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**14. ABSTRACT**
This report includes a book chapter (review article), two of our recent Physical Review B (PRB) articles, and our publication list. In the first PRB article, femtosecond pump-probe spectroscopy and time-resolved photoluminescence were used to investigate the carrier dynamics in an $In_{0.18}Ga_{0.82}N$ thin film photoexcited well above the band gap at 10 K. Optical gain occurring after 2.5 ps time delay caused stimulated emission with a 28 ps decay time. In the second article, femtosecond pump-probe transmission spectroscopy was used to study the nonequilibrium carrier dynamics in a GaN thin film at 10 K with carrier densities ranging from $4 \times 10^{17}$ to $10^{19}$ $cm^{-3}$. Because of hot phonon effects, the carriers were strongly confined in a nonthermal distribution and collectively relaxed very slowly to the band edge for 1 ps. Excitonic resonances persisted at carrier densities well above the Mott density at early time delays, indicating that the excitons do not strongly couple to the nonthermal electron-hole plasma.

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# Optical Properties and Lasing in GaN

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# Contents

# 1. INTRODUCTION

It is well known that wide gap group III nitrides have enormous potential in device applications, particularly in UV-visible light emitters and high temperature and high power electronics. The study of optical properties in these materials has been hampered by the difficulties in obtaining high quality nitride materials. The tremendous recent progress made in nitride growth technology, such as MBE and MOCVD as discussed in previous chapters, has renewed interest in optical investigations in GaN after a relatively long inactive period since the eraly work during the 1970s by Dingle *et al.,* Pankove *et al.,* and Monemar.

In this chapter, we present recent studies of the optical properties of GaN with emphasis on those aspects relevant to photonic applications. We discuss optical transitions associated with excitons and impurities, stimulated emission ar 1 lasing by optical pumping, and optical nonlinearities, with more focus on experimental aspects. The experimental data shown in the figures were selected to represent the most pertinent aspects of the chosen topics. Many are the first of their kind, especially in the optical pumping and nonlinear optical studies. From the viewpoint of optical spectroscopy techniques, they also cover a wide range of procedures. The data presented were taken by absorption, photoluminescence (PL), PL excitation, reflectance, photomodulation spectroscopy, PL using diamond-anvil pressure cells, time-resolved PL measured with a picosecond streak camera and optical pumping for stimulated emission, as well as nonlinear spectroscopy techniques such as second harmonic generation, picosecond four-wave-mixing and tunable femtosecond four-wave-mixing. These data, taken mostly from GaN, will provide valuable reference bases for the study of alloys such as AlGaN and InGaN, as well as quantum structures such as quantum wells and superlattices containing AlN, GaN, InN, and their ternaries and quarternaries, in much the same way as the role GaAs data played in studying its related structures in the past.

There are several difficulties in the optical studies of III-nitrides. Even in GaN, although high quality film can be grown now, there is a great deal of inhomogeneity and imperfections in the samples, which is inevitable in any epifilms grown on such lattice mismatched substrates such as sapphire and SiC. This poses many obstacles to experimental investigations and, more importantly, makes it difficult to compare experimental results and theoretical work, which, in most cases, deals

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with ideal or nearly ideal homogeneous samples. Another area of difficulty is in the lack of conveniently tunable light sources in the wavelength range needed for GaN. Additionally, the lack of precise values of fundamental parameters in GaN, such as the index of refraction in the vicinity of excitons, adds uncertainties in the interpretation of the data and its comparison with theory. This situation is more pronounced in nitride alloys and quantum structures where the growth techniques and their understanding are not as advanced as those of GaN.

During the past few years, we have witnessed a significant increase in the number of publications in optical properties of GaN and related subjects. Even for the several topics we selected in this chapter, it is a challenge to provide a comprehensive, as well as a detailed review in those areas. We have, therefore, chosen to discuss those we thought were quite relevant in practical applications and material characterizations, with the hope that what we present here will ultimately aid in the advancement of nitride growth techniques, photonic device development and general theoretical understanding in nitrides and help develop innovative approaches in experimental techniques.

The organization of this chapter is as follows. Each Section opens with a brief introduction of the topic under discussion. Then in Section 2, we focus on the optical transitions associated with excitons in epitaxially grown GaN. After a brief introduction of excitons, we discuss effects of residual strain on the excitonic transitions and the binding energy for excitons, as well as recent, (and somewhat preliminary) work on exciton-phonon interactions. In Section 3, the discussion focuses on optical transitions associated with impurities and defect states observed in nominally undoped GaN and doped GaN with different doping species. In Section 4, the main topic is stimulated emission and lasing observed in GaN and related heterostructures. The optical pumping discussion is followed by a very brief summary of InGaN current injection laser diodes. The last section is devoted to a relatively unexplored but promising area: nonlinear optical studies of GaN, which not only provide additional understanding of optical properties of GaN but may open another avenue for new device applications.

## 2. OPTICAL TRANSITIONS ASSOCIATED WITH EXCITONS

Many significant optical processes in semiconductors are associated with electronic transitions between the band edges of the valence bands and the conduction band: direct and indirect interband

transitions; intrinsic free excitons and excitons bound to impurities (bound excitons); and the transitions related to impurity states associated with the bottom of the conduction-band valleys (donors or donor-like) and with the valence-band maxima (acceptors or acceptor-like). In this section, we focus on the optical transitions associated with free and bound excitons in GaN. The excitonic processes including excitation, relaxation, formation and annihilation are important in semiconductor physics because they involve a number of basic interactions between excitons and other elementary excitations as well as impurities and defects. Exciton studies are very useful for fundamental understanding of physics involved in those basic interactions in the material systems and deriving some important parameters in terms of electronic structures and optical properties of the materials.

## 2.1. General aspects of excitons in GaN

Gallium nitride crystallizes in a hexagonal wurtzite structure. Its conduction band minimum locates at the center of the Brillouin zone ($\Gamma$-point, $k=0$), and has a $\Gamma_7$-symmetry with a quantum number $J_z=1/2$. The valence band of GaN has its maximum at the $\Gamma$-point as well, which leads to a direct fundamental band gap. The top of the valence band is split into three sub-bands as a result of crystal-field and spin-orbit coupling due to the wurtzite structure of GaN, conveniently denoted by A, B, and C. The A-band has $\Gamma_9$-symmetry, while B and C have $\Gamma_7$-symmetry. Detailed reviews of the electronic band structure and the numerical values of some important parameters can be found in a number of recent review articles (Jenkins, 1989; Gorczyca, 1991, 1993; Min, 1992; Palummo, 1993; Rubio, 1993, 1995; Christensen, 1994; Kim, 1994; Capaz, 1995; Suzuki, 1995; Yang, 1995; Lambrecht, 1995; Sirenko, 1996; Chuang, 1996). We summarize only the structure and symmetries of the lowest conduction band and upmost valence bands in GaN near $k=0$ (the $\Gamma$ point) in Fig.1, which is directly related to the object of discussions in this section.

Intrinsic free excitons (FX) represent the lowest energy intrinsic excitation of electrons and holes in pure materials at low excitation density. (Elliott, 1957; Knox, 1963) In GaN, the free-exciton state can be adequately described by the Wannier-Mott approximation, where the electrons and holes are treated as nearly independently interacting through their Coulomb fields. The interactions result in completely correlated motions of the paired electrons and holes and a reduction of the total energy

of the bound state relative to that of the unrelated free carrier states by an amount corresponding to the exciton binding energy. In the effective mass approximation, the total energy of the two-particle structure involving an electron and a hole bound together because of the Coulombic attraction is given:

$$E_K = E_n + \hbar^2 K^2 / 2(m_e^* + m_h^*),\tag{1}$$

where $m_e^*$ and $m_h^*$ are the effective masses of the electron and hole, and $K$ is the wavevector of the exciton, and

$$E_n = -e^4 \mu / 2(4\pi\hbar\epsilon)^2 n^2,\tag{2}$$

where $n$ is an integer, $\epsilon$ is the low-frequency dielectric constant, and $\mu$ is the reduced effective mass given by $1/\mu = 1/m_e^* + 1/m_h^*$. Eq.(2) is a solution of the hydrogenic wave equation, suggesting that free excitons can exist in a series of excited states similar to the excited states of hydrogen-like atomic systems, with an ionization limit corresponding to the bottom of the conduction band. Due to the existence of excitons, optical transition such as absorption or emission from the discrete states occurs below the band gap $E_g$ at the exciton energy:

$$E = E_g - E_b / n^2.\tag{3}$$

The binding energy ($E_b$), which is the energy necessary to ionize an exciton, apparently is equal to $e^4\mu/2(4\pi\hbar\epsilon)^2$. In GaN, each valence band generates a hydrogenic series of exciton states.(Dingle, 1971(a), 1971(b)) The free excitons associated with the $\Gamma_9^V$ valence band (A-band), the upper $\Gamma_7^V$ valence band (B-band), and the lower $\Gamma_7^V$ valence band (C-band) in GaN are often referred to as $A$-, $B$-, and $C$-excitons, as indicated in Fig.1.

Bound excitons are the formation of a complex involving an impurity and an exciton. The impurity might first capture an electron or a hole and then capture the carrier of the opposite charge, or the impurity might directly capture a free exciton (Lampert, 1958; Haynes, 1960). Excitons can be bound to neutral or ionized donors and acceptors. The combination of bound excitons is an important recombination process in the near-band-edge spectral region. At low temperatures, the bound exciton emission lines are prominent features of luminescence spectra of many semiconductors. The energy of the emitted photon is:

$$\hbar\omega = E_g - E_b - E_{BX},\tag{4}$$

where $E_{BX}$ is the so-called exciton localization energy, that is, the energy required to dissociate the

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exciton from the impurity. Haynes (1960) first found the exciton localization energy in Si linearly depending on the impurity binding energy. The approximation of $E_{BX} \approx 0.1E_i$, where $E_i$ is the impurity binding energy, is called the Haynes rule. A more general relation between the localization energy $E_{BX}$ and the impurity binding energy $E_i$, in the case of neutral impurities, has been empirically found to be

$$E_{BX} = a + bE_i, \tag{5}$$

where $a$ and $b$ are constants, and in general. $a \neq 0$, $b$ depends on whether the impurity is donor or acceptor.(Dean 1982) The variation of the exciton localization energy for different chemical species is clearly a central-cell effect:(Merz, 1972) both the impurity binding energy and the exciton localization energy can be written

$$E_i = E_0 + PV, \tag{6}$$

$$\text{and} \quad E_{BX} = E_0' + P'V, \tag{7}$$

where $E_0$ and $E_0'$ are the effective-mass binding energy, respectively, $V$ is a square-well potential in the central cell of the impurity, which distinguishes the difference of the impurities, $P$ is the probability that the impurity electron (or hole) is in the central cell, and $P'$ is the probability of the bound-exciton electron in the cell. Combining these two equations gives

$$E_{BX} = [E_0' - (P'/P)E_0] + (P'/P)E_i = a + bE_i. \tag{8}$$

In direct gap semiconductors, since the impurity binding energy for donors is generally smaller than that for acceptors, the transitions of the donor-bound excitons are expected to lie closer to that of the free excitons than that of the acceptor-bound excitons. It must be pointed out that caution should be taken when the Haynes rule is used to estimate the impurity binding energy based on the measured energy difference between the free-exciton and the bound-exciton recombinations since it does not apply to shallow acceptors in direct gap semiconductors.(Dean, 1982)

## 2.2. Excitonic recombinations in GaN

The near-band-edge luminescence spectra observed from most GaN samples are predominated by a strong, sharp emission line resulting from the radiative recombination of bound excitons. Fig.2 shows a set near-band-edge photoluminescence (PL) spectra obtained from GaN at various temperatures. Two sharp luminescence lines dominate the emission spectra. The intensity of the

strongest emission line marked by BX was found to decrease with increasing temperature much faster than that of FX$^A$. It became hardly resolvable when the temperature was raised above 100 K. Such effects of temperature on the luminescence intensity indicate that the emission line results from the radiative recombination of bound excitons. The second strongest luminescence line (FX$^A$), together with the weak emission features such as FX$^B$ at higher energies, can be attributed to the emissions from intrinsic free excitons associated with various interband transitions in GaN. Since as-grown GaN is always $n$-type, neutral donors are expected to be the most common extrinsic centers in the crystals. The bound-exciton emission line is from the radiative annihilation of excitons bound to neutral donors. One of the reasons for the predominance of the bound exciton emission line in the low-temperature luminescence spectra is that even a very small population of donor-like centers can have very large capture probability for excitons and make the bound exciton states very efficient recombination channels.

