Light-Emitting Diodes

SECOND EDITION

E. Fred Schubert

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LIGHT-EMITTING DIODES SECOND EDITION

Revised and fully updated, the Second Edition of this textbook offers a comprehensive explanation of the technology and physics of light-emitting diodes (LEDs) such as infrared, visible-spectrum, ultraviolet, and white LEDs made from III–V semiconductors. The elementary properties of LEDs such as electrical and optical characteristics are reviewed, followed by the analysis of advanced device structures.

With nine additional chapters, the treatment of LEDs has been vastly expanded, including new material on device packaging, reflectors, UV LEDs, III–V nitride materials, solid-state sources for illumination applications, and junction temperature. Radiative and non-radiative recombination dynamics, methods for improving light extraction, high-efficiency and high-power device designs, white-light emitters with wavelength-converting phosphor materials, optical reflectors, and spontaneous recombination in resonant-cavity structures, are discussed in detail. Fields related to solid-state lighting such as human vision, photometry, colorimetry, and color rendering are covered beyond the introductory level provided in the first edition. The applications of infrared and visible-spectrum LEDs in silica fiber, plastic fiber, and free-space communication are also discussed. Semiconductor material data, device design data, and analytic formulae governing LED operation are provided.

With exercises, solutions and illustrative examples, this textbook will be of interest to scientists and engineers working on LEDs, and to graduate students in electrical engineering, applied physics, and materials science.

Additional resources for this title are available online at www.cambridge.org/ 9780521865388.

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Note: This book contains many figures in which color adds important information. For this reason, all figures are available in color on the Internet at the following websites: http://www.cambridge.org/9780521865388> and http://www.cambridge.org/9780521865388> and http://www.lightEmittingDiodes.org>.

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SECOND EDITION

E. FRED SCHUBERT

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Preface

During the last four decades, technical progress in the field of light-emitting diodes (LEDs) has been breathtaking. State-of-the art LEDs are small, rugged, reliable, bright, and efficient. At this time, the success story of LEDs still is in full progress. Great technological advances are continuously being made and, as a result, LEDs play an increasingly important role in a myriad of applications. In contrast to many other light sources, LEDs have the potential of converting electricity to light with near-unit efficiency.

LEDs were discovered by accident in 1907 and the first paper on LEDs was published in the same year. LEDs became forgotten only to be re-discovered in the 1920s and again in the 1950s. In the 1960s, three research groups, one working at General Electric Corporation, one at MIT Lincoln Laboratories, and one at IBM Corporation, pursued the demonstration of the semiconductor laser. The first viable LEDs were by-products in this pursuit. LEDs have become devices in their own right and today possibly are the most versatile light sources available to humankind.

The first edition of this book was published in 2003. The second edition of the book is expanded by the discussion of additional technical areas related to LEDs including optical reflectors, the assessment of LED junction temperature, packaging, UV emitters, and LEDs used for general lighting applications. No different than the first edition, the second edition is dedicated to the technology and physics of LEDs. It reviews the electrical and optical fundamentals of LEDs, materials issues, as well as advanced device structures. Recent developments, particularly in the field of III–V nitrides, are also discussed. The book mostly discussed is relevant to other solid-state light emitters such as group-IV, II–VI, and organic emitters. Several applications areas of LEDs are discussed in detail, including illumination and communication applications.

