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Upconversion Due to Optical-Phonon-Assisted Anti-Stokes Photoluminescence in Bulk GaN

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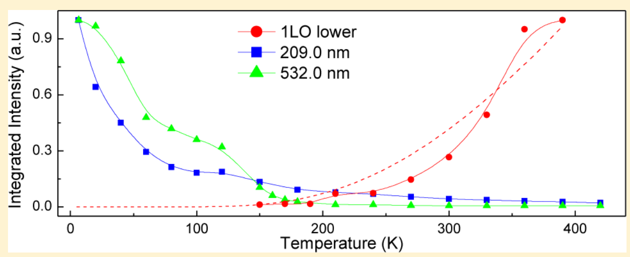
ABSTRACT: We demonstrate that under optimized experimental conditions phonon-assisted anti-Stokes photoluminescence becomes the dominant light emission process in a free-standing GaN sample excited well below the bandgap. Potentially this up-conversion process can be used for efficient removal of phonons generated in the wide range of GaN-based electronic and optoelectronic devices and perhaps laser cooling based on nitride structures.



KEYWORDS: *phonon-assisted anti-Stokes light emission, up-conversion, phonon removal, laser cooling, nitrides*

Optical cooling of solids based on anti-Stokes photoluminescence (ASPL) was first proposed as early as 1929.[1] The basis for this process is straightforward: since the average photon energy emitted in ASPL is larger than that for the absorbed pump photons, the difference between the emitted and absorbed photon energies is made up by the energy of lattice vibrations (phonons). Thus, the temperature of a material can be reduced through the ASPL process. This concept for optical cooling was first realized in ytterbium-doped glass.[2] Nowadays, laser cooling using rare-earth doped materials approaches cryogenic temperatures,[3] and, efficiency-wise, already bests the performance of a typical thermoelectric cooler. However, cooling of some rare-earth doped insulating crystal itself may be of dubious utility as it is the active semiconductor device that needs to be cooled in the end, and most of the rare earth host materials have low thermal conductivity and also make poor thermal contact with semiconductors. Hence, it would be more practical if laser cooling could be implemented directly inside semiconductor material, thus, establishing short thermal pathway to the active region where the heat is generated. Furthermore, optical refrigerators based on semiconductors have a potential for cooling devices down to ∼10 K.[4,5] Such a low temperature may not be reachable using rare-earth doped solids, since the top of the ground state at such a low temperature is significantly depopulated during the light emission. In comparison, semiconductors do not suffer from such an obstacle since valence band is always populated by electrons.

With all the advantages offered by semiconductors for laser cooling, this field has been intensively investigated both theoretically and experimentally.[4−13] In the past, most efforts have been devoted to the exploitation of GaAs since GaAs technology is the most mature among the direct gap semiconductors and the external radiative recombination efficiency, up 99.5% has been observed in GaAs/GaInP double heterostructure.[14] Radiative recombination efficiency plays the key role in laser cooling, since in each act of Antistokes photon emission only about $k_B T$ of energy is being carried away, that is, a small, about 1% fraction of the incident pump photon energy, hence nonradiative loss of just 1% may be fatal for the cooling.

And yet, despite all the aforementioned attractive features of GaAs, no net cooling has been attained in this material, notwithstanding all the persistent efforts that came tantalizingly close to it. Instead, rather unexpectedly, the first observation of laser cooling in semiconductor has been recently made in CdS nanobelts rather than in GaAs.[15] It was suggested in such a paper that the strong exciton-longitude optical (LO) phonon coupling through Fröhlich interaction played an important role in achieving optical cooling in semiconductors. In polar semiconductors such as GaAs and CdS, the dominating mechanism for ASPL is exciton-LO phonon coupling.[10] Thus, compared with III−V materials such as GaAs, more polar II−VI materials such as CdS are expected to produce more efficient ASPL since the corresponding Fröhlich interaction is stronger (the Fröhlich coupling constant is 0.51 and 0.07 for CdS and GaAs, respectively). Indeed, phonon-assisted ASPL has been widely observed in II−VI quantum dots, including CdSe,[16] PbS,[17] PbSe,[18] and CdTe,[16,19] which motivates the discussion of laser cooling on these materials.[20] Besides its strong Fröhlich interaction, the bandgap of CdS is significantly larger than GaAs (2.4 vs 1.51 eV). The idea that wider bandgap materials may hold an advantage when it comes to laser cooling due to

