ATIP-Seminar 2 August 1995

Blue light emitters for displays, data storage, and traffic signals— Recent breakthroughs by Nichia Chemical Industries Ltd., background and implications

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Blue Light Emitters—'Executive Summary'

- Blue (450nm) and blue/green Light Emitting Diodes have been developed by Nichia Chemical Industries (Anan, Tokushima-ken) using InGaN/AlGaN

- Nichia's LED's are about 100 times brighter than previous blue SiC LED's (indirect bandgap!). Competing II-VI devices are bright but have short lifetime.

- Nichia's blue LED's are in commercial service now at large outdoor display screens (e.g. Hachiko-Shibuya). Nichia ships 1 ...2 Million per month. LED's will most likely replace all traffic lights: energy saving 50% to 75%, replacement every 5-10 years instead of once per year. Present half-lifetime: 60 000 hours (7 years)

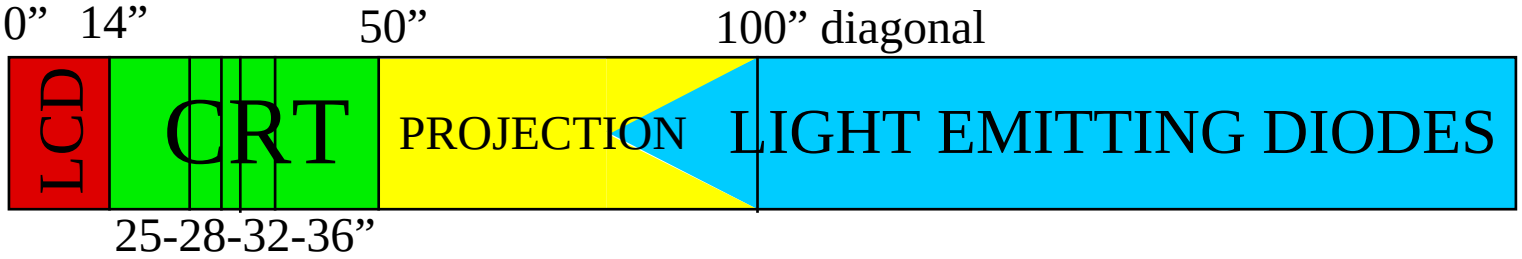
- Other applications: Color Scanners (FAX, Color Copier, Full Color Scanner), data storage, large TV displays, Traffic lights, Displays, Room Lighting ...

- Nichia Chemical Industries: Turn-over: $ 222 Million, 750 Employees (30 in R&D), Privately held Share-Company (23% Directors, 27% Employees, 50% Others), Products: Speciality Chemicals, Ceramics, 25% of World market in phosphor coating for TV-screens, and for fluorescent light tubes

- Future: Gallium-Nitride based laser diodes are expected soon

Applications and Markets for blue LED's

- Full Color TV displays (Display at Hachiko/Shibuya uses 300 000 blue LED's) and smaller indoor full color displays (e.g. Narita Express train, subways etc.)



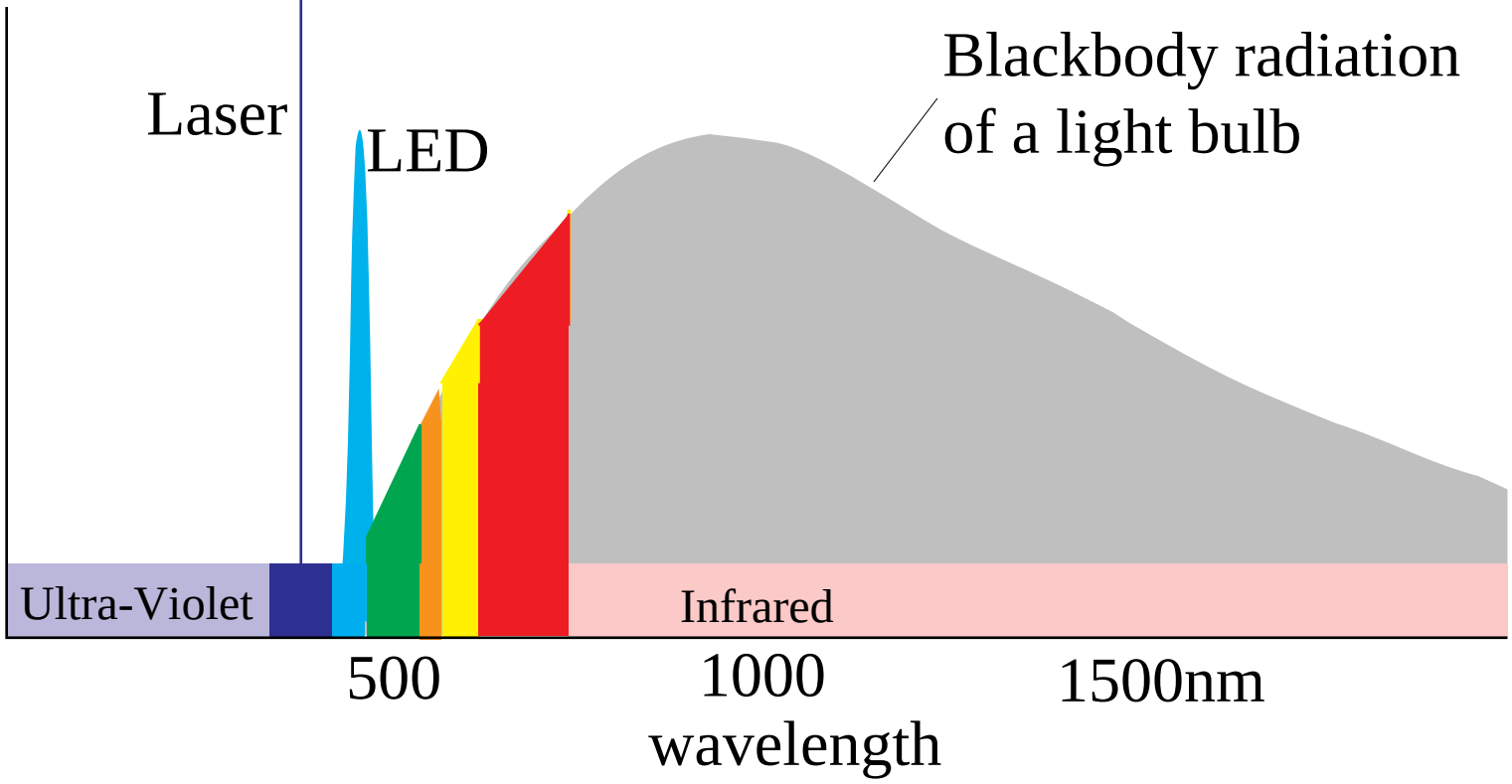
- Full color scanners (FAX, computer printers, copy machines, ...)
- traffic signals (testing under way, total consumption in Japan: $\sim$ Gigawatts):