Many colleagues and collaborators have provided information not readily available and have given valuable suggestions on the first and second editions of this book. In particular, I am deeply grateful to Enrico Bellotti (Boston University), Jaehee Cho (Samsung Advanced Institute of Technology), George Craford (LumiLeds Corp.), Thomas Gessmann (RPI), Nick Holonyak Jr. (University of Illinois), Jong Kyu Kim (RPI), Mike Krames (LumiLeds Corp.), Shawn Lin (RPI), Ralph Logan (retired, formerly with AT&T Bell Laboratories), Fred Long (Rutgers University), Paul Maruska (Crystal Photonics Corp.), Gerd Mueller (LumiLeds Corp.), Shuji Nakamura (University of California, Santa Barbara), N. Narendran (RPI), Yoshihiro Ohno (National Institute of Standards and Technology), Jacques Pankove (Astralux Corp.), Yongjo Park (Samsung Advanced Institute of Technology), Manfred Pilkuhn (retired, University of Stuttgart, Germany), Hans Rupprecht (retired, formerly with IBM Corp.), Michael Shur (RPI), Cheolsoo Sone (Samsung Advanced Institute of Technology), Klaus Streubel (Osram Opto Semiconductors Corp., Germany), Li-Wei Tu (National Sun Yat-Sen University, Taiwan), Christian Wetzel (RPI), Jerry Woodall (Yale University), and Walter Yao (Advanced Micro Devices Corp.). I would also like to thank my current and former post-doctoral fellows and students for their many significant contributions to this book.

History of light-emitting diodes

1.1 History of SiC LEDs

Starting early in the twentieth century, light emission from a solid-state material, caused by an electrical power source, has been reported: a phenomenon termed *electroluminescence*. Because electroluminescence can occur at room temperature, it is fundamentally different from *incandescence* (or heat glow), which is the visible electromagnetic radiation emitted by a material heated to high temperatures, typically >750 °C.

In 1891 Eugene G. Acheson established a commercial process for a new manmade material, silicon carbide (SiC), that he termed "carborundum". The synthesis process was accomplished in an electrically heated high-temperature furnace in which glass (silicon dioxide, SiO₂) and coal (carbon, C) reacted to form SiC according to the chemical reaction (Filsinger and Bourrie, 1990; Jacobson *et al.*, 1992)

 $SiO_2(gas) + C(solid) \rightarrow SiO(gas) + CO(gas)$ $SiO(gas) + 2C(solid) \rightarrow SiC(solid) + CO(gas).$

Just like III–V semiconductors, SiC does not occur naturally. SiC, which has the same crystal symmetry as diamond, has a very high hardness. On the Mohs Hardness Scale, carborundum has a hardness of 9.0, pure SiC a hardness of 9.2–9.5, and diamond a hardness of 10.0. Because of its high hardness and because it could be synthesized in large quantities at low cost, carborundum was a material of choice for the abrasives industry.

In 1907, Henry Joseph Round (1881–1966) checked such SiC crystals for possible use as rectifying solid-state detectors, then called "crystal detectors". Such crystal detectors could be used for the demodulation of radio-frequency signals in early crystal-detector radios. Crystal detectors had been first demonstrated in 1906. Crystal–metal-point-contact structures were frequently tested during these times as a possible alternative to expensive and power-hungry vacuum-tube diodes, which were first demonstrated in 1904 (vacuum-tube diode or "Fleming

valve").

Round noticed that light was emitted from a SiC crystallite as used for sandpaper abrasive. 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. Nevertheless, he immediately reported his observations to the editors of the journal *Electrical World*. This publication is shown in Fig. 1.1 (Round, 1907).

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 pole 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).

Round was a radio engineer and a prolific inventor who, by the end of his career, held 117 patents. His first light-emitting devices had rectifying current–voltage characteristics; that is, these first devices were light-emitting *diodes* or LEDs. The light was produced by touching the SiC crystal with metal electrodes so that a rectifying Schottky contact was formed. Schottky diodes are usually majority carrier devices. However, minority carriers can be created by either minority-carrier injection under strong forward-bias conditions, or 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.



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.

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. Additional light-generating processes in Schottky diodes under reverse-bias conditions have been reported by Eastman *et al.* (1964).

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 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 power-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. Many II–VI semiconductors, e.g. ZnS and CdS, 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 Heinrich Welker (1952, 1953). The class of III–V compounds had been an unknown substance prior to the 1950s and these compounds do not occur naturally. The novel manmade 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 (Hall *et al.*, 1962; Nathan *et al.*, 1962; Pankove and Berkeyheiser, 1962; Pankove and Massoulie, 1962; Quist *et al.*, 1962).

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 lead 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 Laboratories 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), so 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 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; 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).

