A BRIEF HISTORY OF GaN BLUE LIGHT-EMITTING DIODES

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Starting early in the 20th century, there were several reports of light emission from materials due to applied electric fields, a phenomenon which was termed "electroluminescence."[1] The materials properties were poorly controlled, and the emission processes were not well understood. For example, the first report in 1923 of blue electroluminescence was based on light emission from particles of SiC which had been manufactured as sandpaper grit, and which contained accidental p-n junctions.[2] By the late 1960's, SiC films had been prepared by more careful processes,[3] and p-n junction devices were fabricated, leading to blue light-emitting diodes (LEDs). Electrical to optical conversion efficiencies were never more than about 0.005%.[4] In the ensuing decades, blue SiC LEDs were never substantially improved, because SiC has an indirect band gap. Although many blue SiC LEDs were actually sold commercially in the early 1990's, they are no longer a viable product. In the end, the best SiC LEDs, emitting blue light at 470 nm, had an efficiency of only 0.03%.[5]

In a more organized fashion, growth of the III-V compound semiconductors commenced in 1954. For example, in the mid-1950's, large single crystal boules of GaAs were pulled from the melt, and sliced and polished wafers were used as substrates for the growth of p-n junction diode structures, either by vapor phase or liquid phase epitaxy. Infrared light-emitting diodes based on GaAs were first reported in 1962.[6] In order to get visible light emission, GaAs was alloyed with GaP, and red LEDs were quickly demonstrated.[7] It soon became apparent that GaP was not nearly as efficient a light emitter as GaAs, due again to an indirect band gap. It was subsequently determined that at room temperature, the highest efficiency of these alloy device was about 0.2% starting with GaAs, and this value dropped by several orders of magnitude to less than 0.005% when the phosphorus concentration exceeded 44%.[8] By 1968, iso-electronic doping of GaP with nitrogen had been investigated, and much brighter yellow-green (550 nm) LEDs, which eventually reached efficiencies of about 0.3%, were reported.[9]

At this time, the Radio Corporation of America (RCA) was still one of the premier manufacturers of color televisions, which used standard cathode ray tubes to present the images to viewers. At RCA's central research laboratory in Princeton, NJ, James Tietjen had become the director of the Materials Research Division, and he wanted to develop a flat television that could be hung on the wall like a painting. To create a full color image, one must provide red, green, and blue pixels in the display. Tietjen realized that he already had red LEDs available using $GaAs_{1-x}P_x$, and now green ones had entered the scene based on GaP:N technology. Bback in 1968 he recognized that all that was needed for a flat TV based on LEDs was a bright blue LED.

In May 1968, Tietjen approached a young man in his group, Herbert Maruska, and challenged him to find a method for growing single crystal films of GaN, which Tietjen felt would yield blue LEDs. Maruska had been growing $GaAs_xP_{1-x}$ red LEDs using the Halide Vapor Phase Epitaxy (HVPE) approach. In a traditional HVPE reactor, the group III element such as Ga is transported as the monochloride. For example, GaCl is generated *in situ* by passing HCl vapor over liquid gallium at about 850 ^{o}C. The group V element is transported as the hydride, such as arsine. The substrate is held in a tube furnace, and the two gas flows are injected and allowed to mix at the surface of the substrate. An example of one of Maruska's HVPE reactors is shown in Figure 1.

