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Invited

Progress in Crystal Growth and Conductivity Control of Group III Nitride Semiconductors -Seeking Blue Emission-

Isamu Akasaki

Department of Electrical and Electronic Engineering, Meijo University,
1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468, Japan
Phone: +81-52-832-1151(ext.5089), Fax: +81-52-832-1244, E-mail: akasaki@meijo-u. ac. jp

In this paper, crystal growth and conductivity control of group Ⅲ nitrides in the last quarter century are reviewed as the groundwork for recently developed high-brightness light emitting diodes (LEDs) and laser diodes (LDs) based on nitrides.

1. Introduction

Because of their superior physical and chemical properties, group Ⅲ nitrides have been one of the most promising candidates as materials for application to light emitters such as LEDs and LDs in the region from the UV to the visible. They are also applicable to high-power and high-speed transistors, which are able to operate in harsh environments and at high temperatures.

To realize such novel devices, it is essential to grow high-quality nitride crystals, and to control their electrical conductivity. During the last two decades, much pioneering work has been done on GaN from the fundamental point of view and for practical use by many researchers. However, it has been quite difficult to grow high-quality epitaxial nitride films with a flat surface free of cracks. This is mainly caused by the lack of substrate materials with lattice constants and thermal expansion coefficients close to those of GaN and the nitride alloys. Moreover, it has been well known that undoped GaN is of strong n-type conductivity with high residual electron concentrations. Despite doping of acceptor impurities, p-type GaN and GaN p-n junctions had not been realized until recently. These problems had prevented the fabrication of nitride-based devices for a long time.

2. Recent Progress in Crystal Growth of Group Ⅲ Nitrides

A great advance in GaN growth by an effective interface control was achieved by Amano *et al.* in 1986[1]. They used a low-temperature deposited (LT-) thin AlN layer as a buffer layer for the growth of GaN by organometallic vapor phase epitaxy (OMVPE). The essence of this method is to insert a slightly softer material in order to reduce the interfacial free energy between the epitaxial layer and the highly-mismatched substrate. By using this method, not only the crystalline quality, but also the luminescence as well as the electrical properties, have been dramatically improved simultaneously[2]. The effectiveness of the LT- buffer layer on the improvement of the crystalline quality of the nitride alloys such as AlGaN and GaInN and their heterostructures has also been proven. This LT-buffer method was adopted by Nakamura[3], who used a LT-GaN buffer layer in OMVPE growth of GaN.

Today, these LT-AlN or LT-GaN buffer layer methods are indispensable and standard in the growth of GaN and nitride alloys on sapphire by OMVPE.

3. Control of Conductivity

3.1 n-type conductivity

Nominally undoped GaN grown by OMVPE using the LT-buffer layer is generally highly-resistive, which is caused by the decrease in the residual donor concentration. Therefore, in order to obtain more conductive n-type GaN and to control its conductivity, doping with a donor impurity is indispensable.

In 1990, Amano and Akasaki[4] and Murakami *et al.* showed that Si behaves as a donor in nitrides and SiH_4 is suitable for Si doping during OMVPE growth of GaN and AlGaN, respectively using the LT-buffer layer. The electron concentration at room temperature (RT) can be controlled from the undoped level to levels of $10^{19}cm^{-3}$ by changing the SiH_4 flow rate.

Today, SiH_4 or Si_2H_6 doping in OMVPE growth in combination with the LT-buffer layer is widely adopted for the conductivity control of n-type nitrides, GaN, AlGaN and GaInN.

3.2 p-type conductivity

So far, many groups attempted to produce p-type GaN.

No group, however, succeeded until recently. In 1989, Akasaki *et al.* found good controllability of the Mg concentration in OMVPE growth of GaN using the LT-buffer layer by employing biscyclopentadienylmagnesium (Cp_2Mg) as the Mg precursor. However, the added Mg was mostly inactive as-grown.

A low-energy electron beam irradiation (LEEBI) treatment was used to activate the Mg and to yield p-type GaN and p-n junction type LEDs[5]. Free hole concentrations at RT of about $2\times10^{17}cm^{-3}$ were achieved at that time. Today, hole concentrations at RT of more than $10^{18}cm^{-3}$ are achieved. p-type AlGaN and GaInN were also obtained in the same manner. Later, Nakamura *et al.* achieved p-type GaN by thermal annealing in nitrogen atmosphere[6].

At present, in OMVPE, all the p-type GaN and group Ⅲ nitride alloys are prepared by Mg doping using Mg-precursors such as Cp_2Mg followed by the LEEBI treatment or thermal annealing in a hydrogen-free atmosphere.

4. Device Issues

4.1 LEDs

The GaN MIS-type LED was firstly reported by Pankove *et al.*[7]. The first p-n junction LED was developed in 1989[5]. In 1992, the LED with an efficiency of 1.5% was achieved[8] and in 1993 a GaN blue LED with efficiency of about 2.7% was commercialized[9]. The efficiency began to increase steeply soon after the success in producing the high-quality nitrides using the LT-buffer technology, which resulted in p-n junction LEDs. The luminous efficiencies of these LEDs are comparable to those of the AlGaAs- and AlGaInP-based LEDs.

4.2Laser diodes

Similar to the case of the LED, threshold power (Pth) for stimulated emission by optical pumping began to decrease steeply soon after the successes in producing the high-quality nitrides, quantum wells and p-n junctions.

Thus, in late 1995 the onset of stimulated emission by current injection was observed.[10] Today, Several group[11] realize nitride-based laser diodes (LDs). RT CW laser operation has been achieved for nitrides.[12] However, Pth for lasing from nitrides is still higher than those of GaAs-or ZnSe-based LDs. This is mainly due to a high density of states for both conduction band and valence band and high resitivity of p-contact in nitrides.

4.3Electronic devices

Recent progress in crystal growth and conductivity control has also enabled us to realize high-speed FETs[13] and other novel devices.

5. Summary

An accumulation of a lot of outstanding work, in particular, in the area of crystal growth and conductivity control has led to the commercialization of bright blue and green LEDs and to the realization of LDs and FETs based on nitrides. The performances of these devices are still progressing.

Much further improvements of crystalline quality of quantum wells and p-type conductivity as wall as the understanding of intrinsic nature of nitrides will lead to realization of much higher performance devices which are able to operate in harsh environments.

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