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

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.



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.

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-spectrum 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-spectrum LEDs dates back to the year 1962 when Holonyak and Bevacqua (1962) reported on the emission of coherent visible light 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) recalled that when he first had made these LEDs, he had already envisioned many applications these new devices might 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 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 LEDs while Monsanto would provide the raw material – GaAsP. In the mid 1960s, Monsanto had sent one of its scientists from Saint Louis, Missouri, to Palo Alto, California, to help HP develop the 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 LED 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 display (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, who for many years served as Chief Technical Officer, was published by Perry (1995). In 1999, HP spun off parts of its business (including the LED business) into Agilent Corporation which in turn co-founded Lumileds Lighting Corporation in 1999, as a joint venture with Philips Corporation. In 2005, Agilent sold its share of Lumileds to Philips.

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 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 low-cost, lowbrightness 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 AT&T 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). Theses 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 had been 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 spectrum, respectively. GaP LEDs employ the *uncertainty principle* ($\Delta x \Delta p \ge h/2\pi$) which predicts that an electron wave function localized in real space is delocalized in momentum space, thereby making momentum-conserving (vertical) transitions possible.

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 $0.5 \text{ cm} \times 1 \text{ cm}$ 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 Laboratories could immediately reproduce the remarkable results reported by Grimmeiss and Scholz. However, a big research effort in electroluminescence was launched at Bell Laboratories as a result.

In the solution growth of the GaP platelets, the dopants used were Zn and O (the latter from Ga_2O_3), 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 2.5×2.5 cm². 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 isoelectronic impurities (Logan *et al.*, 1968, 1971). The N was added in the form of GaN to the growth melts used to form the p-n junctions. While the external quantum efficiency of green LEDs is less than for the red LEDs, the sensitivity of the human eye to green light is more than 10 times higher than in the red, so the apparent brightness of the LEDs is comparable.

Other research laboratories such as IBM, RCA, and GE also looked into the possibility of making visible-spectrum LEDs that were more efficient than those made of GaAsP. Research on

GaP LEDs was pursued at IBM Corporation's Thomas J. Watson Research Center in Yorktown Heights in New York State. Manfred Pilkuhn and co-workers demonstrated an LPE-grown red GaP LED doped with Zn and O. The picture of a GaP LED with top and bottom contacts is shown in Fig. 1.6. The *IBM Research Journal* proudly reported that "brilliant red light" was emitted from the p-n junction. Note that in the 1960s, monochromatic colors were mostly generated by filtering incandescent light, so that the narrow-spectral-width LED light appeared to the observer as an impressively pure and "brilliant" color.



Fig. 1.6. GaP light-emitting diode grown by liquid-phase epitaxy emitting "brilliant red light" from the Zn- and O-doped p-n junction region (courtesy of Pilkuhn, 2000).

The active regions of Pilkuhn's GaP LEDs were co-doped with acceptors, e.g. Zn acceptors, and donors, e.g. Te, S, or Se donors, so that light was generated predominantly by donor–acceptor pair recombination processes. The energy of the light was below the bandgap of GaP. It was also found that co-doping of GaP with Zn and O resulted in a particularly large wavelength shift so that the emission occurred in the red wavelength range (Foster and Pilkuhn, 1965). Oxygen in GaP is neither donor nor acceptor but was identified as a deep level (see, for example, Pilkuhn, 1981).

Logan and co-workers, and their management team at AT&T Bell Laboratories immediately realized that there were many possible applications for LEDs. Indicator lamps were becoming useful in the telephone business. All such lights used at that time in the USA operated using 110 V. An example is the "Princess" telephone, which was intended to be used in bedrooms – the dial lit up when the phone was picked up from its cradle. The "Princess" was a prestigious telephone and the latest fad in the 1960s but had to be installed near a 110 V outlet. A service call to the local phone company was needed if the bulb burned out. If LEDs were to replace the

110 V light bulbs, the phone line could power the LEDs and a 110 V outlet would no longer be needed. In addition, GaP LEDs had an expected lifetime exceeding 50 years when used in telephones, much longer than 110 V light bulbs, so that this reliability promised substantial cost savings for the "Bell System" or simply "Ma Bell", as the phone company was called at that time.

