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History of light-emitting diodes

1.1 History of SiC LEDs

Starting early in the 20th century, light emission from a solid material, caused by an electrical power source, was reported, a phenomenon termed *electroluminescence*. The first light-emitting diode (LED) had been born. At that time, the material properties were poorly controlled, and the emission process was not well understood. The light-emitting active material was SiC crystallites as used for sandpaper abrasive.

A Note on Carborundum.

To the Editors of Electrical World:

SIRS:—During an investigation of the unsymmetrical passage of current through a contact of carborundum and other substances a curious phenomenon was noted. On applying a potential of 10 volts between two points on a crystal of carborundum, the crystal gave out a yellowish light. Only one or two specimens could be found which gave a bright glow on such a low voltage, but with 110 volts a large number could be found to glow. In some crystals only edges gave the light and others gave instead of a yellow light green, orange or blue. In all cases tested the glow appears to come from the negative pole. a bright blue-green spark appearing at the positive pole. In a single crystal, if contact is made near the center with the negative pole, and the positive contact is put in contact at any other place, only one section of the crystal will glow and that the same section wherever the positive pole is placed.

There seems to be some connection between the above effect and the e.m.f. produced by a junction of carborundum and another conductor when heated by a direct or alternating current; but the connection may be only secondary as an obvious explanation of the e.m.f. effect is the thermoelectric one. The writer would be glad of references to any published account of an investigation of this or any allied phenomena.

NEW YORK, N. Y.

H. J. ROUND.

Fig. 1.1. Publication reporting on a “curious phenomenon”, namely the first observation of electroluminescence from a SiC (carborundum) light-emitting diode. The article indicates that the first LED was a Schottky diode rather than a p-n-junction diode (after H. J. Round, *Electrical World* **49**, 309, 1907).

The first report on light-emitting diodes, shown in Fig. 1.1, was published by Henry Joseph Round (1907). Round was a radio engineer and a prolific inventor who, by the end of his career, held 117 patents. These first light-emitting devices had rectifying current–voltage characteristics;

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that is, these first devices were light-emitting *diodes* or LEDs. The light was produced by touching the SiC crystal with electrodes so that a rectifying Schottky contact was formed. Schottky diodes are usually majority carrier devices. However, minority carriers can be created either under strong forward-bias conditions, or by avalanche multiplication under reverse-bias conditions.

The mechanism of light emission in a forward-biased Schottky diode is shown in Fig. 1.2, which displays the band diagram of a metal–semiconductor junction under (a) equilibrium, (b) moderate forward bias, and (c) strong forward bias conditions. The semiconductor is assumed to be of n-type conductivity. Under strong forward bias conditions, minority carriers are injected into the semiconductor by tunneling through the surface potential barrier. Light is emitted upon recombination of the minority carriers with the n-type majority carriers. The voltage required for minority carrier injection in Schottky diodes is larger than typical p-n junction LED voltages. Round (1907) reported operating voltages ranging between 10 and 110 V.

Light can also be generated in a Schottky diode under reverse-bias conditions through the avalanche effect in which high-energy carriers impact-ionize atoms of the semiconductor. In this process, holes are created in the valence band as well as electrons in the conduction band, which will eventually recombine thereby creating light.

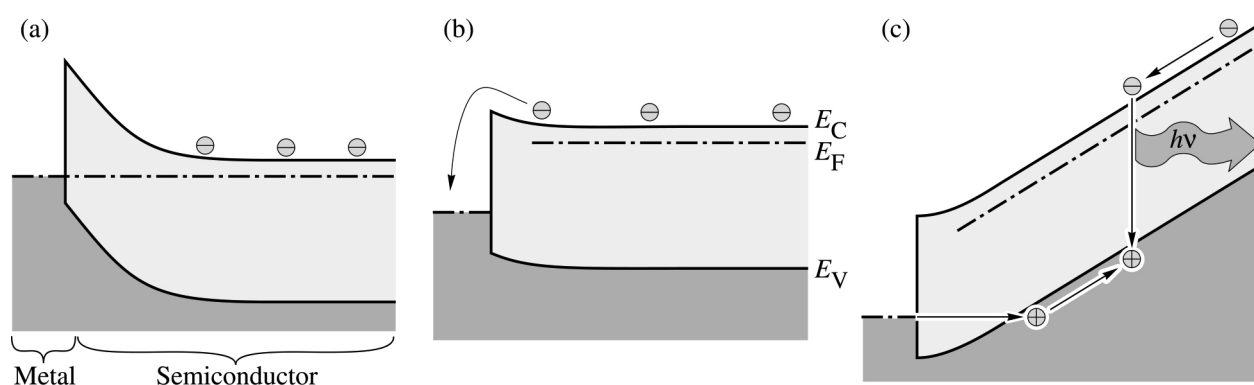


Fig. 1.2. Band diagram of a Schottky diode under (a) equilibrium conditions, (b) forward bias, and (c) strong forward bias. Under strong forward bias, minority carrier injection occurs making possible near-bandgap light emission.

