

GaN and the 2014 Nobel Prize in physics

'LED bulbs India.' If this were the string you were to insert in any search engine and look at the image component, something like Figure 1 would pop up. I wish there was an easy way to do a search in time. If that was possible, then a similar string in the year 2004 would have yielded the response 'No results containing your search items were found'. A 1989 search for commercial light emitting diodes (LEDs) alone would have yielded only red and green LEDs, but not blue and hence not white. One needs red, green and blue to make white light.

If, Figure 1, were not enough, a walk to the local retail outlet would drive home the point. Jostling for space next to the compact fluorescence lamps (CFLs), one would now see LED bulbs promising twice as many lumens per watt (lm/W), with 5000 h of operational lifetime and at 30 times the cost of an equivalent bulb. Well, if you think this is expensive, think again. The first red LED sold by General Electric in 1962 (Figure 2), cost an astronomical US\$ 262. At today's price, this single, inefficient – by today's standards – device, capable of emitting only red light, would have cost you about US\$ 3300 or Rs 2 lakhs, more than the cost of a Tata Nano.

We have come a long way from this first LED, to the white bulbs of today. The packaged white LED market size by revenue is more than US\$ 10 billion today. While there were many who contributed to this development, including Nick Holnyak Jr, the inventor of the red LED¹, the work reported^{2,3} by Akasaki, Amano and Nakamura between 1986 and 1997 could be considered to be the key body of research that can be associated with 'the invention of efficient blue

light-emitting diodes which has enabled bright and energy-saving white light sources' and hence the criterion according to Nobel's will, for '...prizes to those...who have conferred the greatest benefit to mankind' for the Nobel Prize.

It must be remembered that while the Nobel Prize was given for LEDs, that research also laid the foundation for a whole host of gallium nitride (GaN) technologies from blue lasers and hence the blue ray information storage system, to GaN-based high-power and high-speed electronics⁴.

The question would be, 'What is so great about enabling GaN-based LEDs' or for that matter any 'GaN technology?'. There were two problems which we shall call 'the growth challenge' and 'the P-type doping' challenge.

The growth challenge

To begin with it was essentially a crystal growth problem. Si and GaAs, the other two common semiconductor technologies, have been established on bulk Si and GaAs single crystal wafers. This is because one can grow bulk solid Si and GaAs crystals from the melt, using a technique that is not any different, thermodynamically speaking, from growing ice or solid water from the liquid form in a refrigerator. The problem with GaN and the other less known but equally important counterparts like AlN and InN is that if heated they decompose to give the metal and N₂ gas before melting. As shown in Figure 3 (ref. 5), at 1400 K, a typical growth temperature required, N₂ pressure of about 10⁸ Pa or 1000 atm is required to prevent the decomposition of

GaN. Reactors that reach such large pressures are called 'bombs' and while capable of producing tiny crystals for scientific purposes, are not conducive to enabling large-scale commercial technology. Thus, unlike Si and GaAs, GaN melts are not easily made and therefore large GaN crystals cannot be easily grown. Thus, III (Al, In and Ga)-nitride films for device purposes had to be grown on substrates that were not III-nitrides or by a method commonly referred to as heteroepitaxy.

For various reasons including stability at growth temperatures and a symmetry similar to that of the III-nitride crystal structure on the surface, sapphire or aluminum oxide was the substrate that came closest to being used. It is still used today for growing LEDs. In spite of being the 'best' substrate, the interatomic distances in sapphire are different from those of the III-nitrides. To illustrate the problem, the lattice parameter mismatch between sapphire and GaN is 15%. Crystal growth textbooks and crystal growers even today would deem growth of GaN on sapphire impossible as a 1%



Figure 2. The first LED from GE. Source: lamptech.co.uk.



Figure 1. Source: Google Search.