More important was the multi-line "key telephone". This is the multi-line telephone used in large offices mostly by operators and secretaries where indicator lamps tell which line is being called and busy. To switch the telephone lines and the 110 V indicator lamps, a remote switch was used with dozens of wires to each phone. Installing and servicing these phones was very costly. In present-day telephones, the LED indicator lamps are powered over the phone line. A compatible circuit inside the phone handles the switching of the indicator lamps and phone lines. The savings in telephone manufacturing, installation, and service were impressive.

With the demonstration of the reproducible growth of efficient green N-doped GaP LEDs and red Zn-O-codoped LEDs, both of which were about equally bright and useful, the Bell Laboratories Development Department decided to manufacture the LEDs at its Reading, Pennsylvania, facility.

Telephone lines typically operate with a line voltage of approximately 40 V DC with currents of several milliamperes. The only effect of inserting an LED into this circuit is to reduce the drive voltage by approximately 2 V, a negligible effect, while the efficient LED makes a good indicator lamp. As a result, many phone models were equipped with an illuminated dial pad. Both red and green LED illumination was available, and green was the final choice made by telephone designers. Figure 1.7 shows a 1990 version of the AT&T Trimline telephone – still using GaP:N green LEDs for the dial pad illumination. Red and green LEDs were also incorporated in the multi-line "key telephones".

Should the reader ever be near Murray Hill, New Jersey, visiting the Bell Laboratories Museum, located at 600 Mountain Avenue, should be considered. Many technical artifacts including Logan *et al.*'s green GaP:N LED are displayed in the museum.

The Monsanto team applied N doping to GaAsP to attain emission in the red, orange, yellow, and green wavelength range (Groves *et al.*, 1971; Craford *et al.*, 1972; for a review see Duke and Holonyak, 1973). Many parameters, such as the emission and the absorption wavelength and the solubility of N in GaAsP and GaP were investigated. A useful growth method was vapor-phase epitaxy (VPE), because it allowed for N-doping in the vicinity of the p-n junction only. This resulted in less absorption of light in the layers adjoining the p-n junction and higher overall

LED efficiencies (Groves *et al.*, 1977, 1978a, 1978b). Today, GaP:N is the primary material for green emitters used in low-brightness applications such as indicator lights.



Fig. 1.7. AT&T telephone set ("Trimline" model) with the dial pad illuminated by two green N-doped GaP LEDs. The illuminated dial pad was one of the first applications of green GaP:N LEDs.

The first digital wristwatch with an LED display was released in 1972 by the Hamilton watch company. The watch became an instant furor and only its high price prevented it from becoming widely distributed. The digital Pulsar watch with an integrated calculator was released in 1975 and is shown in Fig. 1.8.





Another early application of LEDs was the numeric display in pocket calculators. Figure 1.9 shows two programmable calculators of the mid 1970s, the Texas Instruments Corporation's SR-56 and the Hewlett-Packard Corporation's HP-67. Both used red GaAsP LEDs in the seven-segment numeric display. All calculators using LED displays shared a significant problem: the display could not be read under bright outdoor conditions because the light emitted by the LEDs was simply too dim; furthermore, the power consumption of LED displays was high so that the rechargeable battery running the calculator had to be recharged on a regular basis. Digital wrist

watches using LEDs shared the same problem. Liquid crystal displays (LCDs), introduced at the end of the 1970s, had much lower power requirements. Consequently, LCDs totally replaced LED displays in calculators and watches by the beginning of the 1980s.

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Fig. 1.9. Programmable pocket calculators Model SR-56 of the Texas Instruments Corporation and Model HP-67 of the Hewlett-Packard Corporation, both first manufactured in 1976. Seven-segment numeric characters composed of GaAsP LEDs were used in the display. The SR-56 came with a "huge" program memory of 100 steps. The HP-67 came with a magnetic card reader and had several freely programmable keys.