Lossev (1928) reported detailed investigations of the luminescence phenomenon observed with SiC metal–semiconductor rectifiers. The main use of these rectifiers was in solid-state demodulation radio-circuits that did not employ vacuum tubes. Lossev found that luminescence occurred in some diodes when biased in the reverse direction and in some diodes when biased in

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forward *and* reverse directions. The author was puzzled about the physical origin of the luminescence. He investigated whether light was generated by heat glow (incandescence) by testing the evaporation rate of a droplet of liquid benzene on the luminous sample surface. He found, however, that the benzene evaporated very slowly and correctly concluded that the luminescence was not caused by incandescence. He postulated that the process by which light was produced is “very similar to cold electronic discharge”. The author also found that the light could be switched on and off very rapidly, making the device suitable for what he called a “light relay”. The pre-1960 history of LEDs was further reviewed by Loebner (1976).

By the late 1960s, SiC films had been prepared by more careful processes (Violin *et al.*, 1969), and p-n junction devices were fabricated, leading to blue light-emitting diodes. Electrical to optical conversion efficiencies were only 0.005 % (Potter *et al.*, 1969). In the ensuing decades, blue SiC LEDs were never substantially improved, because SiC has an indirect bandgap. Although many blue SiC LEDs were actually sold commercially in the early 1990s, 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 % (Edmond *et al.*, 1993). SiC, the material of the very first LED, could no longer compete with III–V semiconductors.

1.2 History of GaAs and AlGaAs infrared and red LEDs

Prior to the 1950s, SiC and II–VI semiconductors had been well-known materials. Both materials occur in nature. The very first LEDs had been made using SiC and there had been one publication by Destriau (1936) reporting LEDs made of zincblende (ZnS).

The era of III–V compound semiconductors started in the early 1950s when this class of materials was postulated and demonstrated by Welker (1952, 1953). The class of III–V compounds had been an unknown substance prior to the 1950s that does not occur naturally. The novel man-made III–V compounds proved to be optically very active and thus instrumental to modern LED technology.

Bulk growth of the III–V compound GaAs commenced in 1954. In the mid-1950s, large single-crystal boules of GaAs were pulled from the melt. The sliced and polished wafers were used as substrates for the epitaxial growth of p-n junction diode structures, either by vapor phase epitaxy (VPE) or liquid phase epitaxy (LPE). Infrared (870 – 980 nm) LEDs and lasers based on GaAs were first reported in 1962 by groups working at RCA, GE, IBM, and MIT (Pankove and Berkeyheiser, 1962; Pankove and Massoulie, 1962; Hall *et al.*, 1962; Nathan *et al.*, 1962; Quist *et al.*, 1962).

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A sustained research effort on GaAs and AlGaAs/GaAs devices started in the early 1960s at the IBM Thomas J. Watson Research Center in Yorktown Heights, located about an hour's drive north of New York City. The IBM team consisted of well-known researchers such as Jerry Woodall, Hans Rupprecht, Manfred Pilkuhn, Marshall Nathan, and others.

Woodall (2000) recalls that his work centered on the bulk crystal growth of GaAs used to fabricate semi-insulating substrates for Ge device epitaxy, and n-type substrates to fabricate injection lasers via Zn diffusion. At that time the GaAs-based injection laser had already been demonstrated at IBM, GE, and MIT Lincoln Laboratories. Rupprecht's interests were in impurity-diffusion theory and experiment along with experimental investigations into the newly discovered injection laser. Rupprecht was associated with a laser device physics group headed by Marshall Nathan, a co-inventor of the first injection laser (Nathan *et al.*, 1962).