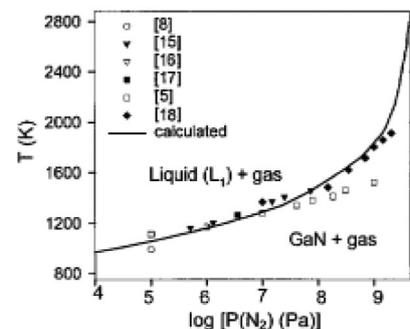


Figure 3. The GaN/GaN equilibrium. (With permission from Davydov *et al.*⁵.)

mismatch translates to a stress of 4 GPa. Mild steel, the heart of RCC (reinforced cement concrete) structures that hold our buildings together, bends at 0.25 GPa. Thus, if one tried to grow GaN on sapphire, crystalline chunks instead of smooth films would be obtained (Figure 4). This is akin to a thin layer of oil on water tending to break up into droplets due to large interfacial energy.

Amano and co-workers^{6,7} used a two-step technique to grow smooth GaN layers (Figure 5), of a particular orientation without stressing them. The two steps involved were a low temperature (<600°C) AlN layer and a high temperature (>1000°C) GaN epilayer. Annealing of the low-temperature AlN layer helps provide stress-free and oriented crystalline seeds for growth of the high-temperature GaN epilayer. Yet, these layers, called textured films, are defective single crystals that contain a dislocation density of $>10^9/\text{cm}^2$. At such defect densities GaAs-based red LEDs would never be expected to perform. In GaN

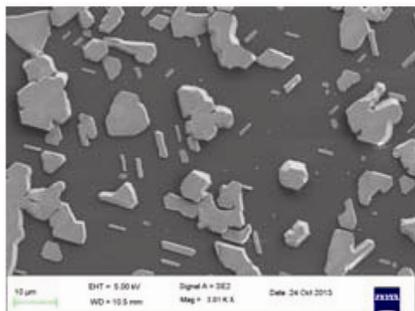


Figure 4. Trying to grow GaN directly on sapphire is like trying to spread oil on water. Instead of smooth films required for devices, crystal chunks are obtained. (Image courtesy: Krishna Srivatsa, Ph D student, IISc, Bangalore).



Figure 5. Smooth featureless films obtained by the two-step growth method of Amano and co-workers^{6,7}. (Image courtesy: Krishna Srivatsa, Ph D student, IISc.)

LEDs, the light-emitting active layer is actually InGaN containing about 10% InN. It has now been shown that hole localization at InN inhomogeneities in InGaN prevents their loss to the dislocations which are non-radiative recombination centres⁸. Radiative recombination at these centres results in high internal quantum efficiencies approaching 80% and in turn efficient blue emission.

On the growth front, Nakamura himself used the two-step growth technique developed by Amano and co-workers^{6,7}. He however made two changes. One, he used GaN low-temperature layers instead of AlN layers. According to him⁹, this resulted in better quality GaN epilayers which then yielded the highest Hall mobilities of $3000 \text{ cm}^2/\text{V}\cdot\text{sec}$ at 70 K then. Two, he developed a ‘two-flow’ reactor (Figure 6)¹⁰ that helped grow smoother layers⁹. The design of a GaN reactor is a challenging process as the precursors used are highly reactive in the gas phase. Various designs currently exist that separate the N-precursor (NH_3) from the Ga precursor ($(\text{CH}_3)_3\text{Ga}$) and allow them to intermix just above the growth surface. LEDs are heterostructures made up of very thin layers, some as thin as 10 nm or lower and separated by abrupt junctions. It is hence essential that this intermixing is uniform over the entire growth surface that can extend from 4 to 8 inches in diameter for high device yield. Without high device yield one cannot buy a LED bulb in the local retail store. Imagine growing a uniform 10 nm thin layer by mixing two ingredients over a $1 \times 10^8 \text{ nm}$ diameter circle. That is what LED technology demands. While Nakamura’s ‘two-flow’ reactor may not be the most commonly used reactor today, it appears from his papers

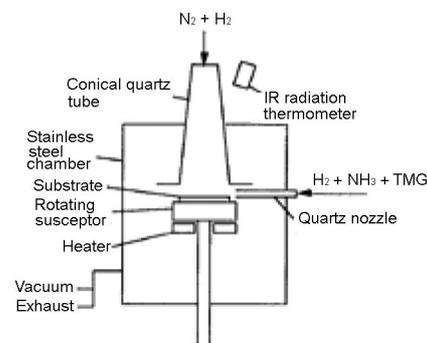


Figure 6. The two-flow reactor. (With permission from Nakamura *et al.*¹⁰.)

that it was critical to helping him grow the layers using which he demonstrated LEDs and laser diodes⁹. Given the difficulties in growing GaN even in today’s modern reactors, it must have been a challenging task in 1991.