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their large joint density of states, lower refractive index, and, most crucially, very weak Auger recombination, was first explored in ref 11. One should stress, that even though, as it was pointed out in ref 6, the cooling efficiency is limited by the ratio mean anti-Stokes shift (roughly k_BT) to the bandgap energy, this obvious drawback of wider bandgap materials is more than outweighed by the impressive list of the advantages mentioned above,[11] and, furthermore, in wide bandgap material the mean anti-Stokes shift of PL peak could be significantly larger than k_BT (ref 10).

It appears that wide gap polar III−V semiconductors, such as GaN and its alloys with AlN and InN, which have been widely used in both electronics (high speed and high power transistors[21]) and optics (LEDs and lasers[22]) combine many attractive properties for laser cooling: strong electron−phonon interaction, large phonon energy, high joint density of states (less saturation), wide bandgap (less Auger recombination) and small refractive index (less light trapping). Compared to II−VI semiconductors, GaN has reached a mature technology where the many technical issues associated with growth, fabrication, and also getting the light out had been already successfully resolved. Hence, it is only natural to start commence experimental effort that 1 day should read to efficient optically driven semiconductor refrigerators monolithically integrated with the electronic and optical devices.

In this article, we report the first step on the road to the laser refrigeration using GaN; experimental demonstration of strong anti-Stokes light emission in a free-standing GaN sample. These results allow us to predict that laser cooling may be eventually achieved in GaN, if the internal quantum efficiency can reach nearly 100%.

The sample used in our experiments is 350 μm free-standing GaN wafer grown by metal organic chemical vapor deposition (MOCVD). The concentration of Si donors is measured to be 2×10^{18} cm^{-3}. Such a sample was mounted on a coldfinger of a continuous-flow cryostat with its temperature being set anywhere from 4.2 to 300 K. The pump source was a Ti:sapphire laser with a 3 ps pulse length, repetition frequency of 76 MHz, and wavelength tunable from 730 to 850 nm. These pulses were subsequently frequency doubled and then quadrupled which allowed us to excite GaN both below and above the bandgap. A typical focal spot area of the pump beam on the GaN sample is 0.02 mm^2. The photoluminescence (PL) signal generated by the GaN material was analyzed with a double-grating spectrometer with and a photomultiplier tube. In ref 23, the investigation was mainly concentrated on the competition between phonon-assisted and two-photon absorption in GaN. In this article, we are primarily focused on the investigation of the optimized experimental conditions under which phonon-assisted anti-Stokes photoluminescence becomes the dominant light emission process amd potential for laser cooling based on GaN.

We first measured PL spectra when the pump photon energy was well above the bandgap of GaN, corresponding to the pump wavelength of 209 nm with an average power of 500 μW. These spectra were obtained under a pump wavelength, which is different from that in ref 23. They are used to understand the mechanisms for the carrier recombination resulting in the light emission. The PL spectrum of GaN obtained at 6 K is shown in Figure 1a. Several peaks were observed by us. These peaks can be assigned to different origins according to their evolutions as a function of temperature.[23−25] The dominant peak located at 357.3 nm corresponds to the recombination of the excitons bound to neutral donors (D-X or I_2), whereas a small peak around 368.13 nm is caused by recombination of electrons bound to the donors with free holes (D-h). It is worth noting that the peak due to the recombination of free excitons appears to be absent. This is due to the presence of the neutral donors. Therefore, majority of the excitons is bound to the neutral donors, resulting in the dominant peak due to the recombination of the bound excitons. The three peaks at