As Woodall developed a technique that led to state-of-the-art horizontal Bridgman GaAs crystals, Rupprecht fabricated the materials into lasers and characterized them. This collaboration paid off immediately and continuous-wave (cw) operation of GaAs lasers at 77 K was attained (Rupprecht *et al.*, 1963). They then learned of the liquid phase epitaxy (LPE) technique pioneered by Herb Nelson at the RCA Labs in Princeton. The employment of LPE to grow GaAs lasers resulted in the achievement of 300 K lasers with lower threshold current densities than for Zn diffused lasers. Stimulated by papers found in a literature search, Woodall set out to grow GaAs p-n junction diodes by using Si as an amphoteric dopant, i.e. Si atoms on Ga sites acting as donors and Si atoms on As sites acting as acceptors. This was an interesting idea, as hitherto LPE had been used to grow epilayers with only a single conductivity type.

The LPE conditions to form Si-doped p-n junctions were found very quickly. Si-doped GaAs p-n junctions were formed by cooling a Ga-As-Si melt from 900 to 850 °C to form Si donors and Si acceptors at the two temperatures, respectively. By examining the cross section of the chemically stained epitaxial layer, the lower layer, grown at 900 °C, was identified as being an n-type layer and the upper layer, grown at 850 °C, as a p-type layer. No loss in crystal quality was found in the regions of lower temperature growth. Furthermore, owing to band tailing effects caused by the highly doped, compensated region of the p-n junction, the LED emission occurred at 900 – 980 nm, far enough below the GaAs band edge (870 nm) that the bulk GaAs substrate and the GaAs epilayer did not absorb much of the emitted light but acted as a transparent “window layer”. LED external quantum efficiencies as high as 6 % were attained, a major breakthrough in LED technology (Rupprecht *et al.*, 1966). Rupprecht (2000) stated: “Our demonstration of the highly efficient GaAs LED is a typical example of a discovery made by

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serendipity”. The quantum efficiency of the amphoterically doped GaAs LEDs was five times greater than that of GaAs p-n junctions fabricated by Zn diffusion. Si acceptor levels are deeper than Zn acceptor levels so that the emission from the compensated Si-doped active region occurs at longer wavelengths where GaAs is more transparent.

Being in the LED research business, the IBM group wondered if this doping effect could be extended to a crystal host with visible emission. There were two candidates, GaAsP and AlGaAs. Whereas Rupprecht tried to do GaAsP epitaxy via LPE, Woodall set up an apparatus for AlGaAs. It was difficult, to form good quality GaAsP epilayers by LPE due to the 3.6 % lattice mismatch between GaP and GaAs. AlGaAs had problems of its own: “AlGaAs is lousy material” was the pervasive opinion at that time, because, as Woodall (2000) stated, “aluminum loves oxygen”. This results in the incorporation of the “luminescence killer” oxygen in AlGaAs layers; in particular, in the vapor-phase epitaxy (VPE) process but less so in the LPE process.

Without the support of IBM management, Rupprecht and Woodall “went underground” with their research, conducting the LPE AlGaAs epigrowth experiments after regular working hours and on the weekends. Woodall designed and built a “vertical dipping”-type LPE apparatus, using graphite and alumina melt containers. As an undergraduate student Woodall had majored in metallurgy at MIT and he remembered something about phase diagrams. He made an “intelligent guess” to select the Al concentrations for the LPE melts. He added Si to the melt for the first experiment, saturated the melt and then “dipped” the GaAs substrate while cooling the melt from about 925 to 850 °C. Finally, the substrate and epilayer were withdrawn from the melt, and the apparatus was returned to 300 K. Although no Si-doped p-n junction was observed, a 100 μm thick high quality layer of AlGaAs had been grown with a bandgap in the red portion of the visible spectrum (Rupprecht *et al.*, 1967, 1968).

