Blue LEDs and Lasers

A report on recent developments with indium gallium nitride.

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Except where specific reference is made to the work of others, this work is original and has not been already submitted either wholly or in part to satisfy any degree requirement at this or any other university.

Abstract

An overview is given of recent advances in wide bandgap device technology. The focus is on In/GaN laser diodes and light emitting diodes, assessing what is currently known about the impact of certain materials issues on device operation. Molecular beam epitaxy, metal oxide chemical vapour deposition and metalorganic vapour phase epitaxy are compared as methods of manufacture. Recombination of excitons in the electron-hole plasma is established as the mechanism for lasing in InGaN devices.

Introduction

Indium gallium nitride has recently been developed as a practical semiconductor for use in blue light emitting diodes (LEDs) and laser diodes (LDs). Such devices have potential uses in traffic signals, full colour displays, data storage (quadrupling the capacity of a CD) and undersea communications[1,2,3,4].

These developments have shown up a number of unexpected semiconductor materials issues, particularly whether the mechanism for lasing is quantum dots or electron-hole plasma (EHP) effects.

The latest commercial LEDs operate with a forward current of 20mA, a reverse voltage of 5V and at 25°C to give an intense blue of 2cd luminosity and chromaticity co-ordinates on the ICI standard colourmetric scale of x=0.130, y=0.015.[5] With a peak at 407.9nm, a full width at half maximum (FWHM) of 0.45nm has been achieved repeatably.

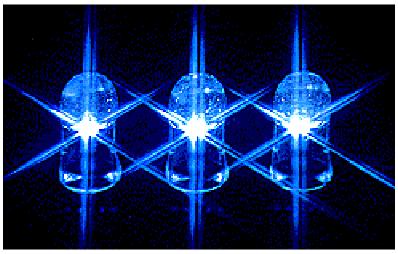


Figure 0a: The latest blue LEDs

Extreme operating temperatures of −30°C and +80°C are quoted.[5] The lifetimes for LDs are over 10^4 hours.[6] Room temperature continuous wave (CW) operation has been demonstrated on several substrates.[7]

This paper will discuss the properties of the materials used, outline the methods of fabricating devices, and evaluate the proposed lasing mechanisms.

Properties

The physical properties of the materials being considered have been the subject of much study over the past few years. Establishing the precise values of these will help explain the behaviour of the devices.

The direct bandgap of GaN is 3.4eV, that of InN is 1.9eV [1]. The lattice parameters of GaN, InN and sapphire (the most common substrate so far) are shown in Table 1a.

	GaN	InN	sapphire
a	3.189	3.54	4.758
c	5.185	5.76	12.99

Figure 1a: Lattice constants in a and c directions (in angstroms)[1]

GaN is very resilient to electrical, mechanical, chemical or thermal attack[8,1,6]. It can withstand current densities of tens of $kAcm^{-2}$ and has a Young's Modulus of 150Gpa [8]. Although this can be useful for building survivable devices for harsh conditions, it does present a problem for etching, discussed in the next section.

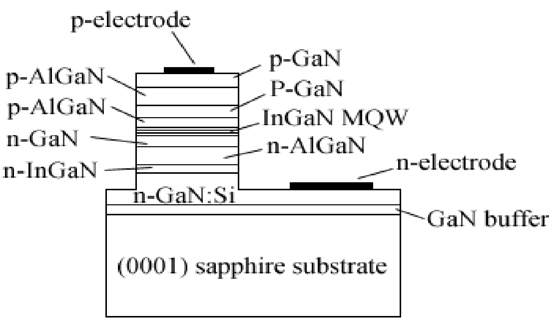
The hole scattering rate in GaN is greater than the electron scattering rate. This isn't surprising given the large hole/electron mass ratio. However, the hole mass has been the source of much debate. This was caused by different applications of the simple hydrogen model. A value of m_h=1.4m (m=9.11×10^{-31}kg, the free electron mass) was initially thought to be required to account for the binding energy (extrapolated from the data available at the time as 190meV). However, measurements of the hole mobility, taking into account the $m^{-3/2}$ dependence on optic polar scattering, give m_h=0.5m. This prompted attempts to reconcile the model and the observations.