1.5 History of GaN metal-semiconductor emitters

In the late 1960s, the Radio Corporation of America (RCA) was one of the premier manufacturers of color televisions, using cathode ray tubes (CRT) with three electron guns to display images. At RCA's central research laboratory in Princeton, New Jersey, James Tietjen had become the director of the Materials Research Division, and he wanted to develop a flat-panel television display that could be hung on the wall like a painting. To create a full color image, the display must contain red, green, and blue pixels. Tietjen realized that red LEDs using GaAsP and green LEDs using GaP:N technology were already available. 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, Paul 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 GaAsP red LEDs using the metal-halide vapor-phase epitaxy (MHVPE) approach. He gained much experience with the promises and perils of III–V compounds including phosphorus, a pyrophoric substance. On a day in 1968, phosphorus caused a garbage truck to catch fire on New Jersey's Route 1 in Princeton shortly after picking up some

phosphorus-containing laboratory waste at the RCA Laboratories. The driver of the truck decided to immediately return the burning and smoking load to RCA and dump it on the front lawn of the research laboratories (Maruska, 2000).

When Maruska started working on GaN, he first went to the library at Princeton University and thoroughly studied copies of all the old papers on GaN from the 1930s and 1940s (Juza and Hahn, 1938). GaN had been prepared as a powder by reacting ammonia with liquid gallium metal at elevated temperatures. He chose sapphire as the substrate because it is a robust material that is not reactive with ammonia. Unfortunately, he misinterpreted the results of Lorenz and Binkowski (1962), who had reported the decomposition of GaN in vacuum at temperatures as low as 600 °C. All of his early GaN films were grown at temperatures below 600 °C to prevent decomposition, and hence were polycrystalline. Finally in March 1969, Maruska realized that in an ammonia environment, growth rather than decomposition would occur, and thus he raised the furnace temperature to 850 °C, the temperature typically used for GaAs growth. The sapphire appeared to be uncoated, because 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 (Maruska and Tietjen, 1969).

Maruska found that all of the GaN films were n-type without intentional doping. He sought to find a p-type dopant so that he could make a p-n 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. But they were never conducting p-type (Maruska, 2000).

During 1969, Jacques Pankove spent a sabbatical year at Berkeley University writing his classic textbook, *Optical Processes in Semiconductors*. When he returned to RCA Laboratories in January 1970, he immediately became interested and strongly involved in the new GaN films. Pankove *et al.* undertook a study of optical absorption and photoluminescence of thin-film GaN (Pankove *et al.*, 1970a, 1970b). The first example of electroluminescence from GaN was announced at RCA in the summer of 1971 (Pankove *et al.* 1971a). The sample consisted of an insulating Zn-doped layer which was contacted with two surface probes, and blue light centered 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 (Pankove *et al.*, 1971b, 1972). This *metal-insulator-semiconductor* (MIS) *diode* was the first current-injected GaN light emitter, and it emitted green and blue light.

The RCA team speculated that magnesium might be a better choice of p-type dopant than zinc. They began growing Mg-doped GaN films using the MHVPE technique, and in July 1972,

obtained blue and violet emission centered at 430 nm as shown in Fig. 1.10 (Maruska *et al.*, 1972). One of these Mg-doped blue light MIS emitters continues to emit light even today. Maruska *et al.* (1973) described these efforts in a paper entitled "Violet luminescence of Mg-doped GaN". Note that the GaN films, even though Mg doped, did not exhibit p-type conductivity, so that the luminescence in these films was probably mediated by minority carrier injection or impact ionization in the high-field insulating regions of the films. Pankove and the RCA team offered a model for the operation of these devices based on impact ionization and Fowler–Nordheim tunneling, because the characteristics were virtually independent of temperature (Pankove and Lampert, 1974; Maruska *et al.*, 1974a, 1974b). Of course, these devices were inefficient, and as a consequence, Tietjen, who had stimulated the work, now terminated it by ordering "stop this garbage" – words that Maruska (2000) still vividly remembers.