The P-type doping challenge

In principle, a LED is a p–n junction (Figure 7), like a solar cell. In a solar cell, light that is incident generates electron–hole pairs which are then harvested to generate a photo-voltage. This voltage in turn helps drive a current through an external load such as a light bulb. In a LED, the reverse happens. Forward biasing the p–n junction injects electrons and holes into an active device region where they combine. Such recombination yields light photons whose energy is equal to the difference in energy between the electrons and holes. This is equal to the band gap of the material, which in the case of GaN, or more accurately $\text{In}_{10}\text{Ga}_{90}\text{N}$, has a value that results in blue light of wavelength from about 450 to 495 nm.

The first blue light emission, for which GaN is famous, was actually reported in SiC as early as 1923 (ref. 11). While SiC has the right bandgap, it is indirect and hence results in LEDs that are inefficient in that <1% of the electrical power injected is converted into light. The earliest reported work on making GaN LEDs can be traced back to the laboratories of the Radio Company of America (RCA), where Maruska and Tietjen¹² showed that GaN has a direct bandgap of 3.41 eV. Back then, at RCA, red and green LEDs based on Ga–As–P–N had been realized and Tietjen was looking for GaN to enable the blue component and hence LED-TVs. GaN layers were deposited on sapphire. They were found to be

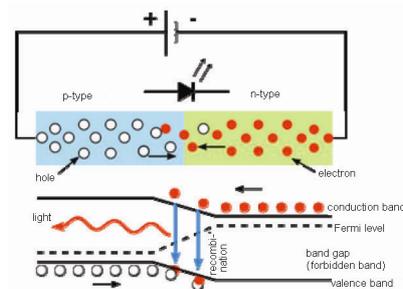


Figure 7. A light emitting diode (source: Wikipedia).

inherently n-type, which is now well known to be due to vacancies in the nitrogen lattice. The search had begun to make it p-type and Zn, from previous Ga-As experience, was the first choice for a p-type dopant. However, Zn-doped GaN resulted in fairly insulating layers and did not display any p-type conduction. In spite of this setback, weak blue light emission at 475 nm was demonstrated by Pankove *et al.*¹³, also from RCA, in 1971, from insulating Zn-doped GaN. By switching over to Mg as a p-type dopant, Maruska *et al.*¹⁴ then proceeded to demonstrate blue to violet emission in the early 1970s. However, these early blue LEDs were inefficient because in spite of doping with Mg, the hole concentrations remained at fairly low levels. For the technically minded, Mg introduces acceptor levels at about 240 meV and Zn at about 360 meV above the valence band edge of GaN. Interest in GaN had faded and the world was focusing on II-VI compounds such as ZnS and ZnSe for efficient blue emission, except for Akasaki and Amano. For those working on GaN, it must have been a lonely world.

Following their success in fabricating smooth layers of GaN, Amano and Akasaki doped GaN layers with Mg and observed that on irradiating the layers with a low-energy electron beam (LEEB irradiation; LEEBI) (<5 kV), they obtained hole concentrations of $10^{17}/\text{cm}^3$ and resistivity of 12 $\Omega\text{-cm}$, the lowest reported till then in 1989–90 (ref. 15). While LEEBI, as it was called, indicated that some activation of Mg was required, it was limited to the penetration depth of the beam and therefore suitable for only converting about 250 nm from the surface to p-type. Using such p-type layers and ‘better’ quality GaN epilayers deposited using the GaN low-temperature nucleation layers, the second GaN p–n junction blue light diodes emitting at 430 nm with an external quantum efficiency (EQE) of 0.18% were demonstrated by Nakamura *et al.*¹⁶ in 1991. EQE is the number of photons emitted to the number of electron–hole pairs injected. Amano and Akasaki had demonstrated blue emission from such LEEBI p–n junctions as well and were thus the first to demonstrate a blue LED.