A critical parameter in determining the PL efficiency of photoexcited carriers is the effective lifetime:

$$1/\tau_{eff}=1/\tau_R+1/\tau_{NR}, \tag{9}$$

where $\tau_R$ is the radiative lifetime and $\tau_{NR}$, the nonradiative lifetime. In addition to spontaneous radiative recombinations, other nonradiative processes rule over the decay of photoexcited carriers. The nonradiative processes which contribute to $\tau_{NR}$, include multiphonon emission, capture and recombination at impurities and defects, Auger recombination effect, and surface recombination, as well as diffusion of carriers away from the region of observation. These processes give rise to fast relaxation of the excited carriers down to lower states from which they decay radiatively or relax nonradiatively. Under low excitation conditions, $\tau_{NR}$ is limited by the presence of nonradiative recombination centers with the energy levels locating at or near the mid-gap, which cause Schockley-Read-Hall recombinations (Pavesi, 1994). There have been a number of time-resolved photoluminescence studies in GaN. The measured decay times for exciton emissions in GaN were found to be generally in the range of several tens of picoseconds to a few hundreds of picoseconds (Harris, 1995; Smith, 1995; Chen, 1995; Shan, 1995a; Eckey, 1996). Shown in Fig.3 is the temporal evolution of spectrally integrated exciton luminescence for both free-exciton and bound-exciton emissions observed in a GaN sample at 10 K. The time evolution for both free-exciton and bound-

exciton luminescence is dominated by exponential decay. The lifetime of the main PL decay was found to be ~35 ps for the free-exciton emissions and ~55 ps for the bound-exciton emissions for the GaN sample at 10 K. These are much shorter than the theoretically-estimated values of radiative lifetime for both free-exciton and bound-exciton recombination in GaN, which are on the order of nanoseconds (Shan, 1995a). The fast decay behavior of the PL intensity indicates that the capture of excitons and trapping of carriers at defects and impurities through nonradiative combinations dominate the decay of the exciton population. The inset shows the decay times for free-exciton and bound-exciton emission of the sample measured as a function of temperature. The bound-exciton PL decay time decreases slightly with increasing temperature before the emission thermally quenched. The free-exciton PL decay time exhibited slow decreasing with temperature for this sample. It is known that for a radiative recombination dominant system, an increase in the radiative lifetime with temperature is expected for the free excitons since their average kinetic energy is increased, while the time-integrated PL intensity remains almost unchanged.('t Hooft, 1987; Feldmann, 1987) The thermal redistribution results in a decreasing number of the excitons close enough to the Brillouin-zone center for radiative recombination. Therefore, the variations of the measured PL decay time for free excitons with temperature is a result of competition between nonradiative capture of free excitons at defects or impurities and thermally enhanced exciton-exciton and exciton-phonon scatterings. Also the lifetime is expected to be independent of temperature for bound excitons, and only the emission intensity is expected to decrease because of thermal ionization of the bound excitons. Such phenomena were observed in a number of III-V and II-VI quantum well systems in the low temperature regime (Feldmann, 1987; Martinez-Paster, 1993). Although recombination from excitons bound to extrinsic states such as defects or impurities can often be very efficient at low temperatures, the measured decay time is still determined by detailed decay kinetics. The observed decrease of PL decay time with temperature for both free and bound excitons in GaN samples suggests that the incremental stronger nonradiative relaxations occur as the temperature is raised resulting in further faster decay of the exciton population.

In addition to the temperature dependent studies on the exciton luminescence in GaN, the dependence of the excitonic recombinations in GaN on pressure has also been studied to verify the theoretical estimates on the pressure coefficients for the band gaps of III-nitrides. (Perlin, 1992;

Gorczyca, 1993; Christensen, 1994)   Pressure-dependent PL measurements were performed using the diamond-anvil pressure-cell technique to study the effects of the application of hydrostatic pressure on bound-exciton and free-exciton emissions.(Shan 1995b, Kim 1995)   The emission lines associated with the radiative decay of a free exciton or a shallow bound exciton shifts with the host semiconductor band gap under hydrostatic pressure at the same rate.   The electron stays in the conduction-band edge state or in the orbit of shallow donor state associated with the conduction-band edge, and the excitonic hole bound in the Coulomb field retains the symmetry of the valence-band edges.   The change of the intense and sharp emission lines of excitonic radiative transitions with pressure therefore provides an unmistakable signature of the direct $\Gamma$ band-gap dependence for wurtzite GaN. Plotted in Fig.4 are the peak energies of observed exciton emission structures as a function of applied pressure (Shan 1995b).   The solid lines in the figure are the least-squares fits to the experimental data using the quadratic-fit function

$$E(P)=E(0)+\alpha P+\beta P^2, \tag{10}$$

where $E(P)$ is the peak energy of exciton emissions under pressure, and $P$ is the applied pressure. The best fits to the data yield a linear slope of $\alpha=3.86\times10^{-3}$ eV/kbar for the BX transition with an extremely small sublinear term of $\beta= -8\times10^{-7}$ eV/kbar$^2$.   Similar results were obtained from fitting the FX transition as well.   The pressure coefficient for the FX emission energies derived from the fittings is $\alpha=3.90\times10^{-3}$ eV/kbar and $\beta= -1.8\times10^{-6}$ eV/kbar$^2$.   The uncertainty of the linear pressure coefficient is $\sim5\times10^{-5}$ eV/kbar and comes primarily from the error bar of pressure calibration (within $\pm0.2$ kbar), as well as the possible pressure-induced change of the exciton binding energy, which arises from an increase in the electron effective mass and a decrease in the dielectric constant with the band gap increase (Samara, 1983; Wolford, 1987; Perlin 1992).   The pressure coefficient of the GaN band gap determined by exciton luminescence measurements is smaller than those reported in other studies involving absorption measurements under pressure reported by Camphausen *et al.*(1971) and Perlin *et al.* (1992), as given in Talbe I.   The discrepancy between the PL results and the absorption results may come from the difficulty in accurately determining the transition energies in broad optical absorption curves.


2.3. Strain effects on excitonic transitions

Early work on epitaxial grown GaN on sapphire and 6H-SiC substrates showed a relatively large difference in the energy positions of excitonic transitions reported by various groups using different spectroscopic techniques (Dingle, 1971a, 1971b; Monemar, 1974; Shan, 1995b; Gil, 1995; Smith, 1996; Chen, 1996; Shan, 1996), which caused a significant amount of confusion. Only recently has the importance of the effects of residual strain in the epilayers due to the mismatch of lattice parameters and coefficients of thermal expansion between GaN and the substrate materials been realized (Gil, 1995; Rieger, 1996; Shan, 1996; Volm, 1996). Listed in Table II are the lattice parameters and coefficients of thermal expansion for GaN, AlN, sapphire, and 6H-SiC (Perry, 1997). Despite the inevitable occurrence of strain relaxation by the formation of a large density of dislocations, the residual strain has a relatively strong influence on the excitonic transition energies. Shown in Fig.5 is a comparison of reflection spectra taken from two GaN epilayers grown on sapphire and a GaN epilayer on SiC at 10 K. As clearly shown by the figure, the energy positions of the exciton resonances associated with $A$-, $B$-, and $C$-exciton transitions are sample dependent.

The differences in the measured exciton transition energies can be attributed to the effects of residual strain in the epilayers due to the mismatch of lattice parameters and thermal expansion coefficients between GaN and the substrate material as mentioned above (Gil, 1995; Rieger, 1996; Shan, 1996; Volm, 1996). The effects of strain can be further evidenced by the variations of the lattice parameters of GaN relative to that of the virtually strain-free bulk GaN as shown in the inset of the figure, where the lattice constants of the $a$-axis measured from a few GaN epilayers grown on sapphire and SiC were plotted against those of the $c$-axis. It is generally difficult to separate the strain effects caused by lattice-parameter mismatch from the ones involving thermal-expansion mismatch so as to exactly determine their influences on the optical properties of GaN epitaxial layers. However, the figure clearly indicates that the overall effects of residual strain generated in GaN on sapphire is compressive, which results in an increased band gap, while the stress induced in GaN on SiC is tensile, which leads to a decrease in measured exciton transition energies. The residual strain induced by thermal-expansion mismatch in GaN based epitaxial layers has the prevailing influence on the energy variations of exciton transitions, since lattice-mismatch induced strain has a completely opposite effect on the variation of GaN band gap (Amano, 1988; Shan,1996).

The introduction of strain changes the lattice parameters and in some cases the symmetry of a

material, which, in turn, generates variations of electronic band structure. The significance of strain effects is often straightforwardly reflected by the variation of the fundamental band gap of the material. The strain Hamiltonian of a material having a wurtzite structure is given by Pikus (1962). Under the assumption of a strain-independent and isotropic spin-orbit interaction, the energies of the three free excitons $A$, $B$, and $C$ can be described as (Sandomirskii, 1964; Gavini 1970)

$$E_A = E_A(0) + D_1 \epsilon_{zz} + D_2(\epsilon_{xx} + \epsilon_{yy}) + D_3 \epsilon_{zz} + D_4(\epsilon_{xx} + \epsilon_{yy}),\tag{11}$$

$$E_B = E_B(0) + D_1 \epsilon_{zz} + D_2(\epsilon_{xx} + \epsilon_{yy}) + \Delta_+[D_3 \epsilon_{zz} + D_4(\epsilon_{xx} + \epsilon_{yy})],$$

(12)

$$E_C = E_C(0) + D_1 \epsilon_{zz} + D_2(\epsilon_{xx} + \epsilon_{yy}) + \Delta_-[D_3 \epsilon_{zz} + D_4(\epsilon_{xx} + \epsilon_{yy})],\tag{13}$$

where $E_i(0)$ represents strain-free exciton transition energy, $D_i$ are deformation potentials, and the $\epsilon_{ii}$ are components of the strain tensor. Since the energy variation given in Eqs.(11)-(13) by $D_1$ and $D_2$ is analogous to the hydrostatic shift of a cubic semiconductor, $\Gamma$ and D are combined hydrostatic deformation potentials for transitions between the conduction and the valence bands, while $D_3$ and $D_4$ are uniaxial deformation potentials characterizing the further splitting of the three topmost valence band edges for tension or compression along and perpendicular to (0001), respectively. The coefficients $\Delta_\pm$ represent the mixing of valence-band orbital states by the spin-orbit interaction and are given by (Sandomirskii, 1964; Gavini, 1970)

$$\Delta_\pm = \tfrac{1}{2}\{1 \pm [1 + 8(\Delta_3/(\Delta_1 - \Delta_2))^2]^{-1/2}\},\tag{14}$$

where $\Delta_1$ is the crystal-field splitting of the $\Gamma_9$ and $\Gamma_7$ orbital states, and $\Delta_2$ and $\Delta_3$ are parameters, which describe the spin-orbit coupling. With the usual definition of the strain tensor, $\epsilon_{ij} = \tfrac{1}{2}(\partial u_i / \partial x_j + \partial u_j / \partial x_i)$, where $u$ is the displacement vector, the elastic properties of hexagonal materials can be described by the simple matrical equation:

$$
\begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{xy} \\ \sigma_{yz} \\ \sigma_{zx} \end{bmatrix}
=
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix}
\cdot
\begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ 2\varepsilon_{xy} \\ 2\varepsilon_{yz} \\ 2\varepsilon_{zx} \end{bmatrix}
\tag{15}
$$

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where the $\sigma_{ij}$ are the components of the stress tensor, and $C_{ij}$ are the elastic stiffness constants. Since the growth direction of most GaN epilayers is along (0001) direction (z-axis), the corresponding strain keeps the wurtzite symmetry of GaN (Gil, 1995). The strain components $\epsilon_{ij}$ can then be described by

$$\epsilon_{xx} = \epsilon_{yy} = \epsilon_\perp = (a_s - a_o)/a_o;$$

(16)

$$\epsilon_{zz} = \epsilon_\parallel = (c_s - c_o)/c_o,$$ (17)

where $a_o$ and $c_o$ are lattice parameters for strain-free bulk GaN, and $a$ and $c$ are those for the strained GaN epilayer. Under biaxial-stress conditions, the components of $\epsilon_{xx}$, $\epsilon_{yy}$, and $\epsilon_{zz}$ are related through the elastic stiffness constants as $\epsilon_\parallel = -2C_{13}/C_{33}\epsilon_\perp$. Listed in Table III are the elastic stiffness constants for GaN.

A number of investigations of the strain effects on the exciton transition have been reported in the past few years. The observed shifts in excitonic transition energies relative to the values of strain-free GaN resulting from an overall effect of strain on the band gap were used to derive numerical values of the uniaxial and hydrostatic deformation potentials of wurtzite GaN (Gil, 1995; Chichibu, 1996; Shan,1996b). Fig.6 shows an example of the fit of the experimentally observed exciton transition energies versus the A-exciton transition by Tchounkeu et al.(1996), which gives an estimate of the values of $\Delta_1$, $\Delta_2$ and $\Delta_3$, as well as the values for the deformation potentials. There have also been some theoretical studies discussing the same topic (Dingle, 1971b; Suzuki, 1995; Gil, 1995; Chen, 1996; Chichibu, 1996; Reynolds, 1996; Chuang, 1996; Shikanai, 1997). Listed in Table IV is a summary of those values published so far. The numerical values of these three band-structure parameters, in principle, have to be used to make estimates of the deformation potentials from experimentally observed strain shifts using Eqs.(11)-(13) above. The individual numerical values of deformation potentials for GaN reported in recently published literature are listed in Table V.


## 2.4. Exciton binding energy

Strong sharp resonances associated with the formation of excitons could often be observed near the band edge of GaN by the various spectroscopic methods including photoluminescence,

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reflectance, and absorption measurements. In fact, the exciton resonances were observed in absorption spectra even with the sample temperature well above 300 K (Song, 1996). Figure 7 shows optical absorption spectra taken from a 0.4-$\mu m$ GaN epitaxial layer grown on sapphire in the vicinity of the band edge at selected temperatures. Three fine exciton-resonance spectral features associated with the $A$-, $B$-, and $C$-exciton transitions between the bottom of the conduction band ($\Gamma_7^C$) and the three topmost valence band edges ($\Gamma_9^V + \Gamma_7^V + \Gamma_7^V$) can be well resolved as marked in the inset of the figure. The excitonic absorption resonances could also be clearly observed in the 300 K absorption curve, although they are thermally broadened and overlapped. These resonances persist well above room temperature up to higher than 400 K, indicating that the free excitons associated with the fundamental band edges of GaN have substantially large binding energy. Note that, under the experimental conditions with the photon wavevector along the $c$-axis of GaN, the intensity of $A$-exciton transition, in principle, should be stronger than or at least comparable to the $B$-exciton as evidenced by the reflection curve, whereas the 10-K absorption spectrum presented in the inset of Fig.7 shows that $B$-exciton transition appeared stronger than that of $A$-exciton. The observed stronger $B$-exciton absorption resonance is not, however, inconsistent with what is expected. It results primarily from an overlapping of the $B$-exciton transition with the higher energy side of the $A$-exciton feature, and the absorption background of the band tail mainly associated with the $\Gamma_9^V$-$\Gamma_7^C$ transition, due to the small energy separation between the $A$- and $B$-exciton transitions (~8 meV) and relatively broad absorption line widths (~10 meV) associated with the respective excitonic transitions observed from this sample, as well as the enhancement of oscillator strength for the $B$-exciton transition under compression conditions (Gil, 1997). A full treatment of excitonic absorption has been given by Elliott (1957), in which the transitions involving discrete excitonic states and band-to-band continuum are considered. By following Elliott's approach, in principle, one should be able to determine the exciton binding energy by fitting experimental data shown in Fig.7. However, the complicated fundamental bands of wurtzite GaN make it rather difficult to derive the binding energy unambiguously from the absorption spectra, primarily because of the mutual overlapping of the spectral features associated with $A$-, $B$-, and $C$-excitons and the structures related to band-to-band absorption continuum.