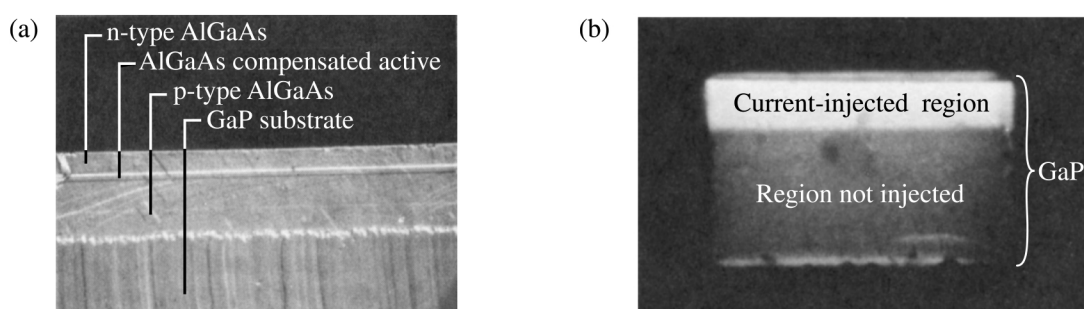


Fig. 1.3. (a) Cross section micrograph of an AlGaAs LED grown on a transparent GaP substrate. (b) Electroluminescence originating from a current-injected region located under a stripe-shaped contact viewed through the transparent GaP substrate (after Woodall *et al.*, 1972).

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Visible AlGaAs were also grown on GaP, a lattice mismatched but transparent substrate. Micrographs of the structure are shown in Fig. 1.3. When AlGaAs was grown on GaP substrates, the thermodynamics of LPE made the initially grown material Al-rich due to the Al distribution coefficient in the melt. As a result, the high-Al-content AlGaAs acts as a transparent window layer for the light emitted from the low-Al-content AlGaAs active region (Woodall *et al.*, 1972).



Fig. 1.4. This classic 1964 mainframe computer IBM System 360 used high-voltage gas-discharge lamps to indicate the status of the arithmetic unit. In later models, the lamps were replaced by LEDs. The cabinet-sized 360 had a performance comparable to a current low-end laptop computer.

Pilkuhn, also an “IBM’er” who had worked with Rupprecht on GaAsP LEDs and lasers (Pilkuhn and Rupprecht, 1965), had built a small battery-powered circuit with an LED emitting visible red light, which he showed to his colleagues and management at IBM (Pilkuhn, 2000). The reactions ranged from “nice but useless” to “great and useful”. However it was soon realized that the latter was true, i.e. that LEDs were extremely useful devices. The first application of the GaAsP LEDs was as indicator lights on circuit boards, where the LEDs indicated the status and proper function of the circuit board. LEDs were also used to show the status of the data processing unit of the classic IBM System 360 mainframe computer shown in Fig. 1.4.

According to Rostky (1997), the first commercial GaAs LED was offered by the Texas Instruments Corporation in the early 1960s. The LED emitted infrared radiation near 870 nm. The manufacturing quantities of the product were low, probably caused by the high price for one LED, which reportedly was 130 US\$.

The *resonant-cavity light-emitting diode* (RCLED) was first demonstrated in the AlGaAs/GaAs materials system (Schubert *et al.*, 1992, 1994). RCLEDs represented a new class

of LEDs making use of spontaneous emission enhancement occurring in microscopic optical resonators or *microcavities*. Enhancement is greatest for wavelengths in resonance with the fundamental mode of the cavity. The emission enhancement is mediated by changes in the optical mode density within the cavity. RCLEDs have higher emission intensities along the optical axis of the cavity, which allows for higher coupling efficiencies to optical fibers.

At the present time, infrared GaAs/AlGaAs LEDs are widely used in video and audio remote controls and as sources for local-area communication networks. In addition, red AlGaAs/AlGaAs LEDs are used as high-brightness visible LEDs with efficiencies higher than the GaAsP/GaAs red LEDs but lower than the AlGaInP/GaAs red LEDs.

1.3 History of GaAsP LEDs

The beginning of visible LEDs dates back to the year 1962 when Holonyak and Bevacqua (1962) reported on the emission of coherent visible light emission from GaAsP junctions in the first volume of *Applied Physics Letters*. Although the emission of coherent light was only observed at low temperatures, the devices worked as LEDs and emitted visible light even at room temperature. This publication marks the beginning of viable p-n junction LEDs emitting in the visible wavelength range.

Nick Holonyak Jr., who in 1962 worked at General Electric in Syracuse, New York, and who later joined the University of Illinois, had used vapor-phase epitaxy (VPE) of GaAsP on GaAs substrates. This technique is suited for large-volume growth of wafers in a research as well as a manufacturing environment. Holonyak (2000) recalls that when he had made these first LEDs, at that time he had already envisioned many applications these new devices may have, including indicator lights, seven-segment numeric displays, and alphanumeric displays.

However, despite the early success of the Holonyak group, the goal of demonstrating a semiconductor laser, working at room temperature, remained elusive (Holonyak, 1963, 1964). It remained elusive for good reasons. The GaAsP material system grown on GaAs substrates has several problems which Holonyak and co-workers discovered.