The next major breakthrough came from Nakamura and it can be considered as the final piece of work that was awarded the Nobel Prize. Nakamura *et*

*al.*¹⁷ found that annealing Mg-doped GaN above 600°C in a N_2 atmosphere yielded hole concentrations in excess of 3×10^{17} – $10^{18}/\text{cm}^3$ and a resistivity of <2 $\Omega\text{-cm}$. It was observed that when the layers were annealed at lower temperatures, the resistivities were six orders of magnitude higher. It was also found that when the layers were annealed in NH_3 , the higher temperatures did not help. These experiments led to the conclusion that the formation of H–Mg complexes prevents activation of the dopant. On annealing in N_2 above 600°C sufficient thermal energy is provided to break these complexes and release H_2 . However, NH_3 itself breaks above 600°C to release H, which prevents complex dissociation.

The final icing...InGaN double heterostructure LEDs

Now that the problems related to growth and p-type doping of GaN had been solved, LED progress was rapid. From the first LED with an EQE of 0.18% demonstrated in 1991, Nakamura increased the EQE to 2.7% through a series of steps that culminated in the first

‘candela class’ LEDs (Figure 8) which were also the first to be commercialized⁹. The EQE in a modern-day blue LED exceeds 50%. A key development that enabled this rapid progress to commercialization was the use of a double heterostructure containing GaN/InGaN/GaN, rather than AlGaIn/GaN/AlGaIn.

The ‘double’ in the double heterostructure stands for the two junctions involved in such a structure. Thus, in GaN/InGaN/GaN structures two GaN/InGaN hetero-interfaces are involved. In such double heterostructures, a small bandgap material, typically intrinsic, is sandwiched between two larger bandgap materials called cladding layers. One of them is p-doped and the other is n-doped. When such a structure is forward-biased p- and n-type carriers are injected into the central smaller bandgap intrinsic layer and confined there by the larger bandgap cladding layers. They combine in this central active layer and yield photons, whose energy being lower results in their passing through the larger bandgap cladding layers as they cannot be absorbed there.

If GaN growth is difficult, InN and InGaN growth is even more difficult. Growing both GaN and InGaN alloys on the same substrate is even more difficult. This is so because AlN and GaN grow well in hydrogen at >1000°C. InN prefers nitrogen at <600°C. Thus, growing InN and GaN or an alloy on the same substrate is a challenge. Hence, most researchers prefer AlGaIn/GaN/AlGaIn heterostructures for LED applications. Nakamura, on the other hand, started working on double heterostructures containing InGaIn as the active low bandgap layer rather than GaN and soon showed that they are much more efficient at light emission. The first blue LED was commercialized on an InGaIn-containing heterostructure¹⁸. Later work, as explained earlier, showed this to be due to carrier localization in InGaIn that prevents non-radiative recombination as it does in GaN⁸.

In summary, LEDs have come a long way from 0.1 lm/W to current devices that generate more than 100 lm/W. As of 23 March 2014, a 303 lm/W LED was announced by Cree Inc, USA. In comparison, Edison’s venerable incandescent lamp generates 15 lm/W and the tube light about 100 lm/W. Truly, the LED made possible by Amano, Akasaki and Nakamura is here to stay... provided of