light bulbs + color filter	**LED's** , better visibility (no color filter)
70 W each	red: 18 W; yellow: 20 W; blue-green: 35 W
Replacement: 1$\times$/year	1$\times$/5 - 10 years (?)
catastrophic failure	gradual decrease (halflife: 60 000 hours = 6.8 yrs)

- Data storage (magneto-optic, and CD)
- room lighting (?)—price question

Light Spectrum of an LED, a light bulb and a laser

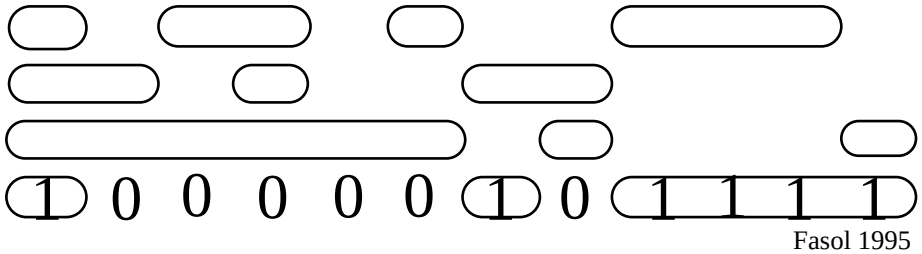
- LED: light is emitted by the transition of electrons between energy levels
- light bulb: tungsten filament at $\sim$ 3000 C emits 'black body' radiation



Blue lasers for optical storage (magneto-optical and CD)

diffraction limits the size of a focussed laser beam to a spot of the order of the wavelength of the light used, therefore the wavelength limits the density of data storage

Schematic of information storage on CD-ROM and magneto-optical disc



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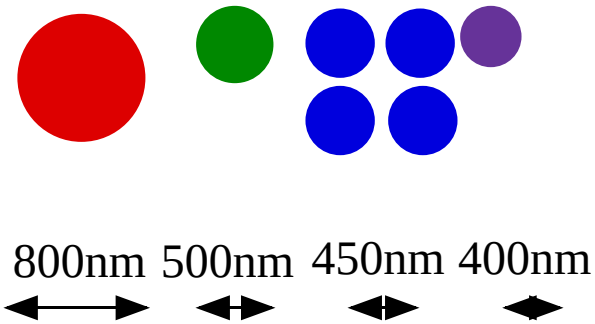
Diffraction spots of
red, green, blue and violet lasers



