

Research on Nitride Semiconductors from the Dawn, through the Present, to the Future

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Abstract

The history of the birth of a blue LED consisted of nitride semiconductors, and the effect in the energy saving by solid state lighting are described. By taking advantage of the characteristics of nitride semiconductors with wide band-gap, the development of the high frequency and the high power transistors are also introduced.

1. Introduction

Since the challenge of the development in Si transistors, the device physics, the technologies of the bulk growth, and the device fabrication process have progressed for more than this 70 years. Integrated circuits (ICs) of Si have realized the present information society. The first light emission from semiconductors was achieved by using SiC [1]. In 1962, reported for the p-n junction red light-emitting-diode (LED) of Ga(As_{1-x}P_x) in 1062 [2] and the green LED of Ga(As_{1-x}P_x) doped N as an isoelectronic trap in 1971 [3] were successively realized. In the development of a blue color LED, II-VI group semiconductors, mainly ZnSe, was closed up instead of SiC. Generally speaking, the conduction-type control in wide band-gap materials is difficult because point defects have to be precisely controlled. After many efforts, a p-n junction diode of ZnSe was fabricated [4], and the first blue laser diode (LD) by ZnCdSe/ZnSe DH structure was fabricated in 1991[5]. For its device lifetime as short as 480 hours, the research on II-VI semiconductors has declined. Nitride semiconductors have become to be earnestly studied. Blue LEDs and LDs have successfully fabricated.

In this paper, the history of the development in LEDs of nitride semiconductors is described. After describing the current status of nitride materials and their applications, Finally, the future prospects of nitride semiconductors are discussed.

2. Development in blue LEDs by nitride semiconductors

The GaN was synthesized in 1932 for the first time [6], however, it was difficult for its high equilibrium vapor pressure of nitrogen because the equilibrium vapor pressure of nitrogen are a several orders of magnitude higher than the equilibrium pressures of As in GaAs and P in InP [7] at their growth temperatures. The gas phase epitaxial growth of a

GaN thin film was also performed on a sapphire substrate for the lack of a GaN substrate in 1969 [9]. The blue emission was obtained from LEDs with MIS-type GaN in 1971 [10]. After this event, the GaN research was focused on the development of the growth technique for high-quality GaN on a sapphire substrate. Differently from the homoepitaxial growth, 13.8% of the lattice-mismatch between GaN and sapphire makes it difficult to grow high-quality GaN. Even the transparent GaN film cannot be obtained for a long time. The first key technology was the growth of GaN through an AlN thin layer by molecular beam epitaxy (MBE) in 1983 [11], because its lattice constant was intermediate between GaN and sapphire, and Al and N of AlN was a component of GaN and sapphire, respectively. By adopting this AlN thin film as a buffer layer, Amano accidentally succeeded in a transparent GaN film with a smooth surface by the metalorganic vapor phase epitaxy (MOVPE) for the first time in 1986 [12], [13]. The epitaxially grown GaN usually shows n-type conduction. Amano *et al.* obtained p-GaN with Mg doping and the electron beam irradiation in 1989 [14]. The mechanism of p-type conduction was explained by Nakamura that the thermal energy generated during irradiation makes hydrogen atoms passivating Mg atoms desorb from Mg atoms in 1992 [15]. This phenomenon is the same as that of the hydrogen passivation of acceptors in Si, which was analyzed in 1983 [16].

To construct a DH structure indispensable for highly efficient LEDs, two more elements in addition of two elements forming compound semiconductors such as GaN are needed because of satisfying two freedoms of controlling the band-gap energy for the band engineering in a DH structure and the lattice-constant for the growth lattice-matching to each layer. Therefore InGaAlN quaternary system was proposed in 1989 because AlN and InN have the same crystal structure of wurtzite as GaN [7]. The relation between the lattice-constant along a-axis and the band-gap energy E_g of InGaAlN is shown in Fig. 1, compared with conventional III-V and II-VI semiconductors. In this figure, the simplest material for a blue emission material in InGaAlN is InGaN because InAlN is thought to have the severe phase separation due to the large difference of atom sizes between Al and In. The growth of InGaN was studied in 1972 [17], however, a single crystal InGaN was not obtained because their procedure followed the common sense for the heterostructure of GaAs and InP, *i.e.*, the constant

growth temperature of 600 °C, the constant flow rate ratio of the group V to the group III (V/III ratio) of 100 to 200,