Although excellent electrical junction characteristics were obtained (Holonyak *et al.*, 1963a), the optical properties degraded. When the phosphorus content in GaAsP was about 45 – 50 %, a strong decrease in the LED radiative efficiency was found. These difficulties were attributed to the direct–indirect transition of the bandgap of GaAsP (Holonyak *et al.*, 1963b, 1966; Pilkuhn and Rupprecht, 1964, 1965). It was determined that the 300 K efficiency of GaAsP alloy devices

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dropped to less than 0.005 % when the phosphorus concentration exceeded 44 % (Maruska and Pankove, 1967).

The first commercial GaAsP LED was offered by the General Electric (GE) Corporation in the early 1960s. The LED emitted visible radiation in the red part of the spectrum. The manufactured quantities of the product were low, probably due to the high price which was 260 US\$ for a single LED. The product was offered in the Allied Radio catalog, a widely distributed catalog for amateur radio electronics (Rostky, 1997).

The Monsanto Corporation was the first commercial entity to start mass production of LEDs. In 1968, the company had set up a factory, produced low-cost GaAsP LEDs, and sold them to customers. The era of solid-state lamps had started. In the period 1968 – 1970, sales were skyrocketing, doubling every few months (Rostky, 1997). The Monsanto LEDs were based on GaAsP p-n junctions grown on GaAs substrates emitting in the visible red wavelength range (Herzog *et al.*, 1969; Craford *et al.*, 1972).

Monsanto developed a friendly collaboration with Hewlett-Packard (HP) Corporation, expecting that HP would make light-emitting diodes and LED displays while Monsanto would provide the raw material – the GaAsP. In the mid-1960s, Monsanto had sent one of its scientists from Saint Louis, Missouri, to Palo Alto, California, to help HP develop an LED business using Monsanto's GaAsP material. However, HP felt nervous about depending on a single source for the GaAsP material. The informal relationship ended and HP started growing its own GaAsP (Rostky, 1997).

For several years, from the late 1960s to the mid-1970s, the emerging market was in numeric displays, driven at first by calculators, then by wristwatches, following Hamilton Watch Corporation's introduction of the Pulsar digital watch in 1972. For a while, the early contenders, Monsanto and HP, took turns leaping into first place with a more advanced multiple-numeric or alphanumeric LED displays (Rostky, 1997).

A key technical innovator and manager at Monsanto was M. George Craford who has made numerous contributions to LEDs including the first demonstration of a yellow LED (Craford *et al.*, 1972). It employed an N-doped GaAsP active region grown on a GaAs substrate. When Monsanto sold off its optoelectronics business in 1979, Craford joined HP and became the key person in the company's LED business. A profile of Craford was published by Perry (1995).

It soon became clear that the large lattice mismatch between the GaAs substrate and the GaAsP epilayer resulted in a high density of dislocations (Wolfe *et al.*, 1965; Nuese *et al.*, 1966). As a result, the external efficiency of these LEDs was quite low, about 0.2 % or less (Isihamatsu

1.4 History of GaP and GaAsP LEDs doped with optically active impurities

and Okuno, 1989). The importance of the growth conditions and thickness of a *buffer layer* was realized by Nuese *et al.* (1969) who pointed out that a thick graded GaAsP buffer layer yields improved brightness red LEDs. It is understood today that the thick graded buffer layer reduces the high dislocation density in the GaAsP epitaxial layer originating near the GaAsP-epilayer-to-GaAs-substrate boundary.

The direct–indirect transitions as well as the high dislocation density limit the brightness attainable with GaAsP LEDs. Today this material system is primarily used for standard (low-brightness) red LEDs for indicator lamp applications.

1.4 History of GaP and GaAsP LEDs doped with optically active impurities

Ralph Logan's and his co-workers' pioneering work on GaP LEDs was done while working at Bell Laboratories in Murray Hill, New Jersey, in the early 1960s, where they developed a manufacturing process for GaP-based red and green LEDs. At that time, semiconductors had been employed to demonstrate both bipolar and field-effect transistors for switching and amplifying electrical currents. Engineers and scientists back then also began to realize that semiconductors would be perfectly suitable for light-emitting devices.