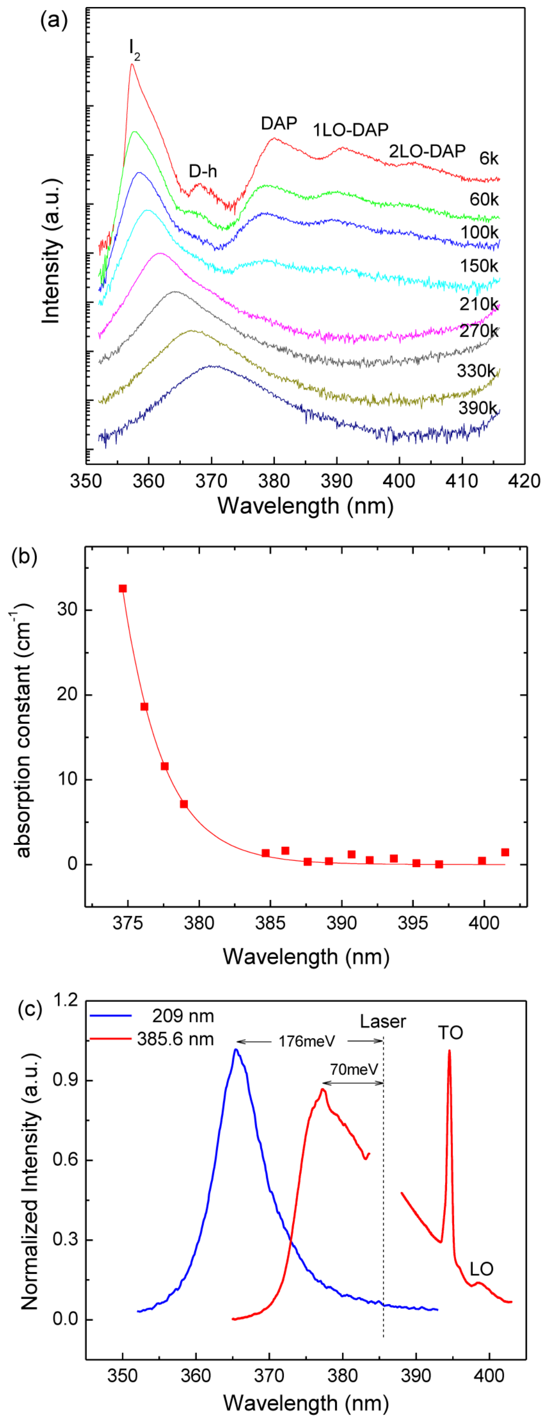

Figure 1. (a) PL spectra excited by 209 nm with an average power of 0.5 mW at different temperatures. (b) Absorption spectrum at 300 K. Squares and curve correspond to data and exponential decay fitting. (c) Normalized PL spectra measured at 300 K. The blue and red curves are excited by 209 and 385.6 nm, respectively.

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380.08, 390.96, and 402.49 nm correspond to the recombination of the donor−acceptor pairs (DAP) and its 1LO-phonon and 2LO-phonon replicas, respectively. The strong intensities of LO-phonon replica of DAP indicate the strong coupling between electrons (or holes) bound to donors (or acceptors) and LO phonons. When the sample temperature is increased, the peak of DAP progressively evolves toward the exciton peek, as also shown in Figure 1a, and eventually, above 200 K all the sharp features in the spectrum disappear. As can be seen from the absorption spectrum at room temperature in Figure 1b at an elevated temperature one can only observe exponential bandtail, devoid of any features, from which the luminescence emerges. The center of PL peak shifts rather substantially toward longer wavelength as temperature increases, in a general agreement with the temperature dependence of the bandgap described by the Varshni equation.[26] It is worth noting that the sensitivity of emission wavelength to the temperature can be exploited to determine the temperature of the optical refrigerator indirectly.[6,15]

Next, after following the evolution of emission peaks with temperature using above-the-gap excitation, we have moved closer to the study of laser refrigeration by setting the pump photon energy below the bandgap and performing all the subsequent measurements at room temperature. The red curve of Figure 1c shows a typical ASPL spectrum measured at the pump wavelength of 385.6 nm. The mean PL wavelength has been determined to be 381.8 nm corresponding to the photon energy separation between the pump laser and PL of 31.41 meV, that is, 21% larger than $k_BT \approx 25.852$ meV at $T = 300$ K, in full agreement with the results published in ref 10. The ASPL occurs as a three step process: the optical phonon-assisted absorption of the pump photon, followed by the thermalization in the band accompanied by releasing acoustic phonons that carry away about 60 meV of energy to the lattice, and the final step of direct radiative recombination that does not involve the phonons. It is also clear that what is observed is ASPL and not anti-Stokes Raman scattering for which the antiStokes shift would always be equal to the phonon energy.