Fig. 1.10. Blue light emission found in 1972 caused by recombining electron-hole pairs created in a highly resistive GaN structure doped with Si and Mg (courtesy of Maruska, 2000).

1.6 History of blue, green, and white LEDs based on GaInN p-n junctions

After the research efforts of Pankove and co-workers had ended, work on GaN virtually ceased. In 1982 only a single paper was published on GaN. However, Isamu Akasaki and co-workers in Nagoya, Japan, refused to give up, and in 1989 they demonstrated the first true p-type doping and p-type conductivity in GaN. The stubborn Mg acceptors were activated by *electron-beam irradiation* (Amano *et al.*, 1989). It was later shown that a high-temperature *post-growth anneal* of Mg-doped GaN also activates Mg dopants in GaN (Nakamura *et al.*, 1994a). Superlattice doping (Schubert *et al.*, 1996) further enhances the activation efficiency of deep acceptors. These p-type doping breakthroughs opened the door to efficient p-n junction LEDs and laser diodes. Today, Mg-doping of GaN is the basis for all nitride-based LEDs and laser diodes.

Subsequent to the attainment of p-type doping, the first GaN p-n-homojunction LED was reported by Akasaki *et al.* (1992). The LED that emitted light in the ultraviolet (UV) and blue

spectral range, was grown on a sapphire substrate. The result was presented at the "GaAs and Related Compounds" conference held in Karuizawa, Japan in 1992. The LED had an efficiency of approximately 1%. This was a surprisingly high value for the highly dislocated GaN material grown on the mismatched sapphire substrate. It was also the first demonstration that nitride LED efficiencies are not affected by dislocations in the same adverse manner as III–V arsenide and phosphide light emitters.

A name closely associated with GaN LEDs and lasers is that of the Nichia Chemical Industries Corporation, Japan. A team of researchers that included Shuji Nakamura and Takashi Mukai has made numerous contributions to the development of GaN growth, LEDs, and lasers. Their contributions included the demonstration of the first viable blue and green GaInN doubleheterostructure LED (Nakamura *et al.*, 1993a, 1993b, 1994b) that achieved efficiencies of 10% (Nakamura *et al.*, 1995), and the demonstration of the first pulsed and cw GaInN/GaN current injection *blue laser* operating at room temperature (Nakamura *et al.*, 1996). Initially, a particular design, the two-flow organometallic vapor-phase epitaxy (OMVPE) growth-system design was used (Nakamura *et al.*, 1991). However, the use of two-flow OMVPE at Nichia Corporation has been discontinued (Mukai, 2005). Detailed accounts of the team's contributions were given by Nakamura and Fasol (1997) in the book *The Blue Laser Diode* and by the Nichia Corporation in the booklet *Remarkable Technology* (Nichia, 2004).



Fig. 1.11. Array of GaInN/GaN blue LEDs manufactured by the Nichia Corporation (after Nakamura and Fasol, 1997).

Blue LEDs made by the Nichia Corporation are shown in Fig. 1.11. A common application of high-brightness GaInN green LEDs is traffic signals as shown in Fig. 1.12. The earlier mentioned GaP:N green LEDs are not suited for this application due to their much lower brightness.

In 1990, when Nakamura entered the field of GaN devices while working for the Nichia Corporation, he was a 36-year-old engineer without a Ph.D., not a single publication, and no

conference contribution (Nakamura and Fasol, 1997). At the end of the 1990s, he had become a Professor at the University of California in Santa Barbara and a consultant for the Cree Lighting Corporation, a fierce competitor of Nichia. In 2001, he strongly criticized the Nichia Corporation and Japanese society. In the book entitled *Breakthrough With Anger*, Nakamura (2001) stated, "There is something wrong with this country. Industry and universities are terribly sick."







Fig. 1.12. Green traffic signals are one of the ubiquitous applications of GaInN/GaN green LEDs.