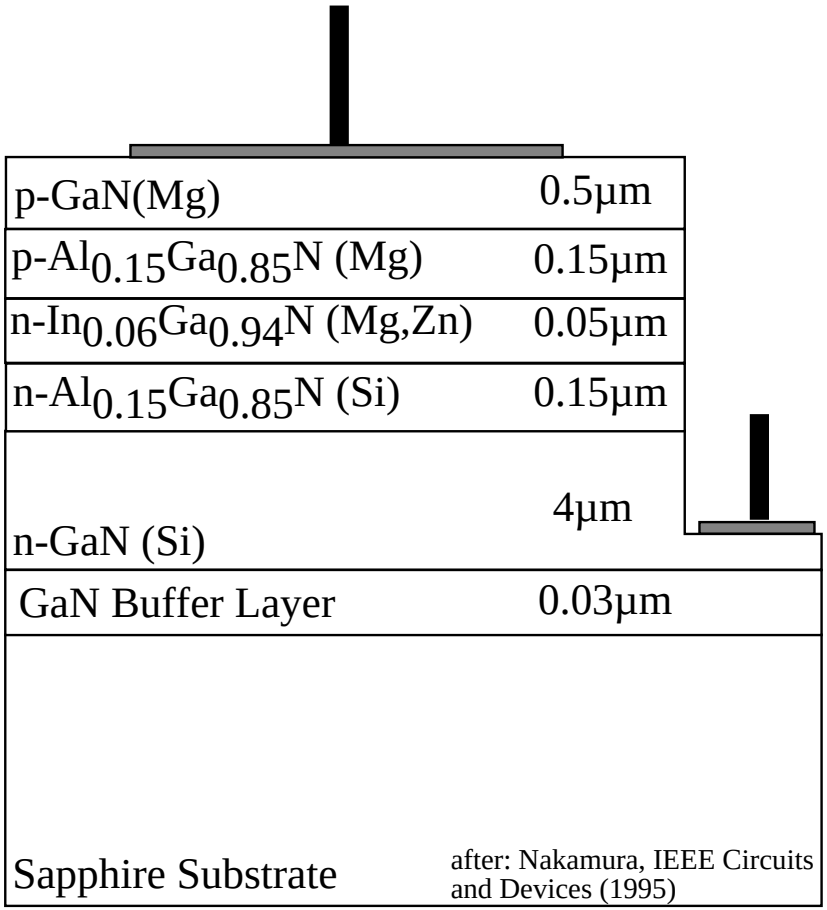
In principle an optical nearfield microprobe allows much higher density of optical storage, however access is VERY slow using current knowledge

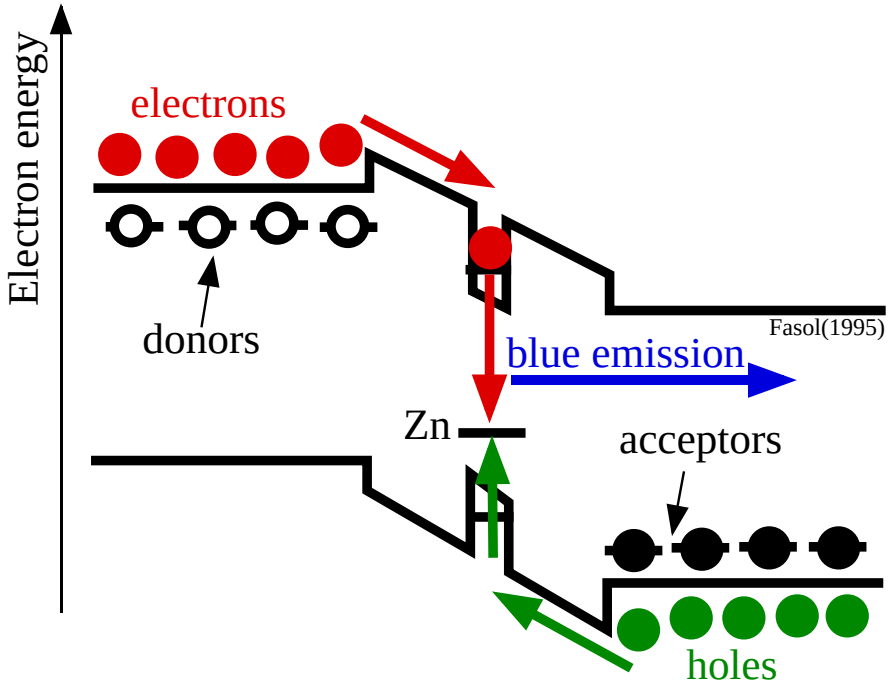
Who are today's key players?—Partial Listing of US-Patents issued 1994/1995

filed	issued	title	assignee
1991	1993	...diodes from GaN	Cree Research, Inc.
1992	1994	LED using GaN group ...	Toyoda/Toyota/Nagoya Univ./JRDC
1991	1994	LED using GaN group	Toyoda/Nagoya Univ./JRDC
1991	1994	Optical semicond. device ...	Toshiba
1992	1994	Crystal growth method ...	Nichia
1992	1994	Method of manufacturing ...	Nichia
1992	1994	AlGaN laser	Khan; Muhammad A. (APA Optics)
1991	1994	Method of vapor-growing ...	Nichia
1992	1994	GaN-based ...LED...	Toyoda/Toyota
1993	1995	TM-polarized laser ...	Xerox Corporation
1993	1995	...insulating GaN thin films	Trustees of Boston University
1992	1995	Light emitting diode	Sharp
1993	1995	Method of fabricating ...	Amano/Akasaki/Pioneer/Toyoda
1993	1995	Buffer ...SiC and GaN ...	Cree Research, Inc.
1993	1995	LED of GaN compounds	Toyoda/Toyota
1993	1995	Blue light-emitting diode ...	Cree Research, Inc.
1994	1995	...LED (GaN on SiC)	Toshiba
1994	1995	Method of depositing ...	Nichia