The standard hydrogen model may only be employed if the dielectric constant can be defined meaningfully. This requires the orbit to include a large number of atoms. In GaN the Bohr radius is 7.5Å, sufficient to enclose about 150 atoms. Thus the model is valid in this circumstance. The calculations so far had used the static value of the dielectric constant, ε(0)=10. This is valid only if the binding energy of the atom is less than the energy of the transverse optic phonon (TOP). In GaN, this is not the case despite the large phonon energy. Thus the high frequency value, ε(∞)=5.35, should be used. This reduces the calculated value to m_h=0.4m, in reasonable agreement with the experimental results. However, calculating the binding energy using this mass puts it below the TOP energy, against the initial statement. The observed m_h=0.5m puts the binding energy just above the TO energy. Another factor could be the large electronegativity of the nitrogen atom causing a central cell correction to the binding energy. [9,10]

Fabrication

The basic building block of optoelectronic devices is layers of different semiconductors. The methods for growing these are described below. An example of the layout of a laser diode is shown in Figure 2a. The easiest shape for the plates are hexagons, due to the molecular shape of the nitrides. The edges have very different morphology, smooth for gallium-terminated ones and rough for nitrogen-terminated ones.[11]

Figure 2a: A schematic diagram of an



InGaN MQW LD[8]

Substrate

The choice of substrate for devices has been difficult for III-V nitrides. The best options so far are shown below, in Figure 2b.

CW operation of LDs has been demonstrated at 20°C on sapphire, SiC, ELOG and GaN substrates.[7]

The latter two materials listed in the table require quite complex manufacture. Bulk AlN is grown by sublimation-recondensation. Polycrystalline AlN is evaporated then condensed at 2300°C. This method can achieve a growth rate of 0.3cm/hr and a high-quality plate of 1.2×1cm.[14]

silicon carbide	sapphire	lithium gallium dioxide	aluminium nitride	epitaxially laterally overgrown gallium nitride
SiC	Al_2O_3	$LiGaO_2$	AlN	ELOG
3.4%	16%	0.2%	2.2%	0%

Figure 2b: Common substrates and their lattice mismatch to GaN[11,12,13,14,15,16]

Lateral epitaxial overgrowth (LEO) involves masking some of a sapphire substrate then growing GaN on top. The mask of SiO_2 is partially removed using ultraviolet photolithography and wet chemical etching before the GaN is grown at 1080°C. This process can reduce the threaded dislocation (TD) density from ~10^{10}cm^{-2} for bulk GaN to ~6×10^7cm^{-2} above the mask. [13,15,16] The masking layer blocks vertically propagating dislocations and alters the direction of others so they travel sideways at the LEO front [16]. A similar procedure called facet-initiated epitaxial lateral overgrowth (FIELO) has been used to grow low dislocation density, crack free GaN on sapphire. The sapphire was then removed to produce 2-inch diameter wafers. The lasing threshold of InGaN devices built on this substrate was found to be much lower than in those grown on sapphire.[7]

There has been some progress in manufacturing pure GaN plates to act as substrates. However, these require a pressure of 2000 atm and have a growth rate so slow that only 5 or 10 10mm-square sections could be made in three days.[14]

Both SiC and AlN have better thermal conductivity than sapphire and so act as good heat sinks for the device. Combined with this is the difference in coefficient of thermal expansion. This is 26-34% greater in sapphire than GaN [1,17]. As the samples cool, the layers will try to contract at different rates, creating strain in the materials[12]. Although on first examination, it would appear that the smallest possible mismatch in both constants would produce the best device. That has not, however, proved to be the case.