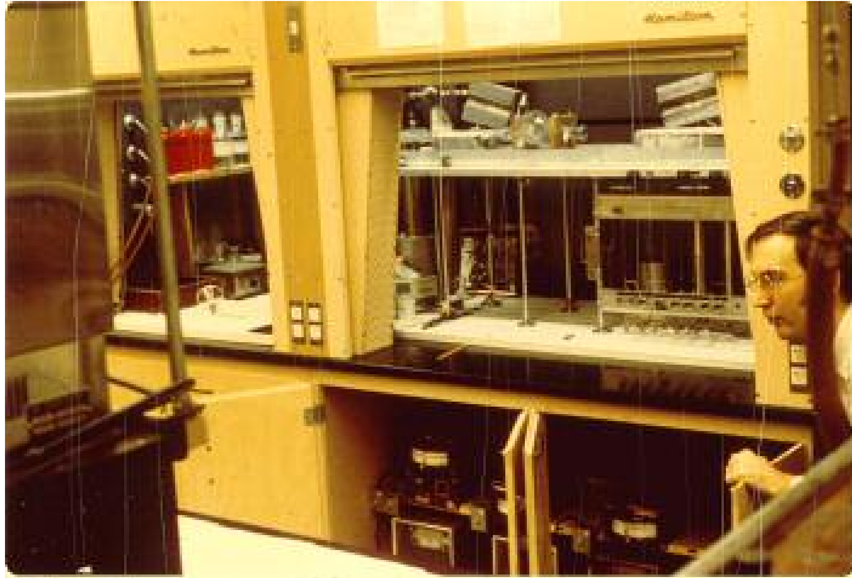

Figure 1. **One of the original HVPE reactors used for growing GaN. Note Maruska at right edge of photo.**

Maruska went to the library at RCA's David Sarnoff Research Center and got copies of all the old German papers on GaN from the 1930's and '40's.[10] To conserve money, RCA employees were encouraged to reuse photocopy pages from the trash basket, turned to the other side. Maruska still has the original copies of the old GaN papers which he made, and the date May 13, 1968 is stamped on the Legal Department memos on the reverse side of the journal pages. So we know the exact date on which the RCA GaN program got started.

GaN had been prepared as a powder by reacting ammonia with liquid gallium metal at elevated temperatures. A number of properties of the material had been reported, including the wurtzite crystal structure. Various dopants had been introduced into these powder samples. No vapor phase epitaxial growth had ever been attempted. To start, Maruska purchased a tank of 99% ammonia, with which he replaced his arsine bottle. He chose sapphire as the substrate because it is a robust material which was not reactive with ammonia. There were centimeter-sized sapphire wafers available at RCA Labs because of an on-going silicon-on-sapphire

program. Sapphire remains a popular substrate for GaN growth to this day.

There was an immediate question concerning the proper growth temperature for GaN. Unfortunately, Maruska and Tietjen misinterpreted the results of Lorenz and Binkowski,[11] who had reported the decomposition of GaN in vacuum at temperatures as low as 600 °C. All of the early GaN films were grown at temperatures below 600 °C, "to prevent decomposition," and hence were all polycrystalline. Finally on March 5, 1969, Maruska realized that in an ammonia environment, as opposed to a vacuum, GaN growth would occur rather than decomposition, and thus he raised the furnace temperature to 850 °C, the temperature typically used for GaAs growth. The GaN film was clear and had a specular surface. He rushed down to the RCA analytical center, and a Laue pattern revealed that the deposit was indeed the first single crystal film of GaN.[12] Better films were grown by raising the furnace temperature to 950 ^{o}C.

Maruska found that all of the GaN films were n-type without intentional doping. Analytical techniques available at the time gave no clue as to the impurities responsible for the conductivity, so Maruska and Tietjen blamed the problem on "nitrogen vacancies." This concept has created much controversy over the years. They sought to find a p-type dopant so that they could make a pn junction. Zinc seemed to be an appropriate acceptor because it worked for GaAs and GaP. With heavy Zn concentrations, GaN films proved to be insulating, and even became orange in color. But the films never became conducting p-type.

During 1969, Jacques Pankove spent a year's sabbatical at Berkeley University writing his classic textbook, Optical Processes in Semiconductors. When he returned to RCA Labs in January 1970, he immediately became interested in the new GaN films. Pankove and Maruska formed a team and together undertook a study of optical absorption and photoluminescence of thin film GaN.[13,14] Back in 1969 the United States was heavily involved in fighting a war in Vietnam, and the GaN work at RCA got funding from agencies of the Defense Department. Maruska was deferred from the conflict because his efforts to grow GaN were judged by his draft board to be contributing to national defense. But in 1970, he turned 26 years old, and was no longer subject to being drafted. Hence Maruska went off to Stanford University to pursue a Ph.D. Ed Miller now joined the effort at RCA, and the first example of electroluminescence from GaN was announced at RCA in the summer of 1971 by Pankove and Miller.[15] The sample consisted of an insulating Zn-doped layer which was contacted with two surface probes, and blue light peaking at 475 nm was emitted. Pankove and co-workers then made a device consisting of an undoped n-type region, an insulating Zn-doped layer, and an indium surface contact.[16] This proved to be the first actual GaN light-emitting diode, and it emitted green light.