Oyo-Butsuri-Gakkai (Spring 1995): 51 papers on Gallium-Nitride compounds

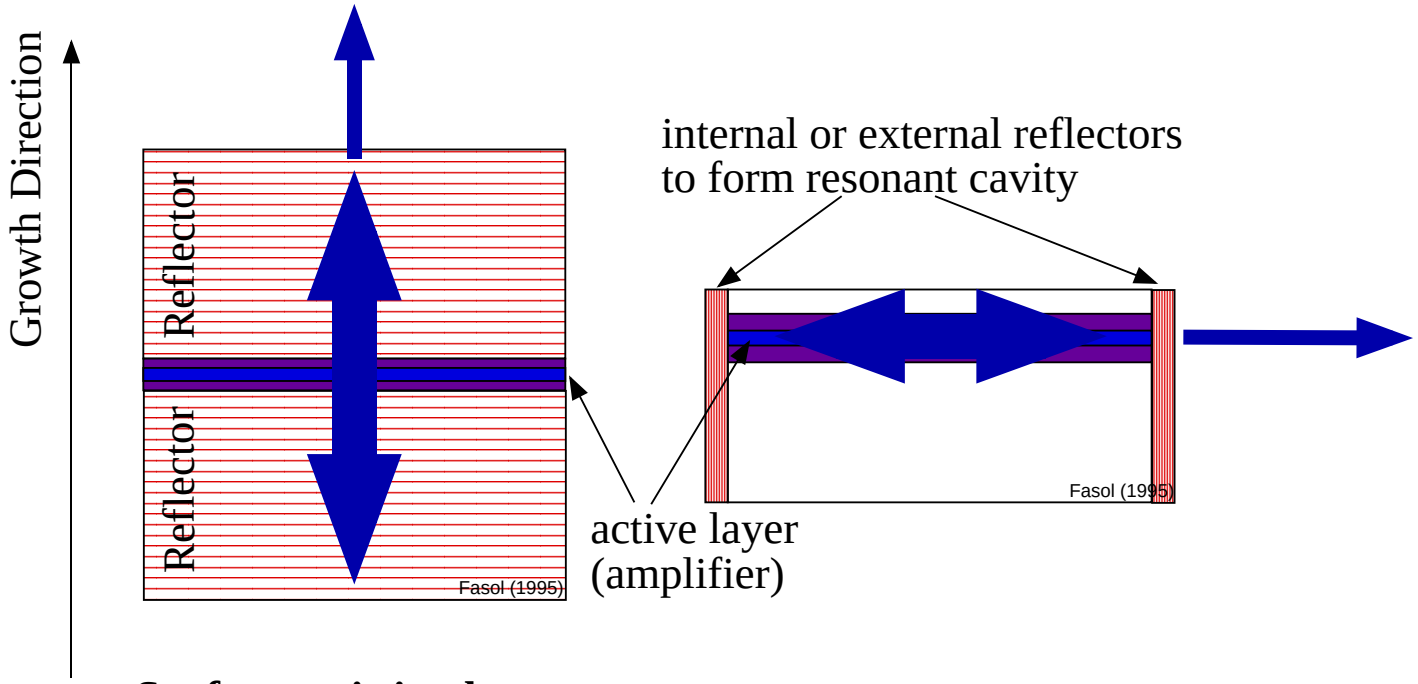
What is a blue Light Emitting Diode (LED)?





What are blue lasers? The race is on ...