Earlier results of photoluminescence excitation by Monemar (1974) suggested a 28 meV exciton

binding energy. Low-temperature photoluminescence (PL) measurements were also reported to provide some information regarding the exciton binding energy in GaN: for instance, the observations of a small PL spectral feature on the higher energy side of the main exciton emission peaks led to the assignment of the feature to the first excited state of A-exciton (n=2), and consequently the estimate of the binding energy of 20 meV for A-exciton and 22 meV for B-exciton by Reynolds *et al.* (1996) and 22.7 meV for A-exciton by Freitas, Jr. *et al.* (1996) Fitting to the Arrhenius plot of temperature dependence of integrated intensity of the free-exciton emission yielded a 26.7 meV thermal activation energy by Kovalev *et al.* (1996). On the other hand, recent results obtained from reflectivity measurements, especially, photoreflectance (PR) measurements, have clearly demonstrated the signatures of transitions related to the 1s and 2s states of *A-*, *B-*, and *C-*exciton transitions, as well as the fundamental band-to-band ($\Gamma_V^9$-$\Gamma_C^7$) transition (Shan 1996c, Chichibu 1996, Tchounkeu 1996). The unambiguous observations of those transitions allow a precise determination of their energy positions and a straightforward estimate of the binding energy for the excitons using the hydrogenic model described by Eq.(3). Fig.8 shows a PR spectrum along with a conventional reflection curve taken from a GaN sample at 10 K. While the spectral features *A*(n=1), *B*(n=1), and *C*(n=1) can be unmistakably identified to be associated with intrinsic free-exciton transitions in the conventional reflectance spectrum, the nature of weak spectral features *a* and *b* are not immediately clear. Fortunately, photomodulation spectroscopy is an alternative approach capable of detecting weak signals so as to accurately determine their transition energies and make a positive identification for the nature of the transitions. As illustrated in the figure, the PR spectra not only consist of a series of sharp structures corresponding to most of the observed spectral features in the reflection spectra, but also exhibit, more strikingly, a pronounced enhancement of the barely observed weak spectral structures on the reflection curves such as the *a-* and *b*-features. Theoretical fits using the Lorentzian functional form to the PR spectra result in an energy separation of 0.008 *eV* between the *a-* and *b*-features marked in the figure, which is almost identical to the *A-B* separation, and a 0.016 *eV* difference for both *A-a* and *B-b* separations within experimental error ($\leq 0.001$ *eV*). Similar properties were also observed in the other GaN samples; while the absolute energy position for the main *A-* and *B*-exciton transitions varies from sample to sample slightly due to the influence of residual strain, the energy differences of the *A-a* and *B-b*

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features were found to be ~0.016 $eV$ for all the samples, and the energy separation between the $a$- and $b$-features was found to closely follow that between the main $A$- and $B$-exciton features at lower energies for each individual sample. These observations indicate that the $a$- and $b$-features are indeed associated with $A$- and $B$-exciton transitions. Therefore, $a$ and $b$ can be attributed to the $n=2$ excited states (2s) of the excitons. Such identifications permit a direct estimate of the binding energy for $A$- and $B$-excitons from the separation between the $n=1$ and $n=2$ states for excitons, assuming that the hydrogenic model based on the effective mass approximation is applicable. A binding energy of $E_b \approx 0.021 \pm 0.001$ $eV$ is obtained using $E_n=-E_b/n^2$ for $A$- and $B$-excitons (Shan, 1996). The binding energy for the $C$-exciton can also be derived from the theoretical fitting to the PR spectrum taken from a GaN sample grown on SiC as shown in Fig.9 using the same approach. A much stronger $C$-exciton transition signal could be observed. In addition to the derivative-like spectral features arising from the transitions associated with the $n=1$ exciton states of the $A$-, $B$-, and $C$-excitons, the spectral features related to the transitions involving the $n=2$ exciton states of the $A$- and $C$-excitons could be clearly observed in the PR spectrum. The best fit yields a 0.0172 $eV$ energy separation between the 1s and 2s states of the $C$-exciton, which corresponds to a binding energy of ~0.023 $eV$, and retains a ~0.016 $eV$ difference between the $A$-exciton ($n=1$) and $a$-feature as indicated in the figure. The values of binding energy for excitons in GaN obtained by various methods including some theoretical predictions are listed in Table VI.

## 2.5. Exciton-phonon interactions

As shown in Fig.7, a weak absorption spectral feature could be clearly visible in the energy region of about 100 $meV$ above the excitonic resonance. This is a real absorption structure though it is weaker and broader than the main exciton absorption structures. Its temperature dependence follows the main absorption edge as shown in Fig.7. A similar feature was first observed in reflectance spectra by Dingle $et$ $al$ (1971b). They suggested that the feature is related to transitions arising from an indirect phonon-assisted absorption process. In such a process, an incident photon simultaneously creates a free exciton in its $n=1$ band and an LO phonon, resulting in an absorption coefficient showing a maximum at the corresponding photon energy. A review of this subject is given by Planel $et$ $al$.(1973) The broad LO-phonon sideband in the absorption spectra with a

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maximum at a higher energy given in Fig.7 is due to the exciton dispersion, or in other words, the recoil kinetic energy $\hbar^2 K^2/2M$ of the exciton (Permogorov, 1975; Ueta, 1986). The indirect absorption process with the simultaneous creation of a nonequilibrium exciton in its n=1 band and an LO phonon followed by a cascade kinetic relaxation process with LO-phonon emissions has been observed in a number of polar materials such as CdS and ZnO by excitation spectroscopy (R. Planel, 1973; Ueta, 1986; Liang, 1968; Permogorov, 1975). There have been few reports, however, on the observation of such phonon structures of excitons directly in the absorption spectra taken from semiconductor materials. Thus the absorption results indicate that phonon-assisted exciton formation is very efficient in GaN, primarily due to strong exciton-phonon coupling in this polar material.

In an indirect phonon-assisted exciton formation process, as illustrated in Fig. 7, the most probable relaxation process in its band is the phonon emission process (Ueta, 1986). When the energy of the incident light is just

$$E = E_0 + n\hbar\omega_{LO}, \tag{18}$$

where $E_0$ is the exciton energy at $K=0$ and $n$ is an integer, excitons created by indirect absorption quickly lose their kinetic energy by emitting LO phonons with an appropriate wave vector $K$ before reaching the minimum at $K=0$ of the exciton band, where they annihilate and emit light with an energy of $E_0$. When the excitation photon energy is

$$E = E_0 + n\hbar\omega_{LO} + \Delta E, \tag{19}$$

where $\Delta E < \hbar\omega_{LO}$, excitons descend toward the bottom by emitting LO phonons until they reach $E_0 + \Delta E$, and then they can relax down only by emitting acoustic phonons to dissipate the excess energy since $\Delta E < \hbar\omega_{LO}$, and virtually become *slow excitons* due to the fact that the relaxation time of the LO-phonon emission ($\tau_o \sim 10^{-13}$ sec.) is four orders of magnitudes shorter than that of the acoustic-phonon emission ($\tau_a \sim 10^{-9}$ sec.)(Ueta, 1986). Such indirect phonon-assisted exciton formation processes can be verified by photoluminescence excitation (PLE) measurements. When the emission intensity at the free-exciton resonance is measured while varying the excitation photon energy $E > E_0$, a change in the PLE spectrum with a period of $\hbar\omega_{LO}$ is expected to be observed if the lifetime of the excitons due to other nonradiative processes is shorter than the relaxation time of the acoustic-phonon emission. This is because that whenever exciton-acoustic-phonon interaction

occurs the number of excitons which reach the $K=0$ state will be small and the intensity of the resonance emission will be weak. The first observation of such PLE spectra due to nonequilibrium excitons (hot excitons) in GaN and detailed discussions were reported by Kodalev *et al.* (1996)

Shown in Fig.10 are the results of PLE measurements from a 2.5-$\mu m$ GaN on sapphire with detection energies at the $A$-exciton (FX$^A$) and bound-exciton (BX) emission peak positions, where the inset is the 10-K PL spectrum of the sample (Shan, 1997). The PLE spectra exhibit a series of emission resonances with 91.7±0.5 meV energy spacing, which corresponds to the excitation energies of $E_0+n\hbar\omega_{LO}$ with the LO-phonon energy $\hbar\omega_{LO}$=740 cm$^{-1}$. The PLE spectra can be clearly distinguished from the spectral structures associated with the formation of electron-hole pairs via thermalization processes by emitting LO phonons. Otherwise, an oscillatory series beginning from the band gap energy $E_g$, rather than from the exciton energy $_0E$, with an energy separation of $\hbar\omega_{LO}(1+m_e/m_h)$, where $m_e$ and $m_h$ are the effective masses for electrons and holes, respectively, would be observed (Permogorov, 1975; Kodalev, 1996). The PLE spectrum detected at the free-exciton (FX$^A$) resonance consisted of two sets of spectral features: the broad features very similar to those exhibited in the PLE spectrum obtained by detecting at bound-exciton (BX) resonance, and the relatively narrower phonon lines highlighted by the dotted lines in Fig.10. While the equidistant phonon lines exhibited in the PLE spectrum can be attributed to the radiative annihilation of those free excitons generated with initial energy at and in the vicinity of $E_0+n\hbar\omega_{LO}$ completing the thermalization process during their lifetime reaching to the $K=0$ minimum of the exciton band, as discussed as above, the nature of the broad spectral features is not immediately clear. It is very interesting to see the broad spectral features with minima approximately at the exciting energies of $E_{BX}+n\hbar\omega_{LO}$, where $E_{BX}$ is the bound-exciton resonance energy, in the PLE spectrum measured at both bound-exciton (BX) and free-exciton (FX$^A$) resonances. The observation at BX resonance suggests that the process of bound-exciton formation is a fast and efficient nonradiative process of trapping slow excitons at impurities and/or defects during the period of excitons interacting with acoustic phonons, rather than a process of resonantly trapping hot excitons with LO phonon emissions, which would otherwise lead to the appearance of a series of equidistant resonant features with maxima at the excitation energies of $E_{BX}+n\hbar\omega_{LO}$. The probability of exciton trapping at impurities and defects decreases with an increase in the kinetic energy of excitons, as demonstrated by the gradual decrease

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of the PLE signal level with excitation photon energy. Fig.11 illustrates the kinetic energy relaxation scheme for excitons within the free-exciton band observed from the GaN samples used in this work. The upper portion of the figure depicts the scheme measured at the $A$-exciton ($FX^A$) emission peak position. The equidistant phonon lines observed in the PLE spectrum detected at $FX^A$ resonance correspond exactly to the case of free excitons with initial energy of $E_0 + n\hbar\omega_{LO}$ reaching the $K=0$ minimum of the exciton band via thermalization process. The lower portion of the figure describes the scheme detected at bound-exciton (BX) resonance. Note that the energy separation between BX and $FX^A$ resonances is only slightly larger than 6 $meV$, a process of repopulation of the n=1 free-exciton band via thermal excitation is likely to occur at a finite temperature right after the free excitons nonradiatively relaxed down to the bound exciton states. Although the occupation ratio of $FX^A$ to BX at 10 K is roughly about $10^{-3}$ given by detailed balance, the density of state of $FX^A$ should be at least a few orders of magnitude larger than that of BX (Chang, 1997). The overall effect of thermal repopulation of the free-exciton band could be very significant, giving rise to the appearance of the broad spectral features at PLE spectrum detected at $FX^A$ reminiscent to those measured at BX resonance. From PLE results shown in Fig.10, one can furthermore infer that the lifetime of both free and bound excitons ($\tau_{ex}$) in the GaN samples is very short compared to the relaxation time of acoustic-phonon scattering, which is the condition ($\tau_o < \tau_{ex} < \tau_a$) necessary for observing a hot-exciton oscillatory spectrum. This is consistent with the results from time-resolved exciton luminescence measurements: the measured PL decay time for free-excitons and bound-excitons was found to be on the order of a few tens to hundreds of picoseconds (Shan, 1995; Harris, 1995; Smith, 1995). This is a clear indication that the lifetime of excitons in the GaN samples is governed by nonradiative processes. The capture of excitons and trapping of carriers at defects and/or impurities through nonradiative relaxation processes dominate the decay of the exciton population. This is also the reason the excitation spectrum, as shown in Fig.10, does not reproduce the shape of the absorption spectrum shown in Fig.7 because of the kinetic phenomena of the nonequilibrium hot excitons.