RCA Laboratories granted Herb Maruska a fellowship to underwrite his graduate studies. He remained an RCA employee while studying at Stanford. RCA stipulated that they would only pay his way if he developed a blue LED as his thesis project. So after he finished passing his qualifying exams, he joined Prof. David

Stevenson's group in the Materials Science Department at Stanford, and began building a copy of the standard RCA HVPE reactor. In April 1972, Maruska decided that magnesium might be a better choice of p-type dopant than zinc: see Figure 2

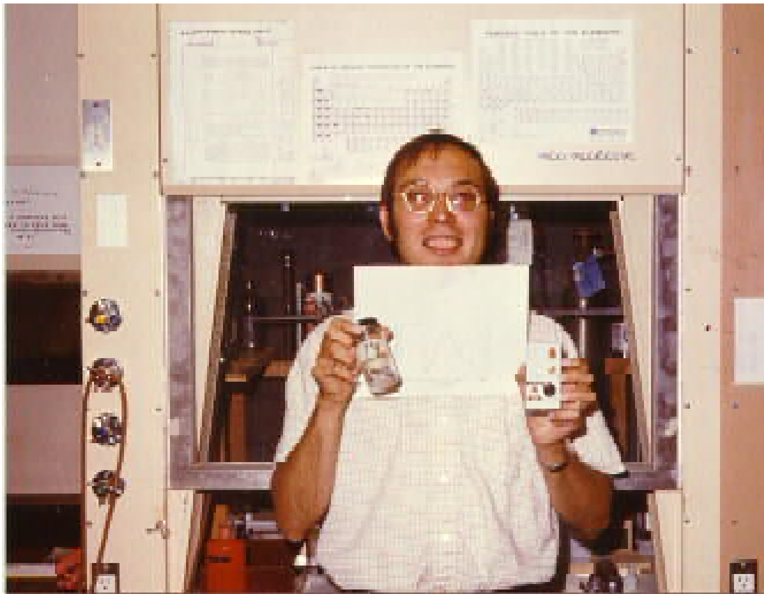

Figure 2. Maruska chooses a new p-type dopant, magnesium, for his GaN LEDs.

. He began growing Mg-doped GaN films using the now-standard HVPE technique, and on July 7, 1972, got a "bright" violet LED emitting at 430 nm.[17] At least it was bright enough to see in a well-lit room. An original photo of the device is shown in Figure 3. Many tests were performed on these LEDs in attempts to define a model for their operation, as shown in Figure 4. Maruska and Pankove described the efforts back in 1972 in the paper, "Violet Luminescence of Mg-doped GaN."[18] Mg-doping of GaN continues to be the basis for all commercial nitride LEDs and laser diodes.

Figure 3. World's first violet LED based on Mg-doped GaN.

The RCA-Stanford team was able to devise a model for the operation of these devices based on Fowler-Nordheim tunneling of electrons through a triangular potential barrier, because the characteristics were virtually independent of temperature.[19,20,21] They proposed that the blue luminescence was due to impact excitation of filled Mg acceptors by hot electrons, followed by recombination. But these tunneling devices were never very efficient, and no successful commercial product ever appeared. Maruska completed his thesis studies by the end of 1973 and returned to RCA. Unfortunately, by the beginning of 1974, RCA Corporation was collapsing as revenues plunged due to inept corporate management. The blue LED project was cancelled.

Figure 4. Preparation and characterization of blue GaN LEDs at Stanford University

Although Maruska was sure that the new blue LEDs would make him rich, as shown in Figure 5, this has never happened. In fact, to this day, he continues to grow GaN films by the HVPE method, now in the Electrical Engineering Department at the University of South Carolina. Jacques Pankove went off to the University of Colorado, where he also continued to grow GaN films. He recently retired.