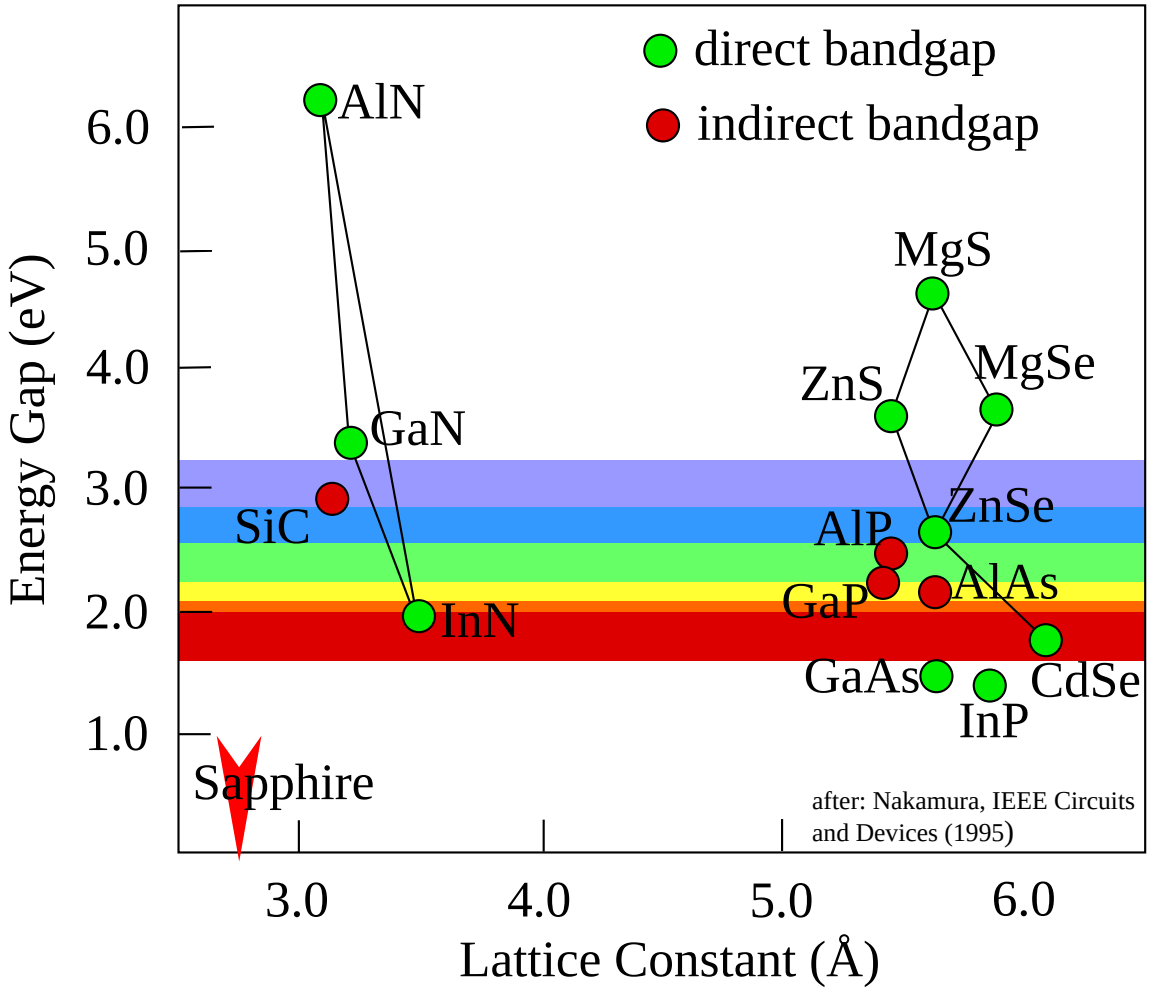
Laser = Light Amplifier + Resonant Cavity



Surface emitting laser
(can be densily packed in a matrix)

conventional semiconductor laser

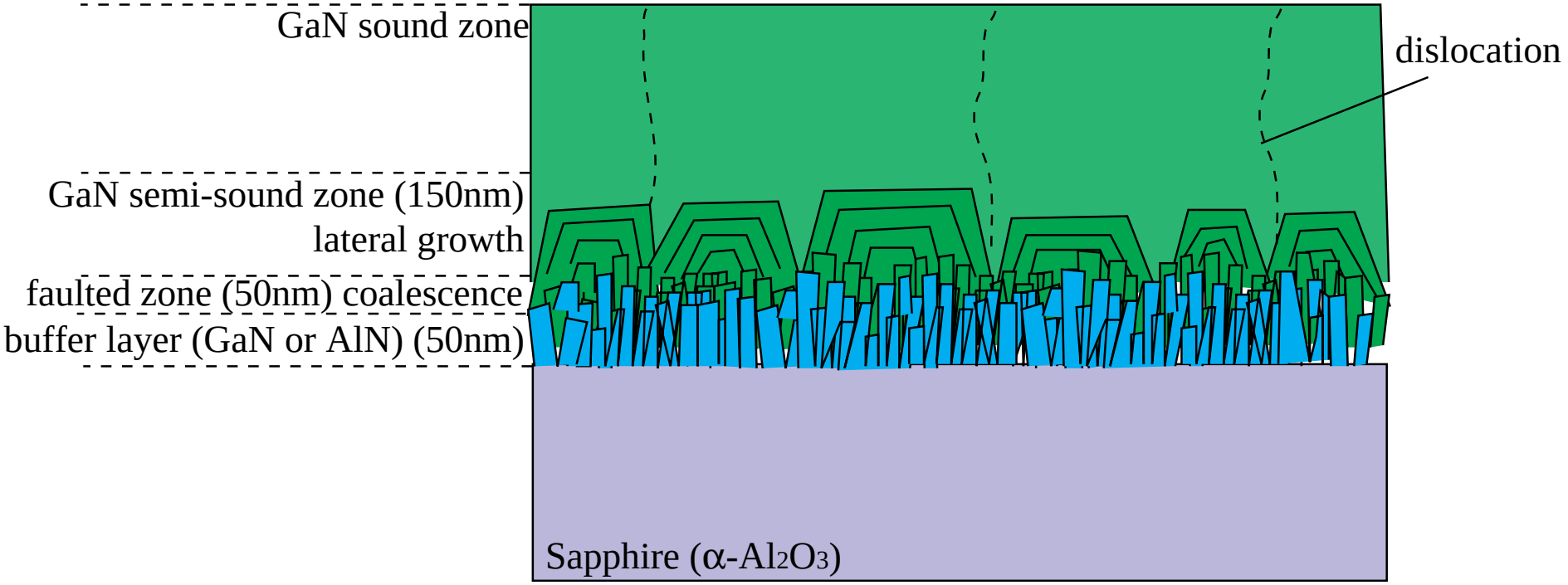
Why AlGaN/InGaN material?