## 3. RADIATIVE RECOMBINATIONS ASSOCIATED WITH IMPURITIES AND DEFECT STATES

The radiative recombination process in semiconductors is primarily determined by the transitions involving band extreme or bound states (excitons, impurities, and defects). The fundamental

properties of transitions associated with band extrema and excitons have been discussed in the previous section. Therefore, this section will focus mainly on the phenomena related to radiative recombination processes involving impurities and defects in GaN, which are most frequently studied by photoluminescence measurements. The non-destructive spectroscopic technique of photoluminescence concerns the radiation emitted after optical excitation and resultantly reveals the intrinsic and extrinsic properties of the material under study.

## 3.1. Properties of nominally undoped GaN

Photoluminescence (PL) spectra taken from nominally undoped (as-grown) GaN samples often, if not all, exhibit a series of emission structures in the energy range approximately 3.27-2.95 eV, and a broad emission band in the yellow spectral region with the peak position around 2.2 eV, in addition to the near-band-edge exciton emissions as shown in Fig.2. The intensities of these two emission bands relative to that of the exciton emissions vary from sample to sample depending on the crystal quality. Fig.12 shows typical spectral signatures of these two emission bands.

The emission structures with a characteristic spectral feature in the energy range of 3.27-2.95 eV have been identified as the radiative recombination processes arising from donor-to-acceptor pair (DAP) transitions and their phonon replicas (Dingle 1971a). The emission energy of DAP transition is a function of the distance ($r$) through the initial state and final state interactions between the donor and acceptor. Assuming a simple electrostatic interaction potential between the charged donor and acceptor through a Coulomb interaction term $e^2/\epsilon_0 r$, the emission photon energy in a DAP transition is given by

$$\hbar\omega = E_g - (E_D + E_A) + e^2/\epsilon_0 r, \tag{20}$$

where $E_D$ and $E_A$ are ionization energies for the donor and acceptor, respectively. The relatively broad spectral structures suggest the emissions resulting mainly from distant pair transitions. A detailed review on the subject is given by Dean *et al.* (1973). The DAP emission structure will evolve to the free-to-bound (FB) recombination with increasing temperature as a result of the thermal ionization of the donor and the increase in the carrier concentration in the conduction band. A characteristic shift of the DAP emission toward higher energies is expected at moderate temperature range. This phenomenon was first observed by Dingle *et al.* in 1971, and the observation, combined

with time-resolved spectroscopic measurements, was used to estimate the binding energies for the donor and acceptor, as well as the Coulomb interaction in GaN (Dingle 1971).

The broad-band emission in the yellow spectral region known as yellow luminescence has been extensively studied for its adverse effects on carrier lifetime and blue emission efficiency. It could be commonly observed regardless of the growth techniques (Ogino, 1980; Singh, 1994; Wetzel, 1994; Fertitta, 1994; Ohba, 1994; Shan, 1995b). More strikingly, this band was observed in samples implanted with a variety of atomic species (Pankove, 1976). These observations have led to the general belief that this yellow luminescence band involves the electronic states associated with defects. Recent theoretic studies on the electronic structures of impurities and native defects in GaN suggested that point defects, such as nitrogen or gallium vacancies, play important roles.(Jenkins, 1989; Tansley, 1992, 1993; Neugebauer, 1994, 1996; Boguslawski, 1995) A few mechanisms were proposed regarding the electronic states involved in the radiative recombination process, which give rise to yellow luminescence. Among them, a model proposed by Glaser *et al.*(1993, 1995), based on the results of optically detected magnetic resonance (ODMR) from undoped GaN epifilms, as depicted in Fig.13(a), suggests a two-stage process involving three distinct states: a process of nonradiative, spin-dependent-electron capture from a neutral effective-mass shallow-donor state to a singly ionized, deep-double-donor state, then followed by a radiative recombination between the deep donor state and a shallow effective-mass acceptor state with peak energy at 2.2 eV. In the meantime, the recombination from the shallow donor state to the acceptor state, which weakly competes with the recombination through the deep donor state, can account for the DAP emission band. However, another model, first proposed by Ogino *et al.*(1980) attributes the yellow luminescence to the radiative recombination from a shallow-donor state to a deep localized acceptor state (Fig.13(b)). Recent high-pressure PL studies found that dependence of the yellow luminescence on the applied pressure follows the band gap of GaN (Perlin, 1995; Shan 1995c). These results are consistent with the model of the recombination resulting from the transition between the shallow-donor state and deep-acceptor state, since a shallow-donor state shifts with the host semiconductor band gap under hydrostatic pressure at the same rate and the effects of hydrostatic pressure on acceptor state is negligible (Wolford, 1985). On the other hand, if the yellow luminescence originates from a transition from a deep-donor state to a shallow-acceptor

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state, its pressure coefficient is expected to be smaller than that of the band gap of GaN. This is because the composition of the wavefunction of a donor-like deep center consists of contributions from the entire Brillouin zone and from many bands and its pressure coefficient will be primarily determined by the pressure dependence of the average conduction band energy, since it is no longer possible to associate a deep donor level to one particular conduction band valley (Chadi, 1988).

Shown in Fig. 14 is the pressure dependence of the peak energy of yellow luminescence observed in GaN by Perlin *et al.*(1995). A pressure coefficient of 3.0 meV/kbar was derived from the experimental data obtained at pressures below 180 kbar, which is very close to that of the band gap of GaN (Shan, 1995c; Kim, 1995). At higher pressures, the peak energy of the yellow luminescence was found to lose its linear dependence and become insensitive to the applied pressure. This experimental observation, together with the observation of free carrier freeze-out at the same pressure range by Raman and infrared absorption measurements, was explained by a pressure-induced resonant-to-deep transition; the applied pressure increases the band gap of GaN and brings a resonant electronic level of a deep center into the forbidden gap, resulting in the capture of effective mass electrons and consequently, the change in the pressure dependence. Their *ab initio* pseudopotential calculations found that the native defects of the nitrogen vacancy and the interstitial gallium are shallow donors at ambient pressure, and each of them introduces a resonance approximately 0.8 eV above the bottom of the conduction band at atmospheric pressure. Based on the results of experimental and theoretical work, they further suggested that the nitrogen vacancy and the interstitial gallium are responsible for the *n*-type conductivity commonly observed in nominally undoped GaN. And moreover, the nitrogen vacancy is energetically favorable to be the dominant donor due to its significantly lower formation energy compared to that of interstitial gallium.

It should be pointed out that whether or not the nitrogen vacancy is mainly responsible for the *n*-type conducting in as-grown GaN is still a subject of debate. Recent theoretical calculations by Neugebauer and Van de Walle (1994, 1996) suggested that the isolated nitrogen vacancy cannot be a source for *n*-type conductivity because under thermodynamic equilibrium conditions, nitrogen vacancy has a very high formation energy, about 4 eV, which is not likely to produce appreciable concentrations. On the other hand, they concluded that it is the Ga vacancy, rather than the N

vacancy, responsible for the broadband yellow luminescence. This is based on the facts that the formation energy of the Ga vacancy depends on the position of the Fermi level and is much lower than that for the N vacancy in $n$-type GaN, and the electronic energy level of this point defect is a deep acceptor state, consistent with the high-pressure experimental results. Some experimental observations did show that the yellow luminescence band was noticeably suppressed by Mg- and Ge-doping or under Ga-rich growth conditions (Nakamura, 1992a; Zhang, 1996). These results are favorably consistent with the theory that the yellow luminescence is closely related to the Ga vacancy. In addition, a number of recent investigations of introducing oxygen into GaN during growth have indicated that O acts as a donor (Seifert, 1983; Chung, 1992; Sato, 1994; Zolper, 1996). The proximity of O to N suggests it to be an effective-mass type defect (Wetzel, 1996). Therefore, O has been considered as one of the most probable candidates account for the $n$-type conductivity in as-grown GaN, and consequently involve in the yellow luminescence. In their theoretical work, Neugebauer and Van de Walle (1996) found that the triple acceptor Ga vacancy and the single substitutional donor O can form very stable $V_{Ga}$-$O_N$ complex acting as double acceptors with a relevant transition energy of 1.1 eV. Thus, the $V_{Ga}$-$O_N$ complex, along with point defect of Ga vacancies, is in agreement with the experimental observations regarding both the electronic properties and the energetic features.

3.2. Properties of doped GaN

Doping $p$ type has been a major challenge to the device applications of wide-band-gap semiconductors including II-VI compounds and III-nitrides. Various potential $p$-type dopants were incorporated into GaN since the early 70s. A detailed review on this subject is given by Strite and Morkoç (Strite, 1992). Currently, $p$-type doping of epitaxial grown GaN is typically using Mg as the acceptor dopant, thanks to the breakthroughs of converting compensated Mg-doped GaN into p-type conducting using low-energy electron beam irradiation (LEEBI) discovered by Akasaki and coworkers (Amano, 1989) and postgrowth thermal annealing pioneered by Nakamura $et$ $al.$(1992b) Currently, free hole concentration well above $10^{18}$ cm$^{-3}$ at room temperature can be achieved for fabrications of $p$-$n$ junction light emitting diodes (Fischer, 1995). The luminescence properties of Mg-doped GaN grown by MOCVD were first studied by Amano $et$ $al.$ (1990) They found that, at

low temperatures (4.2 K), samples with low Mg show DAP emission with the peak position at 3.27 eV and its LO-phonon replicas, indicating that Mg acts as an acceptor. The PL spectra of highly Mg-doped GaN were dominated by broad deep-level emission with the peak at about 2.95 eV. The room-temperature luminescence was found to be doping-concentration dependent as shown in Fig.15. When Mg concentration is lower than $2 \times 10^{20}$ cm$^3$ and higher than $5 \times 10^{18}$ cm$^3$ , blue emission with the peak at 2.7 eV could be observed, together with a much weaker yellow luminescence band. Once Mg concentration is over $2 \times 10^{20}$ cm$^{-3}$, only the yellow band was observed. Therefore, they concluded that it is important to control the Mg concentration in GaN for efficient blue emission. Similar results have also been observed from Mg-doped GaN prepared with other techniques.(Ilegems,1973; Yang, 1996; Kim, 1996)

It is well known that all Mg-doped GaN samples grown with techniques that use $NH_3$ as a nitrogen source or which furnish a hydrogen-rich environment, such as MOCVD, require an additional, deliberate processing step to electrically activate the acceptor dopant in order to dissociate the electrically inactive Mg-H complex. These unpassivating processes are either low energy electron beam irradiation (LEEBI) (Amano, 1989) or $N_2$-ambient thermal annealing above 600°C ( Nakamura,1992). Götz and co-workers reported a systematic study on the activation kinetics of Mg acceptors as a function of postgrowth isochronal rapid thermal annealing temperature (1996). The thermal treatment results in a reduction in resistivity by six orders of magnitude, and the $p$-type conductivity was found to be dominated by the acceptor of the substitutional Mg with an activation energy of about 0.17 eV. They found that PL emission intensities and peak positions of the spectral features, as well as the overall line shapes of as-grown Mg-doped GaN, vary with annealing temperatures (600-775°C), as shown in Fig.16. These observations suggest a correlation between the near band-edge PL lines and activated Mg. The effects of hydrogen passivation on MBE grown Mg-doped GaN using ammonia as the nitrogen source have also been studied. (Yang, 1996; Kim, 1996) While the postgrowth thermal annealing treatment significantly alters the PL emission in MOCVD Mg-doped GaN, it was found to have marginal effects on $p$-type resistivity and PL emission, indicating that fewer Mg-H complexes exist in MBE grown GaN. Nevertheless, a high beam flux ratio of ammonia over Ga was found to affect the PL emissions as well although the amount of Mg-H complexes in the Mg-doped GaN grown by MBE are not as large as that grown by

MOCVD (Yang, 1996).

The incorporation of other common column II acceptors such as Zn, Cd, and Be into GaN to achieve *p*-type doping has been attempted, and the related optical properties have been investigated. (Ilegems, 1973; Pankove, 1973, 1974, 1976; Boulou, 1979; Monenar, 1980; Bergman, 1987) Unfortunately, the results obtained from PL measurements suggested that the doping introduces deep states within the gap and only produces a broad mid-gap luminescence band. The binding energy for Zn (~550 meV) and Cd (~350 meV) was also found to be much higher than that for Mg. Therefore, the effectiveness of these two impurities as *p*-type dopant species will be very limited, even though the accurate thermal ionization energy for them is not definitive (Strite, 1992). Although *p*-type doping of GaN using Be was investigated previously without much success (Pankove, 1974; Ilegems, 1973), recent work of Be-doped GaN grown by reactive MBE using ammonia reported the achievement of *p*-type conduction without invoking any postgrowth annealing and suggested that Be can form acceptor states about 250 meV above the valence band of GaN based on the observation of near U-V luminescence at room temperature. (Salvador, 1996) In addition, Zolper *et al.* recently reported ion implantation doping of GaN using Ca as a *p*-type dopant to test a theoretical argument for Ca to be a shallower acceptor than Mg based on the d-state electron relaxation effects in GaN and the lack of d-state electrons in Ca proposed by Strite (1994). They estimated the ionization level of Ca to be ~169 meV and very close to that reported for Mg (Zolper, 1996).

Controlled *n*-type doping of GaN is commonly achieved by the incorporation of Si. Ge is another dopant used for *n*-doping. Both Si and Ge act as a single donor by substituting Ga in the GaN lattice. Si-doped GaN was primarily characterized by electrical methods such as variable Hall effect measurements. The recently reported values of the donor activation energies are ~17-27 meV (Hacke, 1994; Gaskill, 1995; Götz, 1996). Typical PL spectra taken from Si-doped GaN exhibit features which are usually observed for *n*-type GaN. The most distinguishable part of the PL spectra of Si-doped GaN, compared to that from undoped GaN, should probably be the near-band-edge exciton emission features: the former only exhibits a very strong emission line of excitons bound to neutral shallow donors with the free-exciton emission on the higher energy side hardly observable at low temperatures, whereas the latter shows both emission signatures (Freitas, Jr. 1996; Götz,

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1996). The intensity of near-band-edge emission relative to that of the broadband yellow emission in Si-doped GaN was also found to increase with the dopant concentration (Nakamura, 1992; Hacke, 1994). An optical Si donor level relative to the bottom of the conduction band of GaN was found to be ~22±4 meV by Götz *et al.*, based on their observations of PL features associated with radiative transitions of free carriers in the conduction band to acceptors, as well as donor-acceptor transitions involving the Si donor level as the initial state (Götz, 1996).

