-template through thicker growth. A sharp inversion domain boundary (IDB) between the N- and Ga-polar regions is observed via TEM throughout the extension. A marked reduction in dislocation density has also been observed in the inverted material, beginning at the template/regrowth interface and extending through the regrowth (Fig. 3), as expected due to the dislocation annihilation with increasing thickness mechanism.

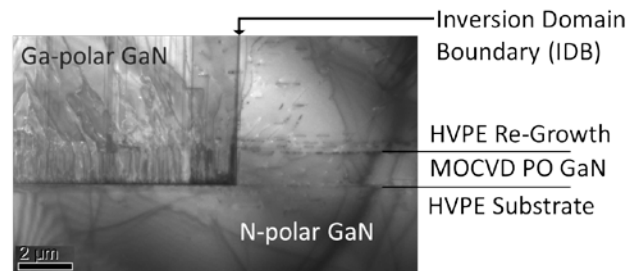


Fig. 3. Cross-sectional TEM of the substrate/MOCVD PO GaN template/HVPE re-growth interface.

In developing the method further, there are a few areas of concern. For example, what is the maximum thickness over which the HVPE regrowth can maintain the polarity of the PO template? We observe a “saw tooth-like” faceting at the surface of the HVPE extension (Fig. 4). This can be partially explained by a difference of growth rates between the Ga- and N-polar materials, with a higher growth rate for the Ga-polar material. If the Ga-polar regions continue to grow faster than the N-polar, these regions may overwhelm the N-polar growth or changes in faceting may initiate polycrystalline growth. Another uncertainty concerns the incorporation of impurities into the GaN. To be useful in NLO, low absorption and scattering losses will be required. HVPE-grown Ga-polar material normally has relatively high concentrations of Si and O impurities, which may act as scattering sites, while N-polar material, regardless of growth method, tends to have impurity levels an order of magnitude higher than the Ga-polar material [24]. For Ga-polar HVPE substrates, low losses have been

previously reported for critical thicknesses of over $80\mu\text{m}$ [25]. Recent measurements of thick (1mm) high quality HVPE GaN substrates have also found that the main absorption losses arise from free carrier absorption rather than scattering.

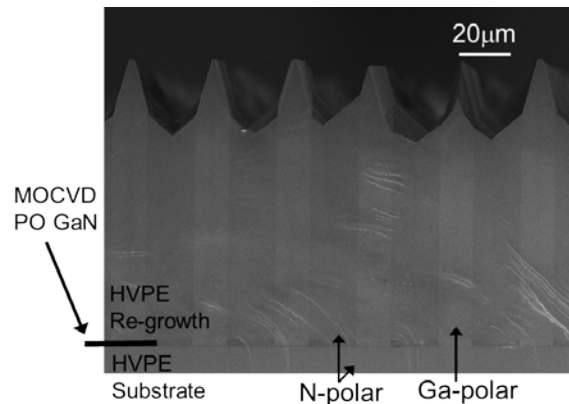


Fig. 4. Cross-sectional SEM of a HVPE extension growth. Ga-polar and N-polar regions are easily distinguished by contrast. The surface exhibits faceting.

4. Conclusions

In conclusion, GaN remains a very promising NLO material. Alternating polarity structures on sapphire have previously shown QPM. High power applications will require thicker periodically oriented material than is possible for epitaxy on sapphire. Recent work at NRL has identified methods to create much thicker PO GaN structures on GaN substrates, using both templates on sapphire and HVPE bulk substrates. Further extension of the template thickness for higher power applications with HVPE has also been demonstrated. To be of practical use, these efforts need to focus on extending the growth to even thicker material, as well as reducing impurities and absorption in the material.

Acknowledgments

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