Key Steps in the Discovery: Materials Issues

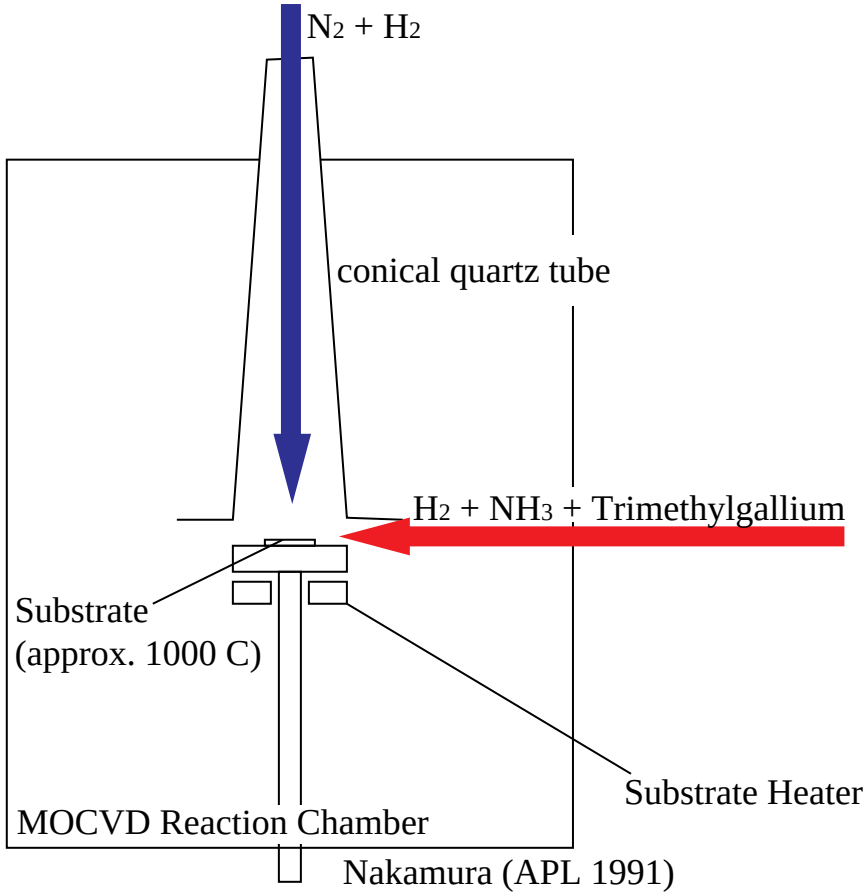
- Substrate is needed: choice of SiC (good lattice matching, very expensive) or Sapphire
- Sapphire: 15% difference in lattice constants, very large difference in thermal expansion $\rightarrow$ Solution: AlN (Akasaki), GaN (Nakamura) Buffer layer
- High Growth Temperature, thermal convection inhibits growth $\rightarrow$ two flow MOCVD
- p-Doping was impossible; solution: $\rightarrow$ E-beam annealing (Akasaki), thermal annealing in N_2 gas (previously Ammonia was used for annealing, Nakamura showed that Ammonia dissociates into N_2 and H_2 at the temperature used, and H makes the acceptors inactive)
- impurity doping (Zn) to obtain right emission wavelength (Pankove)
- Nakamura's work at Nichia could use many results previously obtained by Akasaki (Nagoya), Pankove (RCA), Khan (Honeywell, APA Optics)

- Problem: large lattice mismatch between Sapphire and GaN/AlN
- Solution: AlN Buffer layer (Akasaki, USP. 4855249, Appl. Phys. Lett.)
- Solution: $Ga_xAl_{1-x}N$ Buffer layer (Nakamura, USP. 5290393, J. J. Appl. Phys.)