## 4. STIMULATED EMISSION AND LASING PHENOMENA

The quantum system of a direct gap material described by single electron band structures predicts that the excitation of electrons from the valence band to the conduction band can result in a filling of these bands to levels corresponding to the carrier quasi-Fermi levels. A photon with energy $E_g < h\nu < \Delta E_f$, where $\Delta E_f$ is the difference in electron and hole quasi-Fermi levels, (Bernard, 1961) can stimulate recombination and experience net amplification, or gain, providing the cross section for this process exceeds that for all other absorption processes such as intervalence band transitions or intraband free carrier absorption (Voos, 1980). The very large probability for radiative recombination in direct gap materials provides a tremendous possibility of stimulated emission resulting from the radiative recombination of carriers at reasonable excitation densities.

III-nitrides AlN, GaN and InN and their alloys have direct energy gaps spanning the wavelength range of 200 nm to 650 nm at room temperature and are currently considered to be the most promising UV-blue laser diode materials. The recent demonstration of pulsed InGaN LDs by Nichia was rapidly followed by cw LD demonstration a year later, and now the lifetime of the cw LD is evidently being augmented at an even more impressive pace by the same group. In fact, the optical quality of InGaN, in general, is inferior to that of GaN, and yet InGaN is a very efficient light emitter.

This section is divided into two subsections: (i) optically pumped stimulated emission (SE) and laser action and (ii) current injection laser diodes. In the first subsection, we first discuss widely used experimental configurations for optical pumping and then present experimentally observed SE threshold values reported in the literature and factors affecting the threshold level in GaN and related structures, including the difficulties forming an efficient resonator cavity with commonly used substrate materials. We also mention some of the discrepancies in observed Fabry-Perot interference

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modes and sample dimensions reported. The gain values reported in the literature are presented, along with the mechanisms proposed, including the self-formed quantum-dots playing a role in InGaN lasing. Definitive experimental verification of possible mechanisms is still lacking. Finally, a brief discussion of surface emitting laser action follows. It should be kept in mind that the quantitative values such as SE and lasing threshold and gain can be very much dependent on the samples. And even the relatively good nitride sample that current technology offers still suffer from inhomogeneity and imperfections, which, in part, are related to lattice mismatched substrates and difficulty of incorporating aluminum and indium uniformly in the alloy samples. Additionally, estimating the pumping power density and hence the threshold value can vary with different laser systems and the method of pumping density estimates employed by different groups. In the second subsection, a brief chronological description of the development of the current injection laser diodes is given with the emphasis on their optical performance and spectral output.

### 4.1. Optically pumped stimulated emission and laser action

The optical pumping technique is the method capable of providing very high excitation densities necessary for the occurrence of stimulated emission and lasing. The advantage of the optical pumping technique is that the study of stimulated emission and lasing phenomena can be conducted without electrical contacts on samples so that somewhat complicated device processing procedures can be avoided. Usually a pulsed laser has to be used for optical pumping in order to generate sufficient numbers of carriers in the conduction band. Examples of those pulsed lasers used for optical pumping in III-nitrides include nitrogen laser, 3rd and 4th harmonics of Nd:YAG laser. Tuning of the wavelengths of pump lasers can generally be achieved by doubling dye lasers or Ti:sapphire laser bams to the UV range. The most commonly used pumping schemes are side-pumping and back-scattering configurations. Figure 17 is the schematic depicting these two experimental configurations. In the side-pumping geometry, samples are cleaved or cut into bar-like specimens, and the pumping laser beam is focused on the surface of a bar-like sample under study using a cylindrical lens to form a rectangular excitation spot. The two edges of the sample act as reflective mirrors naturally forming a resonant cavity. The emission signal is collected from the edge perpendicular to the illuminated surface of the sample and then fed into a detection system including

a spectrometer, a photodetector such as PMT or CCD array, and a data acquisition system. In the back-scattering configuration, the emission signal is measured from the same side of the sample as the excitation laser beam direction. In the back-scattering geometry, the sample inhomogeneity in the surface normal to the growth direction can be probed with high spatial resolution by using a short focal length lens such as a microscope objective lens (Song, 1997). The back-scattering geometry is also useful in the feasibility study of surface emitting laser action. With transparent substrate samples such as GaN/Sapphire, a forward scattering, as opposed to a back scattering configuration, can be employed. In this case, the emission can be adversely affected by the inhomogeneity of the sample along the growth direction and the poor quality of the sample in the interface region since the emission passes through the entire sample thickness, as well as the sapphire substrates. This geometry, of course, is not suitable for opaque substrate materials such as GaN/GH-SiC.

The first observation of optically pumped lasing in GaN was made by Dingle *et al.* using needle-like GaN single crystals at the sample temperature of 2 K (1971c). Since then, there have been a number of investigations on optically pumped stimulated emission and laser action in GaN and related heterostructures in recent years (Amano, 1990, 1991, 1994; Yung, 1994; Khan, 1991, 1996; Kim, 1994; Yang, 1995; Zubrilov, 1995; Tanaka, 1996; Schmidt, 1996; Frankowsky, 1996; Aggarwal, 1996; Maki, 1996; Redwing, 1996; Wiesmann, 1996; Zhang, 1996). Fig.18 summarizes the reported values of the pumping threshold for stimulated emission and lasing in GaN and related InGaN/GaN and GaN/AlGaN heterostructures prepared by different growth techniques using various substrate materials. The measured threshold values from double-heterostructure (DH) or separate-confinement-heterostructure (SCH) samples are generally lower than the values for bulk-like GaN epifilms by approximately one order of magnitude. This reduction in threshold is due mainly to the effects of carrier confinement and waveguiding associated with the DH and SCH structures (Schmidt 1996). It is known that in order to achieve lasing in a semiconductor laser structure, a recombination region to produce optical gain by stimulated emission, at least partially overlaps with the optical waveguide region. to confine the optical field (Kressel, 1993). In addition, an optical cavity is required to provide the feedback necessary to produce a self-consistent optical mode with the structure. In the case of the DH structure, the photoexcited carriers are localized in an active region, and an efficient optical waveguide that is contiguous to the recombination region is readily formed.

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In the case of SCH, a larger optical waveguide is incorporated to symmetrically locate around the recombination region. SCH is an optimal structure for low-threshold operation because the peak of the optical field is at the recombination region, the optical-mode size is determined by the spacing and refractive-index step of the outer waveguide layers, and the inner active region can be structured independently to obtain the maximum carrier confinement leading to the minimum lasing threshold (Kressel, 1993).

Shown in Fig.19 are emission spectra taken from a GaN/AlGaN SCH sample grown by MBE at different pumping power densities (Schmidt 1996). Under the conditions of low-excitation power densities, the observed spectra exhibit a relatively weak and broad emission feature with the peak position around 365 nm, and the emission intensities linearly increase with the excitation power density, showing the typical characteristic of spontaneous emission. As the excitation power density increases, a sharp, narrow emission feature appears on the higher energy side of the spontaneous emission peak. The position of the maximum of this new emission feature is ~361.5 nm. Its emission intensity increases superlinearly with the excitation power. This new emission structure becomes the dominant feature as the pumping power density is further increased. Under the conditions of high-excitation power densities, the output of the emission from the GaN SCH samples was very intense. The observations of spectral narrowing and a superlinear increase in intensity with the excitation power density, as well as the complete suppression of the broad emission background, are typical characteristics of the occurrence of stimulated emission. The onset of the steep rise of the emission intensity plotted as a function of pumping power density, as illustrated in the inset of the figure, is defined as the threshold for stimulated emission. The pumping threshold for stimulated emission was determined to be ~90 kW/cm$^2$ for these GaN/AlGaN SCH samples. The measured threshold value is approximately one order of magnitude less than that for MOCVD-grown GaN bulk-like epifilms reported by the same group (Yang, 1995). Note that the SCH sample shown in Fig. 19 was not cut into a bar-like shape to form a cavity, and therefore, the observation of the interference modes cannot be expected in this case. With the proper preparation of sample edges such as cutting and polishing, further reduction in threshold can be achieved.

Generally, the threshold value for stimulated emission and lasing under optical pumping conditions can be affected by parameters which are dependent on the pumping source and sample.

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For a given optical pumping source, the most important influence on the threshold is from the sample itself, with the threshold varying from sample to sample. This can be classified into two groups: one is associated with material properties, such as impurities, crystallinity, and defects; the other is related to the sample preparation such as, in the case of lasing studies, laser cavity length and the quality of sample edge facets. The difficulties associated with forming high quality facets by cleaving wurtzite GaN grown on sapphire are well known. Usually the specimens used in optical pumping experiments were just small pieces simply cut off from the large wafers without too much success in finessing the cut surfaces. Schmidt *et al* demonstrated the improvement of the surface by mechanical polishing of the edge surface of GaN/sapphire, which, however, is a time-consuming process. By attaching external dielectric high reflectivity mirrors to the sample, these authors observed high contrast Fabry-Perot fringes and in some cases, nearly a single mode-like lasing peak with FWHM of ~0.3nm as shown in Fig.20 (Schmidt, 1996). Kuramata *et al.* reported the formation of the optical cavity by cleaving GaN grown on $MgAl_2O_4$ (1996). The use of such spinel substrates allows the cleavage of GaN epifilms on top in some direction to obtain smooth cleaved facets. Stimulated emission was observed from those samples, and the threshold of ~200 $kW/cm^2$ was determined. This value is indeed significantly lower than the reported threshold values of ~800 $kW/cm^2$ for GaN samples without cleaved edge facets (Yang, 1995). Another issue associated with the threshold is the inhomogeneity of the crystal quality for a single piece of GaN. It is known that there is a very large dislocation density (~$10^8$-$10^{10}$ $cm^{-2}$) in GaN epilayers grown on commonly used substrate materials of sapphire and 6H-SiC. Some microstructures such as grains and pillars are often observed to be co-existing with dislocations (Liliental-Weber, 1996). In addition, cracks are easily generated in the GaN layers grown on 6H-SiC. Therefore, the emission spectral lineshape and the pumping threshold values are sometimes found to depend on the excitation spots on a single piece of sample (Song 1997). In some literature, observations of Fabry-Perot cavity modes in stimulated emission and lasing spectra were reported (Aggarwal, 1992; Zubrilov, 1995; Yang, 1995; Redwing, 1996; Tanaker, 1996), but it is rather difficult to associate the observed mode spacings with sample dimensions. One of the reasons for these difficulties is associated with the fact that different groups use different indexes of refraction *n*, and its dispersion *dn/dλ* in calculating the Fabry-Perot interference mode spacings using

$$\Delta\lambda=\lambda^2/(2n_gL), \tag{21}$$

where $n_g=n-\lambda(dn/d\lambda)$ and $L$ is the cavity length. Another difficulty is the pumping laser shot-to-shot noise, together with poor sample edge surfaces, yielding different mode structures at each laser shot. Additionally, mode fringes can also be affected by parallel microcracks in GaN forming a cavity. Zubrilov and coworkers (1995) attributed high quality fringes they observed in GaN on 6H-SiC to such internal microcavities on the order of tens of microns in size.

The knowledge of the dependence of optical gain on optical pumping density or injection current is important for understanding the stimulated recombination processes and developing practical devices such as laser diodes. There have been a number of experimental and theoretical optical-gain studies for GaN and related materials including InGaN/GaN and GaN/AlGaN heterostructures (Fang, 1995; Meney, 1995; Chow, 1995, 1996; Suzuki, 1996; Domen, 1996; Ahn, 1996). Some theoretical calculations predict that the maximum gain value in GaN could be very high (Chow 1995, 1996; Domen 1996). In particular, the calculation results of Domen *et al.* suggested that GaN has a large gain of over $10^4$ cm$^{-1}$ and no gain saturation up to 25000 cm$^{-1}$, although the transparent carrier density is quite high at $5\times10^{18}$ cm$^{-3}$. However, the vast majority of experimentally determined values using the variable-stripe-length (VSL) excitation method are found to be at least one order of magnitude smaller in various samples with different structures (Kim,1994; Song 1996; Frankowsky,1996; Wiesmann, 1996). In the VSL experiment, the excited stripe on the sample surface is varied, and the emission is collected from the sample edge. Then the intensity of emission spectra at every or selected wavelength is analyzed as a function of the length of the excited stripe $L$

$$I_E=I_0(exp\{g\times L\}-1), \tag{22}$$

where $g$ is the optical gain coefficient, at different excitation power densities. Shown in Fig.21 are the variations of emission intensity with the length of the excitation stripe on a GaN sample surface at three different pumping power levels at room temperature. The optical gain values for the GaN sample given in the figure were estimated using Eq.(22)(Song 1996). Fig.22 shows the measured optical gain spectra from an InGaN/GaN double-heterostructure at various pumping power levels reported by Frankowsky and coworkers (1996). The solid lines in the figure are the calculated spectra with a model based on band-to-band transitions. The good agreement between the calculated

and measured gain spectra leads Frankowsky *et al.* to the conclusion that the band-to-band transitions are responsible for the optical gain in their InGaN/GaN double-heterostructure samples, although this needs further verification.