From Figure 1c, one can see that anti-Stokes PL, excited by the radiation at the wavelength of 385.6 nm is red-shifted by as much as 106 meV relative to Stokes PL excited by the radiation at the wavelength of 280 nm. Since absorption at the wavelength of 280 nm is very high, large carrier density is generated that shifts quasi-Fermi levels into the bands and moves the peak PL energy upward. The absorption at 385.6 nm is a few orders of magnitude lower as shown in Figure 1b, and therefore, the carrier density is much lower. (It is worth noting that the PL curves in Figure 1c are normalized and in reality the PL excited by the laser at 280 nm is much stronger.) This strong shift is facilitated by the fact that absorption (and hence the effective density of states) in GaN is exponential near the bandgap due to the presence of LO-phonon-induced Urbach tail.[27] In fact, by comparing with the absorption spectrum of Figure 1b, one can see that not only the absorption of laser light but also the ASPL itself originates in the states below the nominal bandgap in the so-called Urbach tail with an exponential density of states. As shown in refs10 and 28, the exponential density of states is advantageous for laser cooling and the semiconductor should be excited below the nominal bandgap into the Urbach tail whose origin is either of extrinsic (i.e., due to defects/impurities) or intrinsic (phonon-assisted absorption) nature. The extrinsic Urbach tail is less suitable for the laser cooling since it is often accompanied by the background absorption. This background absorption, whose nature is not certain, is very weak but presents a serious obstacle to laser cooling of semiconductors.[4] Furthermore, conceptually using impurity-related Urbach tail for refrigeration is not significantly different from that using the donor−acceptor transition below the gap for the same purpose. The latter concept had been explored in ref 11. While it was found to have an advantage in terms of cooling threshold, the cooling power was found to be very limited due to saturation of the donor−acceptor transition.

At the same time, the Urbach tail originating from the phonon-assisted absorption seems to be a natural match for laser refrigeration, it is almost always guaranteed to produce strong anti-Stokes shift in PL as the joint density of electronic states in the band, that is, above the photon energy is always larger than the density of states below the gap. The potential of using the phonon-assisted Urbach tail absorption for laser cooling had been investigated in ref 10, where it had been shown that while this absorption does get saturated, it usually occurs at relatively high powers. In the same work it was shown that there also exists a Stokes-shifted luminescence due to phonon-assisted electron−hole recombination (the process reverse to phonon-assisted absorption) but with a proper selection of excitation wavelength one can always ensure that it is the anti-Stokes luminescence that dominates, as was indeed observed in our experiments. What makes phonon-assisted Urbach tail particularly attractive for laser cooling is that exists in high-purity materials and, thus, is not inherently accompanied by the bane of optical refrigeration−background absorption.

It is rather evident that the prospective for laser cooling improves when the Urbach tail gets enhanced in both depth and strength. The strength of phonon-assisted absorption is proportional to the strength of electron−phonon interaction in solids: Fröhlich interaction that is particularly effective for LO phonons in polar semiconductors. The depth of the tail, that is, how far below the bandgap it extends in the energy space, is commensurate then with the energy of LO phonons. Under such an analysis, GaN is a good candidate for laser cooling, not only does it have strong Fröhlich interaction (Fröhlich coupling constant is 0.48, 0.51, and 0.07 for GaN, CdS, and GaAs, respectively[26]) but also has very large LO phonon energy (92, 37, and 36 meV for GaN, CdS, and GaAs, respectively).