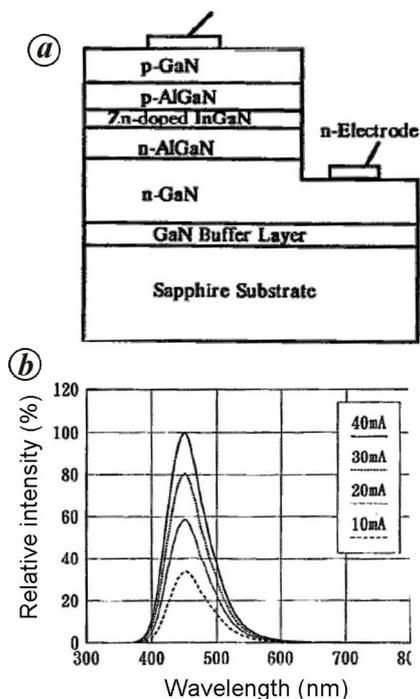


Figure 8. *a*, Nakamura’s first candela class LED that eventually led to commercialization. *b*, Electroluminescence from Nakamura’s first candela class LEDs. (With permission from Nakamura *et al.*¹⁸.)

course the world does not run out of indium. That, however, is a story for another day.

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Field training in glaciology: a way to touch, feel and understand

Glaciers and ice sheets cover approximately 10% of the Earth's surface, out of which 3% is in Asia (IAHS (ICSI)/UNEP/UNESCO 1989). A study of mountain glaciers of the Himalaya has serious implications to understanding climate change and the future of water resources in India. Glaciologists have developed sophisticated techniques to monitor our glaciers. Although there are 9575 glaciers in the Indian part of the Himalaya, only a few have been monitored on a long-term basis. The monitoring is distributed variably and controlled by altitude, orientation and differential precipitation patterns of the Indian summer monsoon and western disturbances¹. Many questions remain about the current status and future impact of these glaciers. Work in extreme climate and high-altitude conditions requires training. Very few organizations in India are conducting training programmes on glacial studies. The Geological Survey of India (GSI) is one of them. GSI initiated snow, ice and glacier studies in 1974, by establishing the Glaciology Division. Since then it has been monitoring the Indian Himalayan glaciers using state-of-the-art techniques¹. During the last few decades, technological advancements have changed the methods of observation and modern high-speed computers and satellite-based approaches are being used for monitoring the glaciers in real time. From time to

time, the Glaciology Division of the GSI has been developing and implementing new concepts and theories intended to develop expertise in the field of glaciology. GSI has been conducting a field training course in glaciology since 1993; till date seven courses have been successfully conducted and 95 students, research scholars and scientists have been trained. In continuation of this series, the 8th training course (4 August–7 September 2014) funded by DST, New Delhi was designed to educate the trainees in various facets of glaciological studies, both theory and practice. An overwhelming response was received and 19 trainees from different universities, academic and research institutions and faculty members of the GSI, participated in the course.

The course was inaugurated on 5 September 2014 by V. K. Raina (formerly at GSI), Deepak Srivastava (formerly at GSI), Subodh Kumar Sharma (Northern Region, GSI), Jogindar Singh (GSI, Chandigarh), Ashwagosh Ganju (SASE), Alok Chitranshi (GSI), S. P. Shukla (GSI) and some other faculty members of GSI and SASE were present. The objective of this training programme was to develop manpower for initiating systematic studies of glaciated region of the Himalaya, which is necessary to understand the glacio-hydrology, meteorology, glacial dynamics, glacial micro-meteo-

rology and suspended sediment loads in head-water regions. An understanding of the complete glacial environment is necessary, including physical and chemical changes and therefore, a multidisciplinary approach is needed for glaciological studies.

Overall, 44 lectures and 10 practical sessions, including field demonstration for collecting the samples and installation of automatic weather stations, were conducted at the GSI office in Chandigarh, SASE Chandigarh/Manali and Hamtah Glacier base camp. This was followed, under the supervision of GSI officers, by a traverse along the Chandra valley and a ~7 km trek along Hamtah Glacial valley to reach the accumulation zone of the glacier. Interactive sessions, including high-altitude trekking and fitness conducted at Hamtah Glacier, helped the students to discuss various problems associated with high-altitude terrain. Hands-on training in the use of various instruments like total station survey equipment, and ground penetrating radar (GPR) was given; data processing was taught in the field. The total station equipment used in modern surveying enabled measurement of angle, distance as well as coordinates and helped record absolute location of the object. GPR is a potentially powerful, non-destructive technique which is widely used to estimate ice thickness, bedrock topography,