The investigation of surface emitting laser action by optical pumping is an important step in the development of the vertical-cavity surface-emitting laser (VCSEL). It can also be used for relatively simple testing of lasing since the emission does not depend on the sample size or the edge conditions. There are several reports of the observation of surface emitting stimulated emission in GaN and InGaN films by optical pumping with a back scattering configuration (Khan, 1994; Yung, 1994; Amano, 1993; Khan 1991). It should be pointed out that caution needs to be taken to block the SE signal emitted from sample edges which could sometimes be unintentionally collected in the back-scattering direction (Bagnatt, 1996; Wiesmann, 1996). Recently, Redwing and coworkers reported the observation of optically pumped vertical cavity lasing *fr* )m GaN (1996). In this case, the 10-$\mu$m thick GaN lasing medium was sandwiched between MOCVD grown $Al_{0.4}Ga_{0.6}N/Al_{0.12}Ga_{0.88}N$ Bragg-reflectors which formed a vertical cavity.

Recently, Narukawa and co-workers (1997) reported the observation of InGaN quantum-dot-like features self-formed, associated with indium concentration inhomogeneity in the well region of purple blue laser diode structures. They attributed the main radiative recombination in these quantum wells to the excitons localized at deep traps probably originating from the indium-rich region of the quantum wells acting as quantum dots. It was suggested that the process of self-formation of quantum dots may be a result of the intrinsic nature of InGaN ternary alloys associated with the indium compositional modulation due to phase separation (Ho, 1996; Narukawa, 1997). These quantum dots are considered to play an important role in the lasing processes of InGaN MQWs at room temperature (Chichibu, 1996; Narukawa, 1997). It is likely that the high quantum efficiency of InGaN-based LDs is due mostly to the large localization of excitons and hence substantially reduced nonradiative recombination channels. Howev-r, the origin of the trap centers of these localized excitons has not been clarified yet. The idea of self-formed quantum dots contributing significantly to InGaN MQW lasing processes is still rather new. Further work is needed to better understand the formation processes of quantum dot like feature and their roles in radiative recombination and lasing processes in InGaN based Laser diodes. The determination of the nature

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of the lasing transition in InGaN MQWs will continue to be of considerable scientific interest and technological importance and require further detailed study.

## 4.2. Current injection laser diodes

The most significant and important application of stimulated emission is the generation of coherent radiation in a laser. Tremendous efforts have been directed to achieving practical current-injection laser diodes using GaN and its related materials. Akasaki $et$ $al.$(1995) first reported the observation of room-temperature stimulated emission in an InGaN/GaN quantum well structure using pulsed current injection. The device used is actually an SCH structure consisting of an InGaN active layer about 7.5 nm thick, GaN waveguiding layers with total thickness of about 0.4-$\mu$m thick, and AlGaN cladding layers about 0.5-$\mu$m thick for both $p$- and $n$-type sides. Strong and narrow stimulated emission with an FWHM of 3 nm was clearly observed, in addition to the broad near-band-edge spontaneous emission at a current density of 1 kA/cm$^2$ for the device.

In December, 1995, fabrication of laser diodes (LDs) using wide-bandgap III-V nitride materials was announced for the first time by Nichia.(Nakamura, 1996a) The LDs emit coherent light at 417 nm from an InGaN based MQW structure under pulsed current injection at room temperature. The first InGaN MQW LD device consisted of a 300 Å GaN buffer grown at a low temperature of 550°C, a 3-$\mu$m $n$-type GaN:Si layer, a 0.1-$\mu$m $n$-type In$_{0.1}$Ga$_{0.9}$N:Si layer, a 0.4-$\mu$m $n$-type Al$_{0.15}$Ga$_{0.85}$N:Si layer, a 0.1-$\mu$m $n$-type GaN:Si layer, a 26-period In$_{0.2}$Ga$_{0.8}$N/In$_{0.05}$Ga$_{0.95}$N multiple quantum well (MQW) structure with the well layer thickness of 25 Å and the barrier layer thickness of 50 Å, a 200-Å $p$-type Al$_{0.2}$Ga$_{0.8}$N layer, a 0.1-$\mu$m $p$-type GaN:Mg layer, a 0.4-$\mu$m $p$-type Al$_{0.15}$Ga$_{0.85}$N:Mg layer, and a 0.5-$\mu$m $p$-type GaN:Mg layer. Sapphire with (0001) orientation was used as the substrate. Reactive ion etching (RIE) was employed to form mirror-like cavity facets. The roughness of the obtained facets was ~500 Å. High reflective coating (60-70%) was used to reduce the threshold current. The device with a stripe geometry was operated at room temperature under pulsed current-biased conditions with a pulse width of 2 $\mu$s and a pulse period of 2 ms. The stimulated emission was observed to occur at a current of 1.7 A, which corresponds to a threshold current density of 4 kA/cm$^2$. Fig. 23 shows the emission spectra of the first reported current-injection InGaN MQW LD. Below the threshold, the emission is characteristic of spontaneous emission with a peak at 410 nm

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and an FWHM of 20 nm. Above the threshold current, strong stimulated emission at 417 nm with an FWHM of 1.6 nm became dominant. An elliptical far-field pattern could also be observed once the stimulated emission occurred.

Shortly after their first report on the achievement of InGaN LDs, Nakamura *et al.* (1996b, 1996c) reported the fabrication of the LDs with the same device structure using spinel (111) $MgAl_2O_4$ substrate. Polished facets with a roughness of about 50 Å were used as the resonant cavity end mirrors for the LDs. Laser action was achieved under similar operating conditions for the first LDs. The threshold current density and differential quantum efficiency per facet were found to be almost the same as the devices grown on sapphire substrates with much rougher facet surfaces. The performance of the LDs was considerably improved after the device geometry was changed from the stripe-geometry to the ridge-geometry and the substrates were switched from the (0001) C-face sapphire to (11$\underline{2}$0) A-face sapphire (Nakamura, 1996d). The number of the active QWs of the new LDs was noticeably reduced, and the layer thickness of the QWs was slightly increased. The threshold current density of the ridge-geometry LDs was found to be half that of the stripe-geometry LDs. The differential quantum efficiency of the former is also much higher than the latter. In addition, the ridge-geometry LDs showed a much higher operation tolerance to the duty ratio of a pulsed current at room temperature. These differences were attributed to the high lateral confinement of light propagation and to the absence of etching damage in the gain region of the active layer due to the ridge geometry. The Nichia group also studied the external differential quantum efficiency as a function of the cavity length of an LD with an $In_{0.2}Ga_{0.8}N/In_{0.05}Ga_{0.95}N$ MQW structure consisting of seven 25-Å-thick undoped $In_{0.2}Ga_{0.8}N$ layers as gain medium (Nakamura, 1996e). An internal quantum efficiency of 86% and an intrinsic loss of 54 $cm^{-1}$, as well as a threshold gain of 110 $cm^{-1}$, were obtained. A minority carrier lifetime of 2.5 ns was derived from the measurement of the pulse response of the LD device, and consequently, a carrier density of $1.3 \times 10^{19} cm^{-3}$ at lasing threshold was calculated. Very recently, the same group again reported continuous-wave (CW) operation of InGaN LDs (Nakamura, 1996f, 1996g, 1997b). Compared to the earlier performance of their LDs, the threshold voltage was significantly reduced from the previous 20-30 V to 11 V for 233 K operation (Nakamura, 1996f) and 6.5 V for room-temperature operation (Nakamura, 1996g, 1997b), respectively, by adjusting growth, ohmic contacts, and doping

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profile conditions. The lifetime of LDs for CW operation at room temperature was first reported to only last 24-40 minutes, due to large heat effects by relatively high operating currents and voltages (Nakamura, 1997b). However, the CW operation lifetime has been improved significantly to be over 35 hours (Nakamura, 1997c, 1997d).

Akasaki et al.(1996) reported the achievement of the shortest wavelength semiconductor LDs. UV lasing at 376 nm was demonstrated by a nitride-based SCH single quantum well (SQW) structure with current injection at room temperature. The SCH LD uses a 1.5 nm-thick $In_{0.1}Ga_{0.9}N$ SQW as the active layer without facet coatings. The device was operated at room temperature under pulse-biased conditions. Strong and narrow stimulated emission at 376 nm with the FWHM of 1.5 Å was clearly observed when the injection current density exceeds 2.9 kA/cm$^2$. Room temperature pulsed operation of nitride based MQW LDs with cleaved mirror facets on conventional C-face sapphire substrates was reported by Itaya et al. of Toshiba (1996). The cleaved facets were carried out by partially scribing along the <11$\underline{2}$0> orientation of the sapphire substrate, after lapping the substrate, to form (1$\underline{1}$00) facet plane. The roughness of the cleaved facets caused primarily by a small tilted angle (approximately 2°) between the cleaved surface of sapphire and nitride layers was determined to be within 50 Å. The lasing emission with a peak position at 417 nm and FWHM of 1.5 Å was observed under high current injection conditions at room temperature. The threshold current density was found to be around 50 kA/cm$^2$ with a 20 V operating voltage for the LD with cleaved facets.

Nakamura et al. have documented their observations of the lasing peak position of the emission spectra at or above threshold showing either red shift or blue shift with respect to that of the spontaneous emission. In general, the red shift of stimulated emission observed from various semiconductors is often attributed to the renormalization of the crystal band gap to lower energy in the presence of high excitation densities (Voos,1980). The peak position of the stimulated emission located at a shorter wavelength, in comparison to that of the broad spontaneous emission spectral feature located at a longer wavelength range and related to the radiative recombination processes associated with the transition from the electronic levels of Si dopants in the GaN active layer to the top of the valence band, was previously observed by Schmidt and co-workers (1996) in GaN/AlGaN SCH. At high pumping power levels, the available density of impurity levels is saturated, and the

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band-to-band radiative recombination process for the majority of photo-generated carriers will lead to a blue shift in this GaN/AlGaN SCH sample. In the case of the blue shift exhibited by undoped InGaN MQWs, transition processes involving impurity levels can be ruled out.

In general, tracing the origin of a blue or red shift in MQWs can be quite complicated due to the inevitable imperfections in MQWs such as interface roughness, well thickness fluctuations, and alloy disordering effects. Growth of high quality homogeneous nitride alloy layers such as AlGaN and InGaN is still a technical challenge. Especially in case of MQWs containing InGaN (thin) layers, further complications arise from the difficulty of incorporating indium in the first place and the intrinsic nature of the current InGaN growth processes. As mentioned in the previous section, it has been suggested by several groups that indium phase separation occurs in InGaN alloys leading to indium compositional modulation (Ho, 1996; Narukawa, 1997). Especially, quantum dot-like features suggested to be present in the MQWs of the Nichia LDs invoked the picture of localized exciton playing a major role in Nichia's current injection LDs (Narukawa, 1997; Kawakami, 1997).

Another interesting observation made in the Nichia LDs is that typically, several more peaks with somewhat irregular separation appeared in the optical spectra when the pulsed injection current densities are above the threshold. For cw operation, however, only one single sharp emission line dominates the spectra even at higher injection current densities. Nakamura et al. suggested that, by comparing the spectra observed under pulsed injection conditions with those under CW operation, the appearance of irregularly-spaced multi-emission peaks is related to the change in temperature at the junction of the LDs, which induces mode hopping at a certain temperature (1997b). Other explanations given in their early papers are that inhomogeneities in the film thickness and in the layer alloy compositions lead to deviations from ideal behavior to asymmetry in the spectrum (Nakamura, 1996f, 1996g). The variations of temperature and electron densities in the LDs alter the reflective index and change the resonant wavelengths of the longitudinal modes.

## 5. OPTICAL NONLINEARITIES OF GaN

Nonlinear optical properties are an important aspect of any materials to be used for optoelectronics. Stimulated emission and lasing processes are, in fact, nonlinear optical phenomena, and as discussed in the previous sections, are being extensively investigated for the development

of practical current-injection LDs operating at the UV-blue spectral region. Although only very limited work has so far been reported in the study of different types of optical nonlinearities of GaN, it is found that the material exhibits several interesting nonlinear optical effects, which provide important information for us to better understand its nonlinear properties and to exploit the intriguing possibilities of its device applications.

## 5.1. Harmonic Generations and Muliphoton Spectroscopy

Optical third harmonic generation spectroscopy was carried out by Miragliotta and co-workers (1994) in MOCVD grown wurtzite GaN on sapphire to measure dispersion and magnitude of the third order susceptibility tensor element $\chi^{(3)}_{xxxx}$, where the x-axis is perpendicular to the GaN growth direction. A resonant enhancement was observed in $\chi^{(3)}_{xxxx}$, near the fundamental energy gap, $E_o$ of GaN when tuning the photon energy in the vicinity of $3\hbar\omega \sim E_o$. The nanosecond photons in the range of 1.00~1.35 eV were generated by stimulated Stokes Raman scattering of tunable dye laser radiation using a pressurized $H_2$ gas cell. The peak value of $\chi^{(3)}_{xxxx}$ was $2.7 \times 10^{11}$ esu at the absorption edge. This is approximately twice as large as the predicted values in ZnSe in the same photon energy region despite the lower band gap energy of the latter. Miragliotta *et al.* attribute this to higher ionicity, hence the less polarizability of ZnSe compared to GaN.

In second-harmonic generation experiments, the second order susceptibility tensor elements were measured in GaN at 532nm. The magnitude of $\chi^{(2)}_{zzz}$ was measured to be nearly twice as large as $\chi^{(2)}_{xxz}$ in the same sample, and approximately 22 times as large as $\chi^{(3)}_{xxx}$ in quartz (~ $1.2 \times 10^{-9}$ esu). (Miragliotta, 1993). Recent calculations of the second harmonic susceptibility by Chen *et al.* (1995) based on Kohn-Shan local density approximation closely agree with the experiments for wurtzite GaN.