Of course, in the end it is the ASPL efficiency that matters for laser cooling, and in our experiments, we have measured only an ASPL output power of 300 nW with the pump power of 30 mW at 385.6 nm, mostly due to the fact that only 5% of the pump beam is absorbed by the GaN wafer and also since most of the photoluminescence can be not directly coupled out due to loss through total internal reflection. Such loss can be greatly reduced by using the optimized collection optics. We have estimated the internal quantum efficiency to be 4.18% at 300 K. Consider the collection efficiency of 1.2%, the net external efficiency is determined to be 0.05%, which is different from the measured value of 0.02% by a factor of 2.5. Such a discrepancy is due to the losses at lenses, gratings, and so on, which can be reduced through optimizations. It is worth noting that our internal quantum efficiency can be significantly improved when the doping is optimized. A previous study indicated that the internal quantum efficiency can reach 93% in ref 29. To confirm that the ASPL of GaN is indeed a phonon-assisted phenomenon, we have measured the intensity of ASPL as a function of the pump power. Besides phonon-assisted

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ASPL, luminescence upconversion in semiconductors can also be induced by two-photon absorption.[30] The intensity of ASPL induced by two-photon absorption is expected to be proportional to the square of the pump power. For the phonon-assisted ASPL, however, the power dependence should be linear since only just one photon is required for each transition. As we can see from Figure 2a, the integrated intensity of ASPL

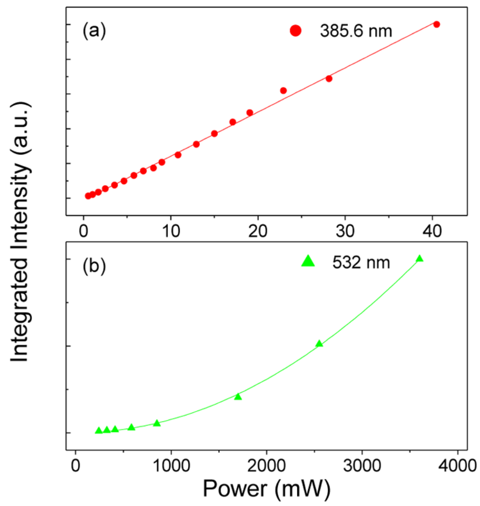

Figure 2. Integrated PL intensity as a function of laser power measured at 300 K: (a) excited by 385.6 nm; (b) excited by 532 nm. The solid red and green lines are linear and quadratic fits, respectively.

is proportional to the pump power for the powers of up to 40 mW. In comparison, Figure 2a shows that when a CW laser beam at 532 nm, that is, well below the bandgap, is used to generate a PL signal from GaN, the dependence of the luminescence intensity on the pump power shows a clearly quadratic behavior. It should also be pointed out that the intensity of PL induced by two-photon absorption is at least 4 orders of magnitude lower than that for the phonon-assisted ASPL pumped at 385.6 nm.

One can see the transition between the phonon-assisted and two-photon ASPL in Figure 3a, where the pump wavelength had been tuned in the range of 383−410 nm, similar to ref 23. As the pump wavelength is increased, the ASPL intensity is decreasing rapidly following nearly exponential decrease predicted in ref 10. This behavior persists when the photon energy is below the bandgap by more than 1 LO phonon energy indicating the gradual switch to the absorption involving two phonons and a photon. Note that a similar behavior was observed on the ASPL experiment of GaAs quantum wells[12] and CdSe quantum dots.[19] However, as the pump wavelength is increased to beyond 400 nm, the PL signal ceases to decrease and more or less stays constant, indicating that in this range two-photon absorption, earlier reported in GaN,[31] is stronger than weak phonon-assisted absorption involving three or more LO phonons. To confirm this assumption of graduate change from phonon-assisted to two-photon absorption, we have measured the ASPL intensity as a function of the pump power at several different pump wavelengths. As shown by Figure 3b, with increasing the pump wavelength from 382.1 to 409.1 nm, the power dependence gradually evolves from linear (phonon-assisted absorption) to quadratic (two-photon absorption), similar to ref 23. Obviously, two-photon absorption leads to