Despite the drastic mismatch, sapphire has become the main substrate. This is due only in part to its availability. It is easy to handle, requiring no specialised equipment, and doesn't need complicated cleaning procedures prior to growth[1]. The hexagonal structure of sapphire (0001) makes binding easier[1,18], but SiC is highly cleavable, making it simple to achieve a smooth surface[8,3]. It has been found that a several-micrometre thick GaN layer on whatever substrate acts as a buffer to allow better quality layers to be grown on top[8].

Etching

As mentioned earlier, etching nitrides has proved very difficult. Several methods of dry and wet etching have been tried. The fastest, with rates of up to 1300mm/min, is electron-cyclotron resonance ion etching (ECR-RIE). This works, like many other processes, by a combination of particle impact and chemical action. It achieves the high speed by having a very high plasma density. [6,19]

Wet etching on the other hand is very slow. However, it has found a use. Photoelectrochemical (PEC) etching using KOH/H_2O allows rapid analysis of dislocation densities in n-GaN. Reduced etch rates around the dislocations, both mixed (m) and edge (e) leave 'whiskers' sticking out of the surface which can be observed with a transmission electron micrograph (TEM).[6]

Figure 2c: TEM image showing dislocations and 'whiskers'[6]

Main Growth

There have been several methods employed in the attempt to grow layers of nitrides. The main examples are metalorganic vapour phase epitaxy (MOVPE), molecular beam epitaxy (MBE) and metal oxide chemical vapour deposition (MOCVD). These all deposit a slow stream of molecules on the surface.

MOVPE is one of the most common methods for growing GaN. Trimethylgallium (or trimethylindium for InN) react with ammonia (NH_3) on a substrate at around 1000°C. This high temperature is required to dissociate the ammonia but causes strain problems in post-growth cooling due to the thermal mismatch of the materials (discussed above). One attempt to reduce the temperature needed has been to supply the nitrogen by microwave plasma excitation. An electron-cyclotron-resonance (ECR) microwave plasma source delivers a stream of atomic, neutral and ionic nitrogen radicals to the growth surface. This can reduce the required substrate temperature to around 500°C. A typical growth rate is 2μm/h.[11,1,19]

In MBE the gallium comes from a solid source effusion cell and the nitrogen, as usual, from high-purity NH_3. Typical growth rate for MBE is 1.2μm/h at 830°C. It has been found that increasing the ratio of Ga to N decreases 3D growth, increases electron mobility, and thus improves the optoelectronic properties of the material. However, growth conditions too rich in Ga lead to gallium droplets forming on the surface, degrading performance. [18,12,20]

Quality

The resulting material is very imperfect. Not only is there a large stress[21] on it, but it is full of defects. In fact, the defect density in an InGaN quantum well (QW) laser diode (LD) is typically of the order of $10^9 cm^{-2}$ [8]. Using the evidence of localised electron-hole pair states, it has been determined that the degree of localisation increases more rapidly as more indium is added than would be expected from a simple random alloy. This suggests lattice disorder which is both structural and compositional.[8] There is a spatial potential undulation, possibly due to fluctuations in the InGaN composition, influenced both by extrinsic and by intrinsic defects[8,22]. These fluctuations take the form of quantum dots (QDs), where pools of indium-rich material, around 35Å in diameter, collect electrons. These dots become more and more ordered, in both size and array, as the layer gets thicker.[8,23,2,24]

Role of Defects

Comparison of GaN LEDs on sapphire and ELOG substrates has yielded important information about the role of dislocations.

The difference in TD density between the samples[15,16] did not produce a significant difference in emission efficiency. Thus the dislocations can't be non-radiative recombination centres, as had been previously thought.[15]

An identical blue shift was observed in both samples with increasing forward current. This was due to localised energy states causing band filling. Again, this could not be due to the TDs, but more likely the In localisation.[15]

The LED on sapphire did have a much larger leakage current than that on ELOG. It seems likely that the TDs are the leakage pathway.[15] The other major benefit of using ELOG in devices is the strain reduction from matched thermal properties.