More recently, Miragliota *et al.* (1996) investigated the optical second-harmonic (SH) response of a reverse biased GaN film grown by MOCVD. In this work, the nanosecond tunable dye laser source was used so as to tune the SH photon energy through the fundamental absorption edge. With the application of a DC field, the nonlinear response can result from coupling two optical fields of frequency $\omega$ and one DC field via third-order nonlinear processes. In this electric-field induced second harmonic (EFISH) generation, the second harmonic polarization at $2\omega$ is linearly dependent

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on the applied DC field and quadratically dependent on the incident laser field $E(\omega)$. It was demonstrated. that the EFISH response from $n$-type GaN films can be resonantly enhanced when $2\omega\sim E_g$ (bandgap). Also the magnitude of the EFISH signal was found to exceed the $2\omega$ contribution from the intrinsic second-order nonlinearity when a field on the order of 100kV/cm was applied to the GaN surface. Fig. 24 shows the SH reflected intensity from the GaN/electrolyte interface for various reverse bias potentials. With the application of a reverse bias DC field, a resonance appeared at 3.43 eV with a linewidth of ~50 meV. This narrow resonance was considered to be due to the resonant behavior of $\chi^{(3)}$, and not to the field-induced dielectric variations. This sharp resonance observed at the critical point $E_O$ suggests that SH spectroscopy may be used to probe the electronic band structure of GaN.

Harmonic generation, as well as multiphoton absorption induced photoluminescence spectroscopy, can also be used to probe the subband gap states using tunable laser sources. Recently, Yang and co-workers (1997) observed extensive spectral structures below the bandgap in the second harmonic generation spectra taken from GaN on sapphire. A strong resonance was observed at $2\hbar\omega\sim 2.85eV$, but its origin is not yet well understood. The subband gap defect states on sapphire were also observed by Libon et al in GaN on sapphire, by using two-color, two-photon excitation spectroscopy technique. The photoluminescence in the UV region was monitored while tuning one of the infrared picosecond pulses generated by an OPO system and the increase in the UV PL intensity was observed when $\hbar\omega$ was resonant with states at ~1.0 eV above the valence band (Kim, 1997). Although the origin of these states is not clean as yet, this work, together with the SHG spectroscopy work mentioned above, demonstrates the usefulness of multiphoton spectroscopy technique in detecting subband gap states.

## 5.2. Picosecond four-wave-mixing: *below bandgap excitation*

Taheri *et al.* reported the performance of degenerate four-wave-mixing (FWM) experiments in GaN grown on sapphire by MOCVD (Tehari 1996). Fig.25 depicts the schematics of the experimental setup. The degenerate wave mixing experiments were performed using frequency-doubled pulses from a mode-locked. Q-switched Nd:YAG laser operating with a repetition rate of 10 Hz. The laser pulse has a quasi-Gaussian spatial and temporal profile with an $e^{-1}$ of 13

picoseconds (*ps*). The second harmonic output of the laser at a wavelength of 532 nm was equally split in energy into two pump beams and one probe beam. These beams were spatially and temporally recombined in the samples in a forward propagating boxcar geometry (Eichler, 1986).

The advantage of this geometry over the conventional counter propagating technique is that the scattered signals are spatially separated from input beams. This enhances the signal-to-noise ratio and allows direct measurement of the absolute scattering efficiency. The two pump beams were $\sigma$-polarized, while the probe beam was $\pi$-polarized in order to increase the signal-to-noise ratio and minimize interactions between the pump and probe beams. At the front surface of the sample, the two pump beams have a small crossing angle ($2\theta \approx 2°$). The probe was incident on the interference region at an angle of 1.7° with respect to the pump beams. Its beam radius was slightly smaller at $400\mu$m. The smaller radius allows the central portion of the pump beams to be monitored, reducing the error that can occur because of the finite radial extent of the pump beams. In such a wave-mixing geometry, the pump beams set up an interference pattern in their overlap region with fringe spacing $\Lambda = \lambda/2\sin\theta$, where $\lambda$ is the wavelength of the beams in free space. Intensity dependence causes the index of refraction in the light regions of the interference pattern to differ from that in the dark region. The overlap region, therefore, behaves as an index grating with spacing of $\Lambda$. An incident probe beam will be diffracted from this grating in the directions satisfied by the phase matching conditions. An energy meter preceded by a polarizer was used to detect the $\pi$-polarized diffracted signal. Fig. 26 shows a photograph of the diffracted signals, together with the three attenuated incident beams when they are temporally overlapped in a thick GaN sample. The picture was taken at room temperature with a total incident irradiance of 1.7 *GW/cm²*. The clearly visible patterned spots are diffracted higher order wave-mixing signals in the phase-matching directions.

By delaying the arrival of the probe beam, the time response of these nonlinear optical changes was measured. Fig. 27 shows the scattering efficiency as a function of the probe-beam delay. The scattering efficiency is defined as the ratio of the scattered to the transmitted probe beam

$$\eta\,(t) \,\cong\, \frac{I_{scattered}}{I_{trasmitted}} \,=\, \sin^2\left(\frac{k\Delta n(t)d}{2}\right) \,\cong\, \left(\frac{k\Delta n(t)d}{2}\right)^2, \tag{23}$$

where $k$ is the probe wave vector. $\Delta n(t)$ is the time dependent index change and $d$ is the sample

thickness. At zero delay, a maximum scattering efficiency of $4 \times 10^{-5}$ corresponding to an index change $\Delta n(0)$ of $1.2 \times 10^{-3}$ was obtained. This change can be related to the pump beam intensity through an effective nonlinear refractive coefficient $n_2$, defined as

$$\Delta n(0) = n_2 I_0. \tag{24}$$

Provided the pump-beam irradiance of 1.2 $GW/cm^2$, a value of $1 \times 10^{-3}$ $cm^2/GW$ was derived for the effective nonlinear refractive index $n_2$ from Eq.(23). Such a value is much larger than the expected range for semiconductors. For example, ZnSe has a value of $6.7 \times 10^{-5}$ $cm^2/GW$ at 532 nm (Sheik-Bahae, 1990, 1991). A large value of $n_2$ in GaN indicates the potential of its technological importance for optoelectronic device applications since for practical applications, the nonlinear refractive index or the nonlinear absorption coeffecient should be large, fast, and convenient to use (Chemla 1987).

Based on the fact that the measured scattering efficiency against the probe-beam delay exhibits a nonexponential decay with two characteristic time constants of $100 \pm 10$ ps and $1.1 \pm 0.2$ ns, as shown in Fig.27, Teheri *et al.* suggested that the change in the refractive index is caused primarily by the generation of free carriers in the conduction band and that the lifetime of index grating is predominantly governed by the decay of free-carrier population through various recombination processes rather than the diffussion of the carriers from the light regions of the grating to the dark regions. diminishing the index modulation.

Since the third order nonlinear optical susceptibility components can exhibit resonance enhancement when the photon energy approaches the energy band gap or excitonic transitions, an even larger diffraction efficiency and hence the larger nonlinear index of refraction than that observed at 532 nm can be expected in GaN at shorter wavelengths. Particularly interesting will be four-wave mixing work in the vicinity of excitons in GaN-based quantum well strctures, as in the case of GaAs-based quantum wells and superlattices (Chemla 1987).

### 5.3. Femtosecond four-wave-mixing: *exciton resonance*

Recently. there has been intense research activity in coherent spectroscopy of semiconductors and their quantum wells. stimulated in part by the ready availability of tunable femtosecond laser sources. Extensive studies have been performed on GaAs, ZnSe, and related materials and their

quantum wells in the coherent regime (Leo, 1991, Fischer, 1994). Fortunately, GaN intrinsic free excitons can be resonantly excited as well using the second harmonic of a self-mode-locked Ti:Sapphire laser in the high energy region of the tuning curve (~700nm). Using this laser system, Fischer and coworkers (1996) performed femtosecond four-wave-mixing (FWM) experiments on the A- and B-exciton transitions in GaN in the reflection geometry. Fig.27 illustrates the experimental arrangements for the coherent-transient degenerate FWM measurement. The second harmonic of 710 nm, 150 fs pulses from a modelocked Ti:Sapphire is used to resonantly excite the intrinsic free excitons in GaN. The FWM signal is detected in the reflection geometry in the phase-matched direction and measured as a function of optical delay between the two pulses in order to obtain the time-integrated (TI) FWM signal. Alternately, the energy spectrum of the signal at zero delay can be measured by sending the signal into a spectrometer to take the spectrally-resolved (SR) FWM signal. Time-integrated (TI) FWM data are shown in Fig.28 at three temperatures (T=10, 70, and 190 K). The decay time at each temperature was fit to a single exponential decay to determine the decay rate as a function of temperature. The homogeneous linewidth can then be determined from the relation $\Gamma_{hom} = 2\hbar/T_2$, where $T_2$ is the pure dephasing time. By performing spectrally resolved (SR)-FWM, as shown in Fig. 29, Fischer et al. determined that the excitons are nearly homogeneously broadened even at low temperatures, and therefore, the FWM decay time $\tau_{FWM}$ is equal to $T_2/2$. The advantage of SR-FWM is that it can give the exciton linewidths without any background, which plagues the analysis of absorption measurement results. In addition, for relatively thick samples, it is virtually impossible to perform absorption. The SR-FWM data at zero delay shown in Fig. 29 represent a clear demonstration of A- and B-excitons without the interference of bound excitons that make the interpretation of photoluminescence spectra difficult.

Fig. 30 shows the quantum beats between the A- and B-excitons observed by TI- and SR-FWM. When the laser is tuned roughly in the middle of the A- and B-exciton, well-defined beating, whose period coincides with (ΔE)/h, where ΔE is the energy separation between the A- and B-excitons measured in SR-FWM. Different curves in Fig. 30 correspond to TI-FWM taken as a function of decay for several different positions across the B-exciton resonance. The phases are completely in synchronization at all the energies, which indicates that the observed beating is due to the true quantum beat associated with the coherent superposition of the A- and B-excitons, rather than to the

so-called polarization beat (Lyssenko, 1993). In Fig. 31, TI-FWM in both the co-linear (solid lines) and the cross-linear (dotted lines) polarization geometries is shown. The maxima at one geometry correspond to the minima at the other, which indicates the existence of a 180° phase shift between the quantum beats. Such observations are very similar to the HH-LH quantum beat observed in GaAs quantum wells (Schmitt-Rink, 1992).

With the advance of the III-nitride growth technology, sophisticated structures such as quantum wells will become readily available, and coherent femtosecond spectroscopy can be extensively applied to the excitons in quantum-well-type structures. However, one of the obstacles in femtosecond spectroscopy in GaN at low temperatures or GaN/AlGaN quantum wells is the difficulty in generating tunable and stable femtosecond UV laser beams in their excitonic region. Finding a way to extend the tunability well beyond 345nm, which is not currently available with commercial femtosecond lasers, is highly desirable in femtosecond laser technology.

## 6. CONCLUDING REMARKS/ACKNOWLEDGMENT

Recent developments in optical studies, particularly in excitonic transitions, optical pumping and four-wave-mixing in GaN were presented. We tried to provide as many references as possible for those who seek more detailed information concerning these topics. However, it is impossible to include all relevant references in the current environment, where new references appear nearly every week through conferences, on the internet web sites and in journal publications. Any omission is unintentional.

We are indeted to our collaborators:

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**Table I.** Pressure coefficients for the exciton emission structures and absorption edge observed in wurtzite GaN.

| | $\alpha{=}dE/dp$ $(10^{-3}eV/kbar)$ | $\beta{=}\frac{1}{2}d^2E/dp^2$ $(10^{-5}eV/kbar^2)$ | References and Methods |
|---|---|---|---|
| Free exciton | 3.90 (10 K) | -0.18 | Shan *et al.* (PL)[a] |
| Bound exciton | 3.86 (10 K) | -0.08 | |
| | 4.4±0.1 (9 K) | -1.1±0.2 | Kim *et al.*( PL)[b] |
| | 4.7±0.1 (300 K) | -1.6±0.2 | |
| Absorption edge | 4.2 (77 K) | - | Camphausen *et al.*(Absorption)[c] |
| | 4.7 (300 K) | 1.8 | Perlin *et al.* (Absorption)[d] |

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**Table II**. Comparison of III-Nitride material properties with 6H-SiC and Sapphire.[a]

| Material | Lattice Parameter at Room Temp. (Å) | In-Plane Mismatch with GaN (%) | Coefficients of Thermal Expansion ($10^{-6}$/K) |
|---|---|---|---|
| GaN | $a$=3.1891[c] <br> $c$=5.1855[c] | - | 5.59; 3.1,6.2[e] <br> 7.75[d]; 2.8,6.1[e] |
| AlN | $a$=3.112[b] <br> $c$=4.982[b] | 2.5 | 4.15 <br> 5.27 |
| 6H-SiC | $a$=3.08[b] <br> $c$=15.12[b] | 3.5 | 4.2; 3.2,4.2[e] <br> 4.68; 3.2,4.0[e] |
| Sapphire | $a$=4.758[b] <br> $c$=12.99[b] | 16.1 | 7.5; 4.3,9.2[e] <br> 8.5; 3.9,9.3[e] |

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**Table III**. Elastic stiffness constants for GaN.

| $C_{11}$(GPa) | $C_{12}$(GPa) | $C_{13}$ (GPa) | $C_{33}$ (GPa) | $C_{44}$ (GPa) | $C_{66}$ (GPa) | References |
|---|---|---|---|---|---|---|
| 296±18 | 130±11 | 158±6 | 267±18 | 241±2 | - | Savestenko et al.[a] |
| 390±15 | 145±20 | 106±20 | 398±20 | 105±10 | 123±10 | Polian et al.[b] |
| 365 | 135 | 114 | 381 | - | - | Chichibu et al.[c] |
| 411 | 149 | 99 | 389 | 125 | 131 | Kim et al.[d] |

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**Table IV.** The crystal-field splitting and the spin-orbit splitting parameters, $\Delta_1$, $\Delta_2$ and $\Delta_3$, for wurtzite GaN.[a]

| $\Delta_1$ (meV) | $\Delta_2$ (meV) | $\Delta_3$ (meV) | References |
|---|---|---|---|
| 22 | 3.7 | 3.7 | Dingle et al.[b] |
| 72.9 | 5.2 | 5.2 | Suzuki et al.[c] |
| 10±0.1 | 6.2±0.1 | 5.5±0.1 | Gil et al.[d] |
| 37.5 | 4 | 4 | Chen et al.[e] |
| 21 | 5.3 | 5.3 | Chichibu et al.[f] |
| 24.7 | 5.8 | 5.8 | Reynolds et al.[g] |
| 16 | 4 | 4 | Chuang et al.[h] |
| 22 | 5 | 5 | Shikanai et al.[i] |

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b) R. Dingle, D.D. Sell, S.E. Stokowski, and M. Ilegems, Phys. Rev. B4, 1211(1971).
c) M. Suzuki and T. Uenoyama, Appl. Phys. Lett. 67, 2527(1995).
d) B. Gil, O. Briot, and R.-L. Aulombard, Phys. Rev. B52, R17028(1995).
e) G.D. Chen, M. Smith, J.Y. Lin, and H.X. Jiang, S.H. Wei, M. Asif Kahn, and C.J. Sun, Appl. Phys. Lett. 68, 2784(1996).
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g) D.C. Reynolds, D.C. Look, W. Kim, O. Aktas, A. Botchkarev, A. Salvador, H. Morkoc, and D.N. Talwar, J. Appl. Phys. 80, 594(1996).
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i) A. Shikanai, T. Azuhata, T. Sota, S. Chichibu, A. Kuramata, K. Horino, and S. Nakamura, J. Appl. Phys. 81, 417(1997).