In the years subsequent to the collapse of RCA, work on GaN virtually ceased everywhere, and in fact in 1982 only a handful of papers were published world-wide on this material. However, Isamu Akasaki refused to give up the cause, and finally in 1989 he solved the p-type doping dilemma, achieving conducting material with electron-beam annealed Mg-doped GaN.[22] Finally in 1995, Nakamura at Nichia Chemical Industries developed blue and green GaN heterostructure LEDs with efficiencies exceeding 10%.[23] One must never give up.

Figure 5. Will blue LEDs ever make Maruska a rich man?

Meanwhile, Maruska's original Mg-doped LED continues to emit light even in the New Millennium, and the 30th birthday was celebrated on July 7, 2002: see Figure 6.

Figure 6. 30th Birthday Party for first Mg-doped GaN violet LED.

REFERENCES

1. H. J. Round, *Electron World,* 19, 309 (1907).

2. O. W. Lossev, *Telegrafia i Telefonia,* 18, 61 (1923).

3. E. E. Violin, A. A. Kalnin, V. V. Pasynkov, Y. M. Tairov, D. A. Yaskov, *Silicon Carbide - 1968*, Pergamon Press, 231-241 (1969).

4. R. M. Potter, J. M. Blank, A. Addamiano, *J. Appl. Phys.*, 40, 2253 (1969).

5. J. A. Edmond, H. S. King, and C. H. Carter, *Physica B*, 185, 453 (1993).

6. M. I. Nathan, W. P. Dumke, G. Burns, F. J. Dill, G. J. Lasher, *Appl. Phys. Lett.*, 1, 62 (1962).

7. N. Holonyak, Jr., and S. F. Bevacqua, *Appl. Phys. Lett.*, 1, 82 (1962).

8. H. P. Maruska and J. I. Pankove, *Solid-State Electronics*, 10, 917 (1967).

9. R. A. Logan, H. G. White, W. Wiegmann, *Appl. Phys. Lett.*, 13, 139 (1968).

10. Robert Juza, Harry Hahn, *Zeitschrift fur anorganische und allgemeine Chemie* 239 282 (1938)

11. M. R. Lorenz and B. B. Binkowski, *J. Electrochem. Soc.*, 109, 24 (1962).

12. H. P. Maruska and J. J. Tietjen, *Appl. Phys. Lett.* 15 327 (1969).

13. J. I. Pankove, J. E. Berkeyheiser, H. P. Maruska, J. Wittke, *Solid State Communications* 8 1051 (1970).

14. J. I. Pankove, H. P. Maruska, J. E. Berkeyheiser, *Applied Physics Letters* 7 197 (1970).

15. J. I. Pankove, E. A. Miller, D. Richman, J. E. Berkeyheiser, *Journal of Luminescence* 4, 63 (1971)

16. J. I. Pankove, E. A. Miller, J. E. Berkeyheiser, *RCA Review* 32, 383 (1971).

17. H. P. Maruska, W.C. Rhines, D.A. Stevenson, *Mat. Res. Bull.* 7 777 (1972).

18. H. P. Maruska, D.A. Stevenson, J. I. Pankove, *Appl. Phys. Lett.* 22 (1973).

19. H. P. Maruska, L. J. Anderson, D. A. Stevenson, *J. Electrochem. Soc.*, 121, 1202 (1974).

20. H. P. Maruska and D. A. Stevenson, *Solid State Electronics*, 17, 1171 (1974).

21. J. I. Pankove and M. A. Lampert, *Phys. Rev. Lett.*, 33, 361 (1974).

22. H. Amano, M. Kito, K. Hiramatsu, I. Akasaki, *Jpn. J. Appl. Phys.*, 28, L2112 (Dec. 1989).

23. S. Nakamura, M. Senoh, N. Iwasa, S. Nagahama, *Jpn. J. Appl. Phys.*, 34, L797 (July 1995).