Chapter 2

Brief Review of Research Works of Dilute Nitrides

From 1994, the investigation on (InGa)(AsN)materials has been carried out intensively and improvements both on theoretical study and device fabrication were achieved. Here, we review briefly some aspects of the investigation and development of this group of materials.

2.1 Growth of (In)GaAsN

The first GaAsN alloy was grown by M. Weyers [1] (1992) with an N concentration of 1.6% by metalorganic chemical vapor deposition (MOCVD) at low pressure, the N source was derived by decomposing NH_3 in a remote microwave plasma. They also observed a strong bandgap reduction of the alloys. In 1994, Kondow *et al.* [2, 3] grew for the first time by gas source molecular beam epitaxy (GS-MBE) with plasma N source the GaAsN alloys with N composition of 4% and suggested that this materials could be used for optoelectronic devices. The application of this group of materials in optoelectronic devices and the theoretical interpretation of the electronic structure of it were both explored intensively since then.

In 1996, Kondow *et al.* [3]obtained GaAsN alloys with N composition of 10% by GS-MBE. In 1997, Bi *et al.* [4] grew GaAsN with N composition of 14.8% on GaP by MBE under low growth temperature. This is the highest N composition obtained till now. In 2000, Toivonen *et al.* [5] reported their growth of GaAsN alloys with N composition of 5.6% by MOCVD. Other growing techniques, such as pulsed laser deposition and N^+ implantation were also used for the GaAsN growth [6,7].

Because the materials quality degrade rapidly with increasing N composition, it is difficult to obtain GaAsN alloy with qualities good enough for working in optoelectronic devices. Even though, in 1996, Kondow *et al.* [8] suggested that InGaAsN could be grown lattice matched with GaAs substrates. After that, in 1998, Xin *et al.* [9] observed photolluminescence of 1.3 μm from the InGaAsN/GaAs multiquantum wells (MQWS) grown by GS-MBE. In 1999, Forrest *et al.* [10] observed PL emission of 1.9 μm from InGaAsN/InP MQWs grown by solid state MBE on InP substrate. In 2000, Tourie *et al.* [11] reported the room temperature (RT) PL emission of 1.43 μm and low temperature (LT) PL emission of 1.68 μm.

2.2 Investigation of the Electronic Structure of (In)GaAsN Materials

2.2.1 Bandgap Energy Bowing

The lowering of the bandgap energy of the whole alloy with the incorporation of N is the most attractive feature of the group of (In)GaAsN materials. This bandgap energy Bowing was well interpreted by the first principle local density approximation calculations (LDA) of Bellaiche *et al.* [12–15]. They showed that the N composition dependent giant Bowing of the bandgap energy is due to the formation in the alloy of spatially separated and sharply localized band edge states. The analysis suggested that band gap variation as a function of x can be divided into two regions: (i) a bandlike region ($x \geq 10\%$) where the bowing coefficient is relatively small and nearly constant, and (ii) an impurity like region ($x \leq 10\%$) where the bowing coefficient is relatively larger and composition dependent.

Shan *et al.* [16, 17] suggested a "band anticrossing" (BAC) model for describing dilute nitride alloys. It calculated a strong interaction between the conduction band and a narrow resonant band formed by nitrogen states. It explained well the fundamental bandgap change under hydrostatic pressure. The significant, practical advantage of the BAC model is that it provides simple analytic expressions for the CB dispersion and allows us to easily calculate, for example, the oscillator strength of the optical transitions [18] in bulk material, the transition energies between electronic states in QWs or the gain in laser structures [19].

ED Jones *et al.* have calculated the pressure dependence of the bandgap energy of InGaAsN by LDA and concluded that the nonlinear dependence of the bandgap on pressure does not resulted from localized N states. Their calculation results were in good agreement with the experimental data, except for an offset of the bandgap energy. However, the other experimental results on ballistic electron emission microscopy [20], ellipsometry measurements [21], and resonance raman scattering [22] appeared to support more the LDA model.

2.3 (In)GaAsN based Optoelectronic Devices

One of the most promising field of application of the (In,Ga)(As,N) system is the 1.3 μm laser for data transmission. Laser Diodes which can be modulated at high frequencies and fabricated at low cost are demanded for this goal.

- In 1996, Kondow *et al.* [23]reported for the first time InGaAsN laser diode(LD) with a pulsed current at RT at 1.2 μm the threshold current density of it is about 0.8 kA/cm^2.

- In 1997, Sato *et al.* [24] realized for the first time with $Ga_{0.9}In_{0.1}As_{0.97}N_{0.03}$ MQWs grown by MOCVD.

- In 1997, Larson *et al.* [25] reported RT continuous wave photopumped operation of 1.146-1.256 μm VCSEL employing InGaAsN MQW active layer grown directly on a GaAs-AlAs distributed Bragg reflector (DBR). The threshold current density was estimated to be 3.3-10 kA/cm^2.

- In 1999, Ellmers *et al.* [26] reported (GaIn)(NAs) vertical-cavity surface-emitting lasers (VCSEL) for room temperature emission at 1.285 μm grown by MOCVD. The optical pumping thresholds are between 1.6 and 2.0 kW/cm^2.

- In the same year, Kondow *et al.* [27] reported InGaAsN MQW based LD works continuously at 1.3 μm for more than 10^5 hours.

- In 2000, Reinhart *et al.* [28] fabricated for the first time an InGaAsN/AlGaAs DFB LD working at 1.3 μm with the threshold current of 120 mA.

- In the same year, Choquette *et al.* [29] reported laser based on InGaAsN MQW working at 1.294 μm, the threshold current density of it is 4 kA/cm^2, the output is 60 μW.

- In 2001, Li *et al.* [30] reported InGaAsN single quantum well (SQW) lasers operating at 1.32 μm, grown by solid state MBE. The threshold current density of it is 546 A/cm^2.

- In 2002, Gollob *et al.* [31] showed InGaAsN single quantum well (SQW) lasers grown by solid state MBE operating at up to 1.304 μm. RT continuous-wave operation was obtained with a threshold current of 28 mA.

- In 2003-04, Bank *et al.* [32] demonstrated the first 1.5 μm InGaAsSbN laser with a pulsed threshold current density of 930 A/cm^2.

- 2003-09, Tansu *et al.* [33] demonstrated an InGaAsN laser with a RT emission wavelength of 1.317 μm. The RT threshold current density is 210-270 A/cm^2.

- In 2004, Wistey *et al.* [34] reported a top-emitting InGaAsSbN VCSEL at 1.46 μm, working at -10°C. The threshold current density of it was 16 kA/cm^2.

- In the same year, Kawamura *et al.* [35] reported InGaAsSbN QW lasers operating at 1.9 μm with the room temperature continuous-wave threshold current density of 580 A/cm^2

- In the same year, Bank *et al.* [36] reported InGaAsSbN QW lasers operating at 1.4 μm with a threshold current density of 250 A/cm^2 at 10 K.

- In 2005, Nishida *et al.* [37] reported an InGaAsN VCSEL emitting at 1.26 μm. The output power at RT was 4.2 mW.

- In the same year, Kawamura *et al.* [38] reported InGaAsSbN QW lasers operating at 2.07 μm with a threshold current density of 1.4 kA/cm^2 at 90 K.

- In 2006, Gupta *et al.* [39] demonstrated continuous wave operation of InGaAsSbN lasers at 1.556 μm. The threshold current density was about 27 mA/cm^2

Besides the applications to LD, other InGaAsN based devices, such as solar cells, resonant-cavity-enhanced photodetectors [40], and heterojunction bipolar transistors (HBT) were also developed in this period [41–44].