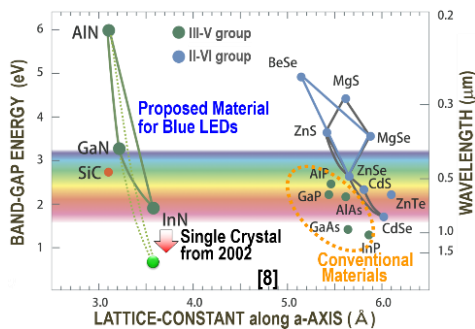


Fig. 1 Lattice-constant along a-axis and band-gap energy [7].

and the usage of hydrogen as a carrier gas through all the growth processes. The growth conditions have to be severely controlled based on the equilibrium vapor pressure of nitrogen in InGaN. Although the ammonia as a nitrogen source makes it more difficult to grow InGaN because of the low dissociation rate of ammonia, this dissociation is suppressed in the hydrogen ambient. To promote the dissociation of ammonia, nitrogen has been adopted as a carrier gas. The growth temperature has been felt down to 800 °C for lowering the equilibrium pressure of nitrogen. The V/III ratio has been raised up to 16,000 for supplying the much quantity of nitrogen. Finally, the growth of a single crystalline InGaN film has become available for the first time [7]. The control of In mole-fraction in InGaN has been realized and the photoluminescence from InGaN grown at 800 °C was successfully observed [18]. These growth conditions have been widely used in the LED mass-production. However, all the composition from GaN to InN cannot be obtained because there is the severe phase separation [19].

The blue LED with a DH was designed in 1992 by Matsuoka [20], fabricated in 1993 by Nakamura [21], and became commercially available in November 1993. The green LED also became commercially available in 1996.

A white LED was invented by Nichia Corporation in 1996 [22]. It has been consisted of a blue LED and yellow phosphor including in the resin. This white LED was sold as reported. The efficacy of white LED commercially available in 2012 reached 180 lm/W which was much higher than that of 15 lm/W and 95 lm/W for incandescent lamps and fluorescent ones, respectively. The efficacy for the research level reached 315 lm/W in 2014 [23]. The penetration rate of white LEDs for lighting was 12% in 2015, and has been forecasted to increase 55 % in 2025 [24]. This means the energy saving is the almost same as the total electric capacity generated in Japan. This energy saving is the reason why the invention of blue LEDs won the Nobel Prize in physics 2014 [25].

The laser diodes (LDs) have been also developed, and a blue LD was reported on the oscillation in 1997. Presently, the optical output power of the 455nm blue LD has been obtained above 4.7 W at the injection current of 3A [26].

3. Current status of nitride semiconductors

The wurtzite nitride semiconductor has a polarity as shown in Fig. 2 [27]. This polarity strongly influences the

crystalline quality in particular In-including materials because the efficiency in the capture of nitrogen atoms. The polarity is also the important factor determining the device characteristics because the polarity and the polarization engages. Presently, the device design considering the polarity has been progressed.

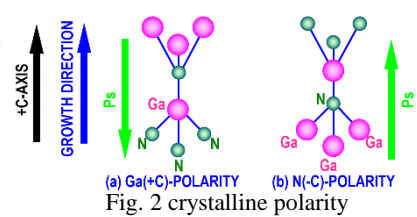


Fig. 2 crystalline polarity

4. Future prospects

Taking the material characteristics of nitride semiconductors, the transistors as well as optical devices have been fabricated. The first field-effect-transistors (FET) of nitride semiconductors was fabricated in 1993 [28]. The high electron mobility transistor (HEMT) has been already used in the base stations of cellular phones. The development of high power and high frequency transistors have been increasingly promoted for realizing the sustainable society.

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