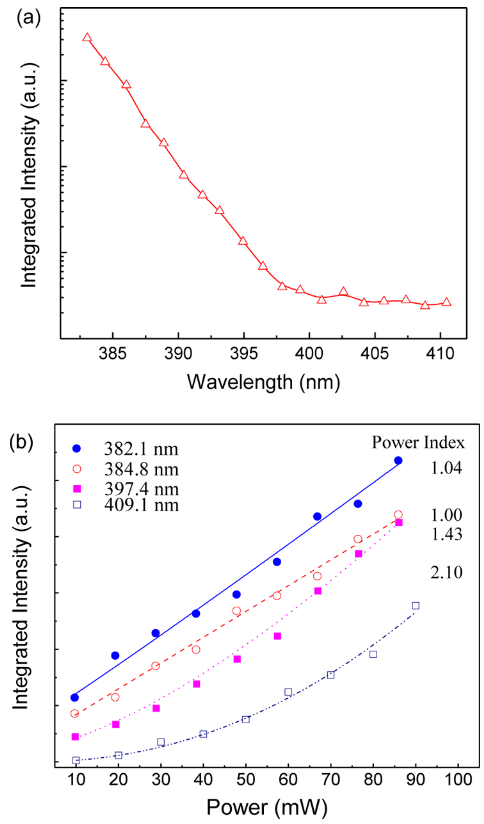

Figure 3. (a) Integrated PL intensity as a function of pump wavelength measured at 300 K. The laser power is set as 20 mW, the solid line is a guide for the eye. (b) Integrated PL intensity as a function of laser power for four wavelengths measured at 300 K. The experiment data have been fitting by $I \propto P^{\alpha}$, where I is integrated PL intensity, P is laser power, and α is power index.

heating rather than cooling of sample and it is desirable to reduce it which suggests using CW rather than pulsed pump.

Perhaps, the clearest signature of the phonon-assisted ASPL is the increase of the intensity with the temperature rise.[19] As shown in Figure 4, the intensity of ASPL scales up quickly with the temperature from 150 to 390 K. It is worth noting that since the intensity of phonon-assisted ASPL is very sensitive to

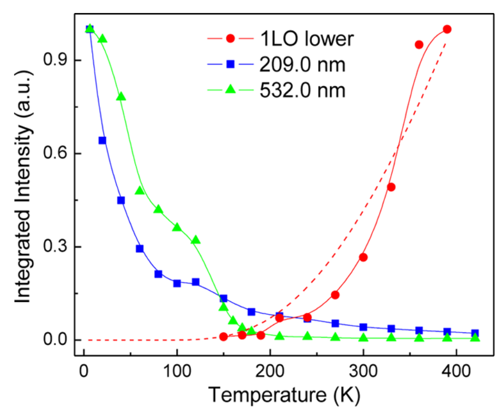

Figure 4. Integrated PL intensity as a function of temperature for different laser wavelengths. Each curve is normalized by its highest value. The solid lines are a guide for the eye. The dashed line is a fitting curve assuming that intensity of ASPL is proportional to number of LO phonons defined by Bose−Einstein statistics.

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the separation between the pump and emission photon energies (see Figure 3a), during such a measurement, the pump laser is tuned to set its photon energy always to about 1LO phonon energy lower than the emission peak of ASPL. Below 150 K, since the ASPL signal is significantly reduced in power and strongly overlaps with the laser emission tail, hence given limitations of our experimental setup, the peak cannot be clearly distinguished from the laser spectrum. The observed temperature dependence of course follows from the Bose–Einstein distribution of optical phonons as shown by the dashed curve in Figure 4. We have also measured the PL intensity as a function of the temperature when the laser wavelength is set to 209 and 532 nm, and the carriers are excited directly well above the bandgap rather than into the phonon-assisted bandtail by either one or two photon absorption. The results shown in Figure 4 indicate that the PL intensities generated by these two pump wavelengths are reduced with increasing the temperature, in all probability due to an increase in the nonradiative recombination. Thus, the temperature behavior of ASPL of GaN strongly supports the fact that the upconversion process is assisted by LO phonons.

In conclusion, we have observed ASPL of GaN. By measuring the power and temperature dependences of ASPL intensities, the mechanism has been attributed to phonon-assisted upconversion. Observation of phonon-assisted ASPL raises the prospect of GaN for laser cooling, although a considerable effort must be devoted for improving the internal quantum efficiency to nearly 100% from 93% reported previously.

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Notes

The authors declare no competing financial interest.

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