Logan (2000) recalls that his interest was stimulated by the first reports of GaP p-n junction LEDs by Allen *et al.* (1963) and Grimmeiss and Scholz (1964). These devices emitted red light at a useful efficiency so that the light could be clearly seen with the naked eye under ambient daylight conditions. The Grimmeiss–Scholz junctions were reported to be made by alloying Sn, an n-type dopant, into p-type GaP.

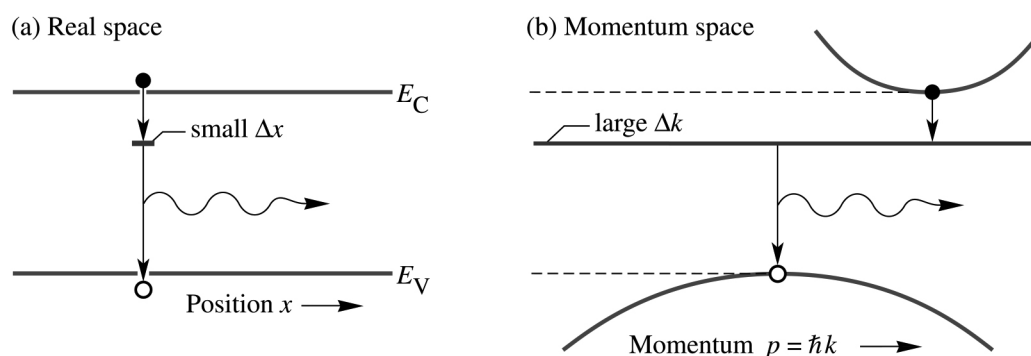


Fig. 1.5. (a) Real-space and (b) momentum-space optical transitions in GaP doped with an optically active impurity such as O or N, emitting in the red and green parts of the visible spectrum, respectively. GaP LEDs employ the *uncertainty principle* ($\Delta x \Delta p \geq \hbar$) which predicts that an electron wave function localized in real space is delocalized in momentum space, thereby making momentum-conserving (vertical) transitions possible.

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GaP is an indirect-gap semiconductor that does not emit significant amounts of light due to the requirement of momentum conservation in optical transitions. Figure 1.5 shows the band diagram of GaP illustrating that the band extremum points occur at different values in momentum space. If GaP is doped with an *optically active isoelectronic impurity* such as N, strong optical transitions are obtained, as shown by Thomas *et al.* (1965), because the impurity levels are smeared out in momentum space. GaP doped with optically active impurities is a wonderful example of a practical device based on the *Heisenberg uncertainty principle*, which predicts that an impurity with a strongly localized wavefunction in position space (small Δx) will have a delocalized level in momentum space (large Δk), so that optical transitions can occur via the deep level state.

The growth of GaP was accomplished by using platelets grown from a solution containing Ga and P. The platelets had lateral dimensions of 0.5 cm \times 1 cm and were grown to a thickness of about 1 mm. This was the standard initial method of growing GaP and overcame the problem of dealing with the P overpressure required when growing GaP at high temperatures. No one at Bell Labs could immediately reproduce the remarkable results reported by Grimmeiss and Scholz. However, a big research effort in electroluminescence was launched at AT&T Bell Labs as a result.

In the solution growth of the GaP platelets, the dopants used were Zn and O (the latter from Ga₂O₃), but it was not generally realized that ordinary ambient air usually contains enough S to be a good n-dopant. The growth kinetics of the platelets had the intriguing result that the compensated melts generally produced an n-type layer on one platelet surface so that a p-n junction was formed under the GaP platelet surface. This was thought to explain Grimmeiss' results. Logan *et al.* (1967a) published these findings at once.

Logan's research group also reported the first demonstration of reproducible growth of efficient LEDs (Logan *et al.* 1967b). These junctions were formed by growing an n-type GaP layer onto Zn-O-doped GaP wafers that were polished out of large solution-grown wafers with typical sizes of 1 \times 1 inch². Logan *et al.* found that post-growth annealing in the range 400 – 725 °C could increase the LED efficiency by as much as an order of magnitude, yielding efficiencies exceeding 2 %. The annealing was thought to diffuse the Zn to the O atoms, thereby increasing the density of isoelectronic Zn-O centers that mediated the electroluminescence.

At the end of the 1960s ingots of GaP grown from melts at high temperature and pressure were becoming available, suitable for being cut into real substrates as we know them today. Green LEDs were formed with efficiencies as high as 0.6 % by doping the GaP with N