Lasing Mechanism

There has been much debate as to the cause of lasing in nitride devices. Early on the research mainly concentrated on attributing minor peaks in the emission spectrum to particular causes. Thus the peak at 3.47eV was believed to be caused by excitons bound to neutral donors, that at 3.45eV to excitons bound to neutral acceptors. Free hole recombination with electrons bound on impurity centres (probably oxygen) was suggested as the origin of the 3.42eV peak. The 3.269eV peak is separated from the band edge emission by 204meV, the difference between the bandgaps of wurtzite (w) and zinc blende (zb) forms of GaN. These have been seen to exist in the same sample and the peak was tentatively ascribed to the DBE transition in zb inclusions in the w film.[18,12] NB: the energies listed above are only valid for the samples used in the experiments. The line positions in GaN on sapphire depend on the thickness of the layers. This is due to the in-plane biaxial strain[21] decreasing with increasing thickness.[17] There is also a red-shift of the lines in QW diodes with increasing temperature[26].

EHP vs. QDs

There are two main candidates for the stimulated emission mechanism. Direct band-band transitions in the electron-hole plasma (EHP), enhanced by excitonic effects is the first. A 3-level pumping scheme is set up between a degenerate state and the non-degenerate excitonic one[22]. Recombination of excitons localised by microscopic crystalline disorder aids the optical gain[8,22]. The other proposal is quantum wells formed by quantum dots. This was suggested in 1997 by Nakamura after concluding that the laser emission came from excitons bound at potential minima[8,2,24].

Most of the evidence appears to support the EHP theory. Firstly, the aforementioned red shift with temperature [26] is in contradiction of the finding that a QD laser has a very weak temperature dependence[27].

More significant have been studies of the mode spacing. Spectral analysis has shown observed mode spacings around an order of magnitude greater than those calculated from the known cavity length. Initially this was attributed to small cracks forming cavity mirrors. These have not been observed in InGaN LDs. The deviation from the calculated value decreases as the carrier density decreases. It has been shown that a carrier-reduced refractive index produces the required mode spacing. Naively, the mode spacing, $\Delta\lambda$ is given by:

$$\Delta\lambda_{\lambda} = \frac{\lambda^2}{2nL}$$

Equation 3a

When the lasing conditions are satisfied, a high free-carrier density alters the refractive index, n, so it is not longer just a function of wavelength, λ.

$$\Delta\lambda = \Delta\lambda_{n_e=0}\left[1+\left(\frac{2L}{\lambda}\right)\left(\frac{2\pi e^2}{n_0 m^* \omega^2}\right)n_e\right]$$

Equation 3b

For a carrier density of 10^{19}, this gives a mode spacing 9 times that given by Equation 3a. This fits with the measured value. This reduction in refractive index is only predicted by an EHP state and so helps to prove that this is the cause of the optical gain. [28,24]

A recent study (published 29 March 1999) has raised some interesting points regarding hole localisation. A theoretical calculation using large supercell empirical pseudopotentials demonstrated that homogeneous InGaN alloys would exhibit electronic clustering even without chemical clustering. Indium-localised hole wave-functions with short-range localisation and long-range delocalisation would still lead to excitonic localisation. It concludes that this phenomenon also explains the strong dependence of optical properties on atomic arrangement. [25]

However, the possibility of lasing in the quantum dots must not be disregarded. A mathematical model of QDs in a hexagonally symmetrical host crystal has been created. When strain effects and coulomb interactions were included, it was concluded that "InGaN QDs should provide a viable gain medium to achieve laser emission in the visible … range".[29]

Conclusions

Efficient devices have been constructed and in some cases, are commercially available. Some of the debated properties of the materials have been discussed, particularly the hole mass. LEO and FIELO appear to be very promising methods for manufacturing substrates. Dry and wet etching techniques have been developed that work fairly fast, and some also have added effects, such as locating dislocations with PEC. Various epitaxy methods have been used to grow high-quality layers of GaN, InN and InGaN for LEDs and LDs. It has been suggested that the TD density does not significantly affect the optical properties of InGaN. After much disagreement, the mechanism for lasing is currently attributed to EHP effects, with hole localisation predicted even in homogeneous InGaN.

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