**Table V.** The interband hydrostatic deformation potentials ($D_1$ and $D_2$) of $E_0$ and uniaxial deformation potentials ($D_3$ and $D_4$) of the valence band for wurtzite GaN.

| $D_1$ ($eV$) | $D_2$ ($eV$) | $D_3$ ($eV$) | $D_4$ ($eV$) | References |
|---|---|---|---|---|
| -8.16 | -8.16 | 3.71 | 3.71 | Gil et al.[a] |
| $D_1$-$D_2$ = -5.73 | | 5.73 | -2.86 | Chichibu et al.[b] |
| -8.16 | -8.16 | -1.44 | 0.72 | Tchounkeu et al.[c] |
| -6.5 | -11.8 | -5.3 | 2.7 | Shan et al.[d] |
| - | - | 8.82 | -4.41 | Shikanai et al.[e] |
| 0.7 | 2.1 | 1.4 | -0.7 | Chuang et al.[f] |
| - | - | 3.03 | -1.52 | Suzuki et al.[g] |

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**Table VI.** The values of binding energies for the intrinsic free A-, B-, and C-exciton in GaN determined by various experimental methods.

| A (meV) | B (meV) | C (meV) | References and Methods |
|---|---|---|---|
| 28 | - | - | Monemar (PLE)[a] |
| 27 | - | - | Ogino et al.(PLE)[b] |
| 18.5;20 | - | - | Smith et al.(PL)[c] |
| 20 | 22 | - | Reynolds et al.(PL)[d] |
| 26.1±0.7 | - | - | Volm et al.(PL)[e] |
| 22.7 | - | - | Freitas et al. (PL)[f] |
| 25.3 | - | - | Chichibu et al.(PR)[g] |
| 21±1 | 21±1 | 23±1 | Shan et al.(Reflection, PR)[h] |
| 20 | 18.5 | - | Tchounkeu et al.(PR)[i] |
| 26 | - | - | Shikanai et al.(PR)[j] |

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e)  D. Volm, K. Oettinger, T. Streibl, D. Kovalev, M. Ben-Chorin, J. Diener, B.K. Meyer, J. Majewski, L. Eckey, A. Hoffmann, H. Amano, I. Akasaki, K. Hiramatsu, and T. Detchprohm, Phys. Rev. B53, 16543(1996).
f)  J.A. Freitas, Jr. K. Doverspike, and A.E. Wickenden, Mat. Res. Symp. Proc. vol.**395**, 485(1996).
g)  S. Chichibu, A. Shikanai, T. Azuhata, T. Sota, A. Kuramata, K. Horino, and S. Nakamura, Appl. Phys. Lett. **68**, 3766(1996).
h)  W. Shan, B.D. Little, A.J. Fischer, J.J. Song, B. Goldenberg, W.G. Perry, M.D. Bremser, and R.F. Davis, Phys. Rev. B54, 16369(1996).
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**Figure 1**. Structure and symmetries of the lowest conduction band and the upmost valence bands in wurtzite GaN at the $\Gamma$ point ($k \approx 0$).

**Figure 2**. Near-band edge exciton luminescence spectra taken from a 7.2-$\mu$m GaN epifilm grown on sapphire by MOCVD.

**Figure 3**. Temporal evolution of spectrally integrated PL for intrinsic free-exciton and bound-exciton emissions in a GaN sample at 10 K. The inset plots the measured decay times for the emissions as a function of temperature.

**Figure 4**. Dependence of the peak energies of exciton emissions on pressure for GaN at 10 K. The solid lines are the least-squares fits to the experimental data.

**Figure 5**. Comparison of reflection spectra of near-band-edge excitonic transitions in one GaN/SiC and two GaN/sapphire samples at 10 K. The curves are vertically displaced for clarity. The inset plots the measured in-plane GaN lattice constants ($a$-axis) versus the lattice parameters along the growth direction ($c$-axis) by high-precision X-ray differaction. The lattice constants of strain-free GaN is shown in the inset for reference.

**Figure 6**. The measured transition energies of various free excitons versus the energy position of $A$-exciton. The solid and dotted lines are fits to the data which lead to the estimates of the crystal-field splitting and the spin-orbit splitting parameters, $\Delta_1$, $\Delta_2$ and $\Delta_3$, for wurtzite GaN. (From Tchounkeu *et al.*, 1996.)

**Figure 7**. Absorption spectra of a 0.4-$\mu$m GaN epitaxial layer in the vicinity of the fundamental absorption edge at various temperatures. The curves are vertically displaced for clarity. The inset details the near-band-edge exciton resonances. The spectral structure indicated by a vertical arrow is due to the contribution of the indirect exciton formation process which creates an exciton and an LO phonon simultaneously.

**Figure 8**. Comparison of conventional and photoreflectance spectra taken from a 7.2-$\mu m$ GaN/sapphire at 10 K. Open circles are experimental data, and solid lines represent the best result of the least-squares fit to the PR data. The identifications of the various spectral features are given by the notations.

**Figure 9**. Photoreflectance spectrum of a GaN/SiC sample. The sample exhibits much stronger transition signals associated with the 1s and 2s state of the $C$-exciton in the sample. A 0.0172 eV energy separation of theses two states is obtained by the best fit to the experimental data.

**Figure 10**. Photoluminescence excitation spectra taken from a 2.5-$\mu m$ GaN epilayer on sapphire with the detection position at the $A$-exciton and the bound-exciton emission resonances,

respectively. The inset shows the 10-K exciton luminescence spectrum of the sample.

**Figure 11**. The decay scheme of excitons in the free-exciton band with an incident photon energy (a) $E=E_0+n\hbar\omega_{LO}$ and (b) $E=E_0+n\hbar\omega_{LO}+\Delta E$. The upper portion depicts the scheme measured at free-exciton emission peak position ($FX^A$), and the lower portion describes that detected at bound-exciton resonance (BX).

**Figure 12**. Typical luminescence spectral signatures of nominally undoped epitaxial GaN samples.

**Figure 13**. Schematic diagrams of two models for interpreting the broadband yellow luminescence. (a) Radiative recombination involving transitions from deep donor to shallow acceptor as proposed by Glaser *et al.*(1994); (b) recombination process associated with shallow donor and deep acceptors.

**Figure 14**. Pressure dependence of the energy of the yellow luminescence for a bulk sample and an epitaxial film of GaN. (From Perlin *et al.*, 1995)

**Figure 15**. PL spectra at room temperature of Mg-doped GaN layers. The Mg concentrations are (a) $1.3\times10^{19}\text{cm}^{-3}$; (b) $5.2\times10^{19}\text{cm}^{-3}$; (c) $8.0\times10^{19}\text{cm}^{-3}$; and (d)$1.8\times10^{20}\text{cm}^{-3}$. (From Amano *et al.*, 1990)

**Figure 16**. PL spectra of Mg-doped GaN in the as-grown state and after annealing at incremental temperatures T. Zero phonon lines (ZPL) are labeled as L1 (382 nm) and L2 (414 nm). The inset shows the near-band-edge region of the spectrum after annealing at 775°C. The lines are labeled L3 (369.55 nm), L4 (376.25 nm), and L5 (377.55 nm). (From Götz *et al.*, 1996)

**Figure 17**. Schemes of optical pumping: (a) Excitation beam; (b) Side-pumping geometry: a laser beam is focused on a variable width slit onto the sample front surface to form a rectangular excitation spot. The length of excitation stripe (L) can be varied by changing the slit size. The emission signal is collected from sample edge; (c) vertical-pumping configuration: emission can be collected from sample front surface in a back-scattering geometry. The inset shows an example of an optical pumping experimental setup for wide gap III-nitrides. The primary excitation source is a tunable dye laser pumped by a doubled Nd:YAG laser at 532 nm. Its output is then frequency-doubled into UV for high-power excitation in either side-pumping or vertical-pumping geometry.

**Figure 18**. A brief summary of most of the results of stimulated emission and lasing in GaN and related materials published since 1994. The solid circles represent optical pumping results and the arrows mark important events regarding electroluminescence and current-injection laser diodes.

**Figure 19**. Emission spectra taken from a GaN/AlGaN SCH sample at different pumping power

densities. The spectra were vertically displaced for the clarification. $I_{th}$(=90 kW/cm$^2$) represents the pumping threshold for stimulated emission.The change of emission intensity as a function of pumping power density is shown in the inset. The onset of the superlinear increase of emission intensity is defined as the pumping threshold. (From Schmidt *et al.*, 1996)

**Figure 20.** Lasing spectrum taken from a 4.2-μm GaN epilayer at room temperature (300 K). The sample edges were fine polished, and external mirrors were imposed to form a resonant cavity. The full width at half maximum of the laser emission line is 3 Å.

**Figure 21.** The variation of the peak emission intensity with the length of the excitation stripe on an GaN sample surface at selected power levels at room temperature. The estimated optical gain values for the GaN sample are given in the figure. The pumping threshold $I_{th}$=800 kW/cm$^2$.

**Figure 22.** Measured optical gain spectra at various pumping power levels and comparison with calculated spectra (solid lines). The carrier density is determined by fitting the spectra. (From Frankowsky *et al.*, 1996)

**Figure 23.** The optical spectra for the first Nichia InGaN MQW LD: (a) at a current of 2.1 A; (b) at 1.7 A; and (c) at 1.3 A. The intensities of the spectra scales are in arbitrary units and are different. (From Nakamura *et al.*, 1996a)

**Figure 24.** The second harmonic reflected intensity from the GaN/electrolyte interface for various reverse bias potentials. (From Miragliotta *et al.* 1996)

**Figure 25.** Picosecond four-wave-mixing experimental setup. A boxcar geometry is used. The insets show the cross-section view of beam spots in front of and behind the sample.

**Figure 26.** Photograph of the wave mixing signals showing three attenuated pump and probe beams and higher order nonlinear diffracted signal spots. The laser photon energy (2.33 *eV*) is well below the room-temperature GaN band gap (3.42 *eV*).

**Figure 27.** Scattering efficiency, η, as a function of the delay of probe beam. Two characteristic time constants of 100±10 ps and 1.1±0.2 ns can be derived from the nonexponential decay.

**Figure 28.** The experimental arrangements for the coherent-transient degenerate FWM measurement.

**Figure 29.** Time integrated four-wave-mixing (TI FWM) signal in the reflection geometry near the B-exciton resonance at 10, 70 and 190 K for a 7.2-μm epilayer of GaN grown on sapphire.

**Figure 30.** (a) Spectrally-resolved (SR) FWM signals from the A and B exciton resonances near zero delay at 10, 50, 100, 150, and 190K plotted together with CW reflectivity data from the same sample. The *B* exciton linewidth of 2.5meV (FWHM) at 10K, together with the FWM

decay time of 300fs ($T_2$=2 $\tau_{FWM} \Rightarrow \Gamma_{hom}$ = 2.2 meV), indicates that the excitons in this sample are mostly homogeneously broadened even at low temperature. (b) SR-FWM linewidth of the *B*-exciton plotted as a function of temperature. The solid line is a least-squares fit to the formula $\Gamma(T)=\Gamma_0+\gamma T+\Gamma_{LO}/[exp(\hbar\omega_{LO}/k_B T)-1]$ with paramenters $\gamma$=13$\mu$eV/K and $\Gamma_{LO}$ = 470meV.

**Figure 31**. TI-FWM data at 10K at different detunings $\delta\omega=\hbar(\omega_d-\omega_2)$ around the *B* exciton. ($\omega_d$=detection frequency). The laser is set to excite both the *A* and *B*-exciton resonances. The fact that no phase shift was observed as a function of energy position across the *B*-exciton resonance indicates that the observed beats are true quantum beats. The curves taken at different detunings are offset for clarity.

**Figure 32**. TI-FWM signal at 10K for co-linear (solid) and cross linear (dashed) polarization geometries.