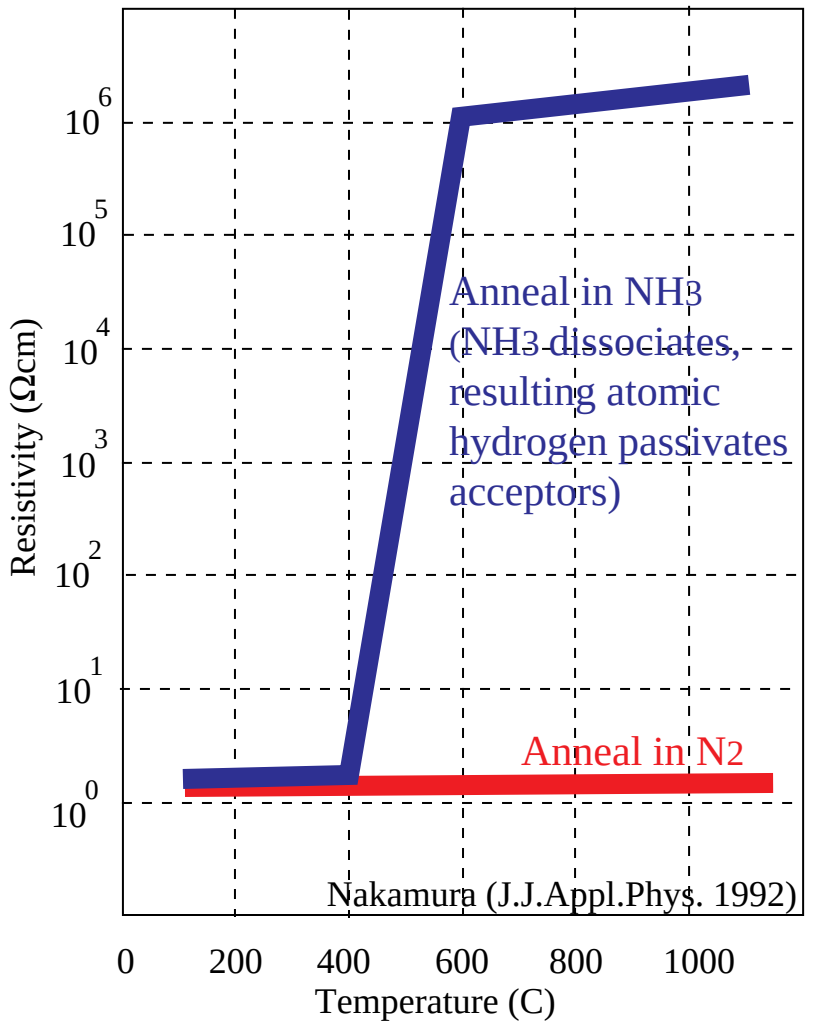


after: Akasaki (APL, 1986)

- Problem: thermal convection (substrate temperature $\sim 1000C$), poor flow
- Solution: Two-Flow MOCVD (Metal Organic Vapor Phase Epitaxy) [Nakamura, Appl. Phys. Lett. (1991), US Pat. 5334277]



- Problem: Pankove (1971, RCA) reported metal-insulator-semiconductor-LED, but p-type doping found impossible
- Solution: Akasaki (1988, Nagoya Univ.) Low Energy Electron Beam Irradiation (LEEBI)
- Solution: Nakamura (1992, Nichia, and US-Patent 5306662) found that during thermal annealing in ammonia (NH_3) athmosphere,(NH_3) dissociates above 400C, and the resulting atomic hydrogen passivates acceptors. $\rightarrow$ anneal in N_2



Why did Nichia succeed where many MUCH larger multinationals failed?

- Quick Answer: Other labs all looked at II-VI compounds (ZnSe/ZnS)—and had given up Gallium-Nitrides as hopeless. Disadvantages of II-VI's: low growth temperature, low stability. Except: Professor Akasaki (Meijo-Univ., Nagoya) continued systematic work

- Nichia's Chairman (N. Ogawa) gave Dr. Nakamura + 2 Assistants 3 Oku Yen ($ 3.3 Million, i.e. 1.5% of annual sales) to 'gamble' on Gallium Nitride + Nakamura one year in Florida (with Prof. Ramaswamy) to learn MOCVD.

- large companies tend to avoid risks and tend to take a more conservative approach to research—even in fundamental research ('jumping on the band-wagon phenomenon')

- large companies and research institutes tend to spend less research budget per research personnel on average, e.g. companies like NTT or AT&T spend of the order of $ 150 000 to $ 400 000 per researcher per year on average.

Nichia Chemical Industries, Anan, Tokushima-ken
Chairman: Nobuo Ogawa, President: E. Ogawa

- Chairman Nobuo Ogawa founded his first company 1948 and *after the expenditure of great personal effort and endurance of significant personal hardship ... the first steps have been taken toward the founding of a modern manufacturing company.* Nichia Chemical Industries Ltd. was established 1956 to fabricate calcium phosphate for fluorescent lamp phosphors.

- Private Stock-Company: Directors 23%, Employees 27%, Others 50%.

- Sales:

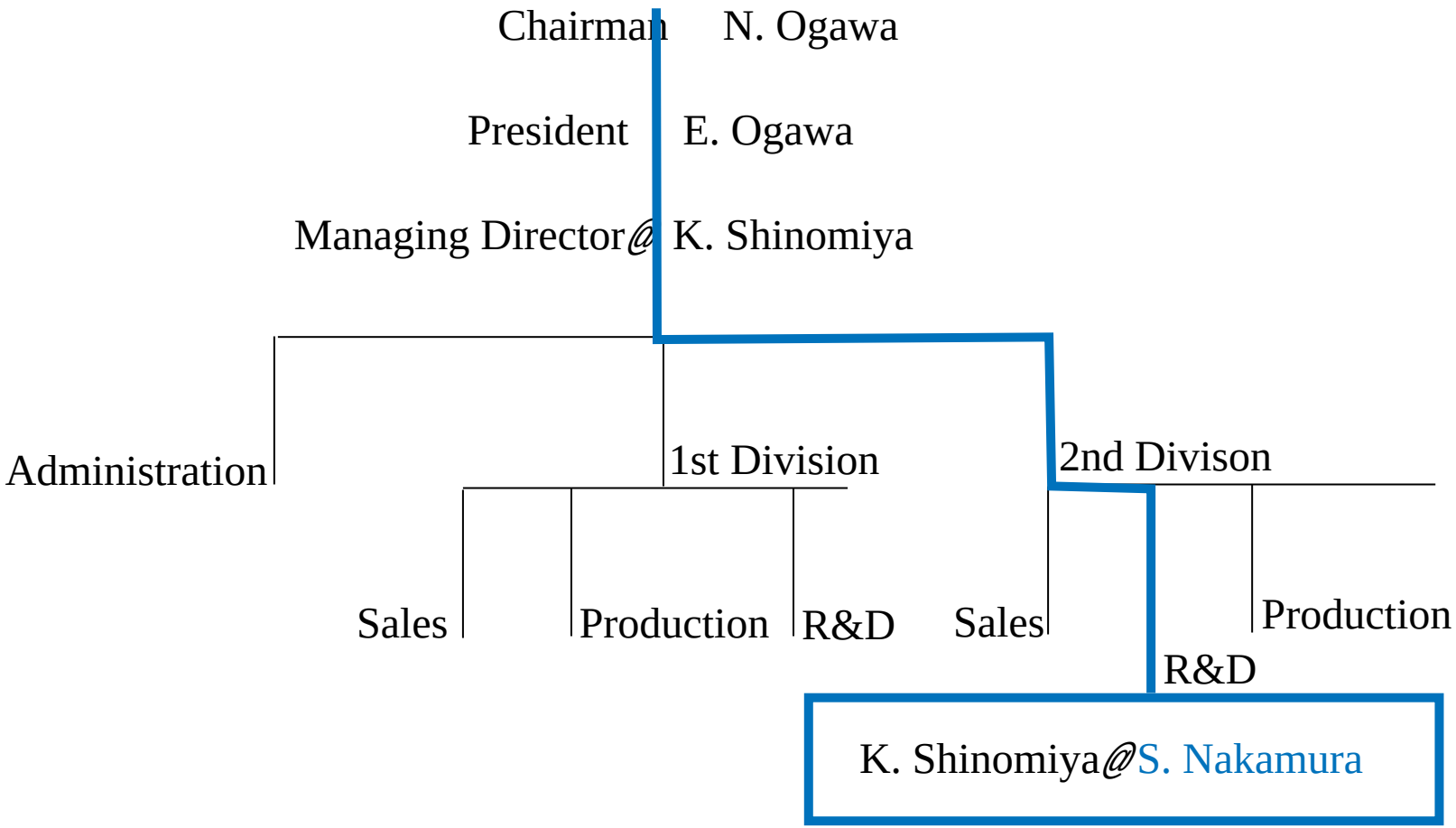
1983	7 Billion Yen	230 Employees
1994	19 Billion Yen ($ 210 Million)	750 Employees (30 in R&D)

- Products: Phosphors (50% of Market in Japan, 25% of intl. market) for TV-screens, for fluorescent lamps, and for X-ray screens, Speciality Chemicals (Electronic materials, catalysts, fine ceramics, optical films, high purity metals (Ga, In), compound semiconductors (GaAs, InP), epitaxial wafers, blue LED).

- R&D Results: 300 patents

- *'Chairman does not want to licence Gallium-Nitride technology, but provide work for the people of Anan'*

Nichia's Organization Diagram→ quick decisions



Slogan of the Nichia - Group

- Let's study
- Let's think hard and work hard
- And let's make the world's best products

From Nichia Chemical Industries Ltd.'s 'Company Profile':

At the beginning

Having 'Ever Researching for a Brighter World' as our motto, Nichia has grown in the field of manufacturing and sales of fine chemicals, particularly inorganic luminescent materials (phosphors).

While further strengthening Nichia's leading edge technologies through active research and development efforts, we hope to maintain our contribution to the world by supplying high quality chemical products which reflect the consequence of strenuous efforts.

Some more comments on the blue LED story.

- The higher the expected reward, the higher the risk in fundamental research
- Note that Dr. Nakamura worked for over 10 years with no commercial reward for the company (and low salary for himself)
- To quote Mr. Klaus Diehl (Chairman of Merck-Japan): In the past large size was an advantage for a company—in the future it will be the speed
- Note that much of the recent publications and conference contributions on blue Gallium-Nitride LED's are in Japanese language. As Japan and South-Korea step up fundamental research, increasingly, European and US companies will need R&D presence in Japan and South-Korea in order not to be caught by surprise as in the case of the blue GaN LED's. Even to catch up now, reading the Japanese papers, conference contributions, and patents will be necessary.

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