

The Blue Laser Diode

The Complete Story

Second Updated and Extended Edition With 256 Figures and 61 Tables



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2.5 Key Steps in the Discovery 15



Fig. 2.3. For a long time it was thought impossible to obtain p-type GaN. Akasaki et al. demonstrated that p-type GaN can be obtained by electron beam annealing. Nakamura finally elucidated why p-type GaN was never found before: researchers had always used animonia for annealing which dissociates during the thermal annealing, dissociation of animonia yields atomic hydrogen which passivates the acceptors (such passivation is of course highly undesirable for most device production in this case here)

- elucidation of the annealing process, and demonstration of p-type doping without electron beam irradiation by thermal annealing (Nakamura et al., see Fig. 2.3)
- two gas flow MOCVD technique (Nakamura)

As research on the GaN group of materials is now rapidly scaled up at many laboratories throughout the world, it is expected that there will be rapid improvements in material quality, and possibly the development of alternative growth procedures.

2.5.1 Research History of Shuji Nakamura and Selected Steps in the Development of the Commercial Blue GaN LED

- 1971: Pankove (RCA, Princeton) demonstrates blue GaN metal-insulatorsemiconductor LED
- 1974: Pankove and Temple demonstrate cubic GaN

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- March 1979: Nakamura graduates from Tokushima University
- April 1979: Nakamura enters Nichia Chemical Industries
- 1979–1982: Nakamura refines metallic gallium for liquid phase epitaxy applications and develops polycrystalline GaP
- 1981: GaN MIS LED (10 milli-Candela) Akasaki and others at Matsushita (quantum efficiency = 0.12%), first flip-chip type
- 1982-1985: Nakamura develops polycrystalline and single crystal GaAs
- 1985–1988: Nakamura develops crystal growth technology of GaAlAs for red and infra-red light emitting diodes by liquid phase epitaxy

16 2. Background

- 1986: Akasaki grows high quality GaN using a-AlN buffer layers, Mizuta et al. grow cubic GaN
- 1988: Akasaki discovers p-type conducting GaN using low energy electron beam irradiation
- March 1988–March 1989: Nakamura works as visiting research associate at the University of Florida (Professor Ramaswamy's group) to learn MOCVD. Research on MOCVD growth of GaAs on Si
- April 1989: Nakamura begins research towards blue LED
- Sept. 1990: Nakamura develops new 'two-flow' MOCVD equipment for growth of high quality single crystal GaN layers
- Feb. 1991: Nakamura grows high quality p-type GaN
- 6 May 1991: Nakamura secretly publishes his first scientific article [Appl. Phys. Lett. Vol. 58, (1991) p. 1021] on his MOCVD equipment
- March 1991: Nakamura fabricates GaN pn-junction light emitting diode, confirms light emission
- June 1991: 3M reports ZnSe-CdZnSe based blue semiconductor laser
- 1992: Akasaki demonstrates GaN based blue pn-junction LED (light output: 1.5 mW at room temperature, quantum efficiency: 1.5%)
- Feb. 1992: Nakamura begins to grow InGaN single crystal layers for the production of double heterostructures
- June 1992: Nakamura successfully grows InGaN single crystal layers
- Sept. 1992: Nakamura fabricates InGaN double heterojunction light emitting diode
- Dec. 1992: Nakamura succeeds in fabrication of InGaN double heterojunction light emitting diode with high light output
- Nov. 1993: Nakamura demonstrates 1 candela InGaN blue light emitting diode product
- Nov. 1993: Nichia announces commercial blue InGaN LEDs
- -May 1994: Nakamura demonstrates 2 candela InGaN blue green light emitting diode product
- from 1994: Nichia employs 100 people in the commercial production of blue LEDs
- Sept. 1995: Nichia announces commercial green InGaN based LEDs
- -Jan. 1996: Nakamura reports pulsed blue InGaN injection laser at room temperature
- 1996: Nichia sells several million blue indium gallium nitride LEDs per month
- Nov. 1996: Nakamura announces the first CW (continuous wave) blue gallium nitride based injection laser at room temperature
- 1991–1999: Nakamura improves laser lifetime through improved layer design and growth (ELOG)
- 1999: Nichia announces sample shipment of violet InGaN laser diodes
- 1999: Nichia announces commercial violet InGaN laser diodes

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