Electronic properties of GaNAs alloy

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Abstract

A brief review on the present knowledge of the electronic properties of the GaNAs alloy is given mainly from an experimental perspective. The paper is focused on GaNAs with low N composition less than ten percent where a large amount of experimental work has been done. Important fundamental electronic properties of the material system are described with the emphasis on the nature of the giant band gap bowing in the alloy and nitrogen-induced modifications of the electronic structure of the conduction band. The current knowledge of the key material parameters, relevant for the device applications, such as electron effective mass, recombination processes and band alignment in GaNAs/GaAs heterostructures, is also reviewed.
1 Introduction

\( \text{GaN}_x\text{As}_{1-x} \) has recent years emerged as a new semiconductor alloy opening a wide range of possible electronic device applications because of it’s unique physical properties. This alloy commonly with \( N \)-containing anion mixed III-V alloys exhibit a huge bowing in the band gap energy\([1][4]\). For example, the addition of only two percent of nitrogen to GaAs causes a dramatic decrease in band gap energy by about 0.4 eV. These remarkable fundamental properties of the GaNAs alloy, in combination with the possibility to vary the lattice constant of the alloy material in a wide range by optimizing the \( N \) content, provide an opportunity to tailor the material properties for desired applications in optoelectronic devices based on III-V materials. First of all, the incorporation of nitrogen has made possible to synthesize III-V compounds that are lattice matched to Si. For example, with 20% \( N \) incorporation into GaAs or 2% \( N \) in GaP, \( \text{GaN}_2\text{As}_{8.8} \) or \( \text{GaN}_{0.92}\text{P}_{0.08} \) can be lattice matched to Si\([1]\). Thus a drastic improvement in the quality of III-V epitaxial films grown on Si substrates can be achieved, providing the possibility of integrating direct band gap III-V compounds with Si. This would fulfill a long sought desire for fabrication of optoelectronic and photonic devices based on the most developed and most mature Si technology, which not only offers advantages of large area substrates, large scale and low cost fabrication, but also opens the door for integration of microelectronic and optoelectronic devices on a chip\([1]\).

![Figure 1: Variation of Bandgap energy with N content \( x \) in GaNAs\([4]\).](image_url)

Incorporation of higher \( N \) content (\( x > 10\% \)), unfortunately, causes severe degradation of the alloy quality resulting in the formation of highly inhomogeneous material with inclusions of GaN, GaNAs and GaAs phases\([1][6]\). The same applies to the GaN rich side of GaNAs, where severe phase separation occurs with As composition as low as 0.005. This is because of an extremely large miscibility gap between GaN and GaAs caused by the large differences in lattice constant and in lattice structure (GaN: wurtzite, GaAs: zincblende).

2 Fundamental Band Structure properties

2.1 Giant bowing of the band gap energy

the GaNAs alloy has shown a considerable red shift in absorption and photoluminescence (PL) near the band edge, suggesting a decrease in the bandgap energy with increasing \( N \) composition- see Fig 1. In figure 1, solid lines are experimental results and broken lines are calibrated without strain.
The deviation of the bandgap energy from the composition weighted linear average of the band-gaps of the parental binary compounds forming the alloy is usually described by a correction term,

\[ \Delta E_g = bx(x - 1) \]  

(1)

Where 'b' is the bowing coefficient. However, in contrast to the conventional III-V alloys, the optical bowing coefficient in III-V-N is huge, i.e. of the order of 18 - 20 eV for \( x < 5\% \) and strongly depends on N content. The bowing coefficient also depends on the internal strain in the GaNAs epilayer.

The reduction of the bowing coefficient has been explained by the first-principle local-density approximation (LDA) calculations of the band structure \[7\][12]. Based on analysis of the highly localized nature of the perturbations introduced by N atoms due to a large chemical and size difference between N and the other column V anions it replaces, two regions in the bandgap variation of the III-V-N alloys has been predicted. An impurity-like region with a large and compositional dependent bowing coefficient is expected for the low N compositions up to 10\%, whereas a band-like region with a much smaller and nearly constant bowing coefficient is predicted for the intermediate compositions \( x = 10 - 40\% \).[12].

