

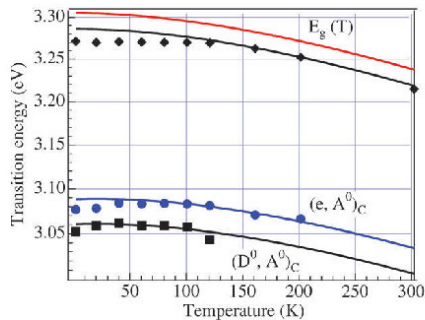


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## A Study of Growth and Doping of cubic Group III Nitride Structures

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# Chapter 1

## An Introduction

### or, Physicists and the Quest for the Holy Grail

Ever since the inception of light emitting semiconductor devices, the replacement of the everyday incandescent bulb lamp has been something akin to the Holy Grail of semiconductor physics. The incandescent lamp of old basically dates its design, which is still visible in the vacuum glass bulb, back to the days of Thomas A. Edison. Although the concept has been much improved, the principal weaknesses remain: glass shatters easily, the filament is made of brittle materials, so that the overall susceptibility to shock is relatively high. Furthermore the radiation is produced thermally (as black body radiation of the filament), so that the vast majority of the radiative energy, approximately 95–98% for ordinary bulb lamps, is emitted in the infrared spectral region which is in most cases unwanted and thus the cause of a rather low efficiency.

Solid state lighting technology however appears to be the perfect replacement: it offers a rugged, simple design without any brittle parts. Moreover, the departure from light generation by means of thermal radiation means that light emission covers only a small fraction of the spectrum. This can of course be turned into an advantage, as it leads to an increase in efficiency, but is also a disadvantage, for example with respect to the generation of white light which inherently covers a greater spectral range.

For a long time however solid state visible lighting has been limited to red, amber and green LEDs (and IR/red laser diodes). Although the Pankove group reported a Gallium Nitride based blue LED thirty years ago this achievement was still hampered by a extremely low efficiency due to the lack of an adequate p-type dopant [1]. Therefore this diode was rather designed as i-n junction.

Only the last decade witnessed an extraordinary increase in Gallium Nitride related research activity culminating in commercially available room temperature *cw* laser diodes [2]. This research activity concerned not only Gallium Nitride, but also the related compound semiconductors Indium Nitride and Aluminum Nitride plus their ternary and even quarternary compounds, eventually covering the spectral range of

2eV—6eV, i.e. the whole visible spectrum and an appreciably large portion of the UV. The emission of UV light enables the use of color conversion using phosphors very similar to the light generation in fluorescence lamps.

The application of III Nitride semiconductors does not stop at light-emitting devices; they are for example equally well-suited as photodetectors or amplifiers with high current densities and large breakdown voltages. This is especially interesting in the case of solar-blind  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  sensors. The possible future use of the III Nitrides is even more attractive given the mechanical hardness and chemical inertness that make those semiconductor devices seem ideal candidates for devices operating at high temperatures or under otherwise harsh and adverse conditions [3, 4]. Their large piezoelectric coefficients suggest their use as actuators. As opposed to Silicon Carbide, which offers similar properties, Gallium-based Nitrides possess a direct band gap, thus increasing the optical efficiency. In summary, III Nitrides offer all the capacities of being truly optoelectronic materials.

The group III Nitrides are known to have two crystal phases under ambient conditions, wurtzite and cubic. The latter however is found to be the metastable phase, which is the reason why most of the scientific and commercial effort has been devoted to and consequently most progress has been reported for hexagonal phase material. Because of the higher crystal symmetry, cubic III Nitrides are expected to exhibit superior properties, such as smaller carrier scattering coefficients, lower dopant activation energies, and a smaller band gap [5]. Cubic phase III Nitrides can be grown on readily available Gallium Arsenide substrates (or even 3C-SiC). Those substrates can be doped, thus facilitating the electric device layout without the need for mesa etching or similarly difficult technological steps. Furthermore both substrate and epilayer possess the same crystal orientation and can therefore be cleaved easily, opening up a way for the manufacture of edge-emitting lasers without post-processing the laser facets.

For optoelectronic devices, controlled p-type doping is essential. The use of Magnesium, although widely applied, presents several drawbacks: the room temperature hole concentration usually reported lies in the middle  $10^{17}\text{cm}^{-3}$ . In MOCVD growth, Mg forms a complex with hydrogen, necessitating an extra thermal treatment. In MBE growth, Magnesium is extremely volatile, causing memory effects in the system. Moreover, it substitutes Gallium, so that the growth process proceeds under Nitrogen-rich conditions, which are disadvantageous for the growth of high-quality epilayers. Carbon however, as will be shown in this work, is an acceptor when substituting Nitrogen and therefore readily incorporated under favourable Gallium-rich growth conditions. It does not cause any unwanted side effects in the MBE growth, and possesses a lower activation energy [6].

Advanced semiconductor devices make use of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  layers or quantum well structures, which may serve several purposes.

Firstly, layered structures of the  $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}$  type can act classically as (multi) QW structures or superlattices [2]. In this way, the layers are the optoelectronic active structures, either for generating or detecting light. The large band gap even makes it possible to build sensor devices which are insensitive to ambient light, as mentioned above. Secondly, because of their different indices of refraction,  $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}$  heterostructures may be used as light guiding elements of optoelectronic

devices, e.g. as Bragg reflectors that may be grown *in situ* [7, 8]. Thirdly, it has been shown that the variation of the chemical environment because of partial Gallium and Aluminum sublattices — evident in the varying position of valence and conduction band — increases the doping efficiency [9]. Lastly, in analogy to the case of GaAs-based devices, it might be possible to reduce the defect density by means of stacking several (dozen)  $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}$  layers [10].

Cubic QW structures grown in [100] direction do not exhibit spontaneous and piezoelectric polarization which result in a strong quantum-confined Stark effect, which in turn deteriorates QW efficiency severely because of the spatial separation of the hole and electron wave functions [11, 12].

This thesis is organized as follows:

Chapter 2 gives a general overview of the known material properties of c-GaN and c-AlN, along with a short discussion. It also contains a description of the principal experimental methods used in the course of this work, i.e., MBE setup and characterization by means of Photoluminescence and Cathodoluminescence as well as X-ray diffraction. Additionally the growth process itself and the influence and optimization of the nucleation are discussed.

Aspects of doping cubic Gallium Nitride using Carbon are dealt with in chapter 3. This covers the commissioning and characterization of the Carbon sources and the optical and electrical characterization of the GaN:C films. The results are discussed using a model of Carbon incorporation onto N lattice sites, interstitials and Dicarbon complexes.

Cubic Aluminum Nitride films and GaN/ $\text{Al}_x\text{Ga}_{1-x}\text{N}$  multi quantum well structures are treated in chapter 4. The structural properties are revealed through X-ray and TEM measurements. GaN quantized states are modelled in effective mass theory, showing good agreement with the experimental values from CL measurements.

The results are summarized in chapter 5.

The nomenclature which has been used throughout this thesis is explained on the preceding pages xiii through xvi. This comprises abbreviations, usually in capital letters, on pages xiii and following, symbols listed on pages xiv f., and physical constants found on page xvi. Therefore, in any case of uncertainty the reader is kindly referred to this chapter.