2.2 Conduction band states: Nitrogen activated E+ and E- levels

Adding nitrogen to GaAs has negligible effect on the electronic structure of the valance band states in the alloy but it provides a change in conduction band states by splitting it into two E+ and E- sub bands. The Fig 2 shows the behavior of E+ and E- with respect to nitrogen addition\[1\][8][9].

![Figure 2: Compositional (left) and pressure (right) dependence of E- and E+ Transition energies of GaNAs\[1\][8][9]](image)

2.3 Pressure dependence

In sharp contrast to the parent GaAs material an unusual pressure behavior of the bandgap energy in GaNAs has been detected both via photocurrent \[1\] [9] and photoluminescence [1] [10] measurements and some representative experimental data for GaNAs are shown in Figure 2 (right). The nitrogen-induced interaction between the E- and E+ levels causes the
reduction of the alloy bandgap. However, the physical origin of this interaction remains a subject of ongoing debate[1].

Figure 3: Left: Temperature dependance of band gap energy. Right: Variation of electron effective mass with N composition[1]

2.4 Conduction band dispersion. Electron effective mass

Electron effective mass $m_e^*$ increases as nitrogen composition N increases in the low composition range[1]. This is opposite to conventional semiconductors in which $m_e^*$ decreases as band gap energy decreases. This leads to a strong energy dependence of the electron effective mass. Based on the clear compositional dependence of the GaNAs Figure 3. The electron effective mass has been found to increase up to 0.19 $m_e^*$ with $N = 2\%$. According to P.N Hai et.al[11] there is at least 50% decrease in scattering time in the GaN$_{0.2}$P$_{0.8}$ alloy as compared with GaAs. Thus both effects, i.e. increase of the electron effective mass value and the decrease in the scattering time have been concluded to contribute to a decrease of the electron mobility in GaNAs[1].

2.5 Band alignment in GaNAs/GaAs heterostructures

One of the remaining unsolved issues regarding the electronic properties of the GaNAs/GaAs quantum structures involves the band edge alignment. But a type I band line-up has been concluded based on the experimental findings of I.A Buyanova et.al[13]

3 Recombination processes

3.1 Radiative recombination

This is a very important process for optoelectronic devices and according to Buyanova et. al the dominant PL mechanism is the recombination of excitons trapped by potential fluctuations of the band edge. The low-temperature PL spectra of the GaNAs alloys in the near band-gap spectral region are usually dominated by a rather asymmetric PL band (Figure 4-left) with the position of the PL maximum shifting towards lower energies with increasing N composition in the structures[1].
Figure 4: Low temperature PL spectra of GaNAs in the near bandgap region [1]

3.2 Non-Radiative Recombination

From numerous optical experiments it is concluded that the radiative efficiency of the GaNAs alloy rapidly degrades with incorporation of nitrogen (Figure 4-right). Presence of the nonradiative channels in the GaNAs/GaAs structures depends on the growth temperature and by improving the crystal quality using post growth rapid thermal annealing or high temperature growth this effect can be reduced [1].

4 Conclusion

GaNAs alloy represents a novel material which has many exciting physical properties and a great potential for applications in optoelectronics and photonics. The majority of the discovered fundamental physical properties can be referred to as unusual and fascinating. These include the giant bowing in the band gap energy, the appearance of the E- and E+ subbands in the CB, a sub-linear pressure dependence of the band gap energy, a strong increase of the electron effective mass with decreasing band gap energy (increasing nitrogen content), etc. These nitrogen-induced modifications of the CB structure have been shown to be attributed to the highly localized nature of the perturbations induced by the N atoms. However, the exact physical mechanism behind this remains a subject of ongoing debate. The radiative recombination processes in the GaNAs is much better understood [1].

References