The GaInN material system is also suited for *white LEDs*. There are different approaches to white LEDs, including white LEDs based on phosphor wavelength converters (see, for example, Nakamura and Fasol, 1997) and on semiconductor wavelength converters (Guo *et al.*, 1999). Much progress is expected in the area of white LEDs, since they have the potential to deliver a substantially higher luminous efficiency compared with conventional incandescent and fluorescent light sources. Whereas conventional light sources have typical (demonstrated) luminous efficiencies of 15–100 lm/W, white LEDs have the potential for luminous efficiencies exceeding 300 lm/W.

1.7 History of AlGaInP visible-spectrum LEDs

The AlGaInP material system is suited for high-brightness emission in the red (625 nm), orange (610 nm) and yellow (590 nm) spectral range and today is the dominant material system for high-brightness emitters in that wavelength range. Figure 1.13 shows some of the common signage applications of red and yellow AlGaInP LEDs.

The AlGaInP material system was first developed in Japan for visible-spectrum lasers (Kobayashi *et al.*, 1985; Ohba *et al.*, 1986; Ikeda *et al.*, 1986; Itaya *et al.*, 1990). Efforts started with AlGaInP/GaInP double-heterostructure lasers using Ga_{0.5}In_{0.5}P as the active material, which

is lattice matched to GaAs substrates. The bandgap energy of lattice-matched GaInP is approximately 1.9 eV (650 nm), making the material suitable for visible lasers emitting in the red. These lasers are used, for example, in laser pointers and in digital video disc (DVD) players.



Fig. 1.13. Examples of red and amber AlGaInP/GaAs LEDs used in signage applications.

The addition of Al to the GaInP active region allows one to attain shorter emission wavelengths including the orange and yellow spectral region. However, $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ becomes an indirect semiconductor at Al compositions of $x \approx 0.53$, so that the radiative efficiency strongly decreases at wavelengths near and, in particular, below 600 nm. Consequently, AlGaInP is not suited for high-efficiency emission at wavelengths below 570 nm.

Subsequent to the AlGaInP laser development that occurred in the early 1980s, AlGaInP LED development started at the end of the 1980s (Kuo *et al.*, 1990; Fletcher *et al.*, 1991; Sugawara *et al.*, 1991). In contrast to the AlGaInP laser structures, the LED structures typically employ current-spreading layers so that the entire p-n junction plane of the LED chip lights up and not just the region below the top ohmic contact. Further improvements were attained by using multiple quantum well (MQW) active regions (Huang and Chen, 1997), coherently strained MQW active regions (Chang and Chang, 1998a, 1998b), distributed Bragg reflectors (Huang and Chen, 1997; Chang *et al.*, 1997), transparent GaP substrate technology (Kish and Fletcher, 1997), and chip-shaping (Krames *et al.*, 1999). Comprehensive reviews of the AlGaInP material system and AlGaInP LEDs were published by Stringfellow and Craford (1997), Mueller (2000), and Krames *et al.*, 2002).

1.8 LEDs entering new fields of applications

As devices with higher power capabilities have become available, new application areas emerge constantly. Figure 1.14 shows the use of LEDs integrated into medical goggles worn by a surgeon during an operation (Shimada *et al.*, 2003). The LED-based light source promises substantial weight savings and fulfills the stringent requirements of high-quality color rendition required during medical operations.



Fig. 1.14. (a) First goggle with integrated white LEDs used for (b) illumination during medical surgery (after Shimada *et al.*, 2001; Shimada *et al.*, 2003)

LED-based automotive headlights were first introduced by Audi Corporation in 2004 using Lumileds Lighting's Luxeon devices. The car is shown in Fig. 1.15.



Fig. 1.15. First automotive daytime running lights based on LEDs.

The use of LEDs in large-scale display and signage applications continues unabated. A seven-story high display and an animated pedestrian traffic signal are shown in Figs. 1.16 and 1.17.

LEDs have also entered the domain of the arts. Figure 1.18 shows the accent-lighted Stone Bridge across the Danube River located in Regensburg, Germany. A line of 21 900 red lightemitting diodes stretches brightly across the bridge, thereby emphasising the link between the two banks of the river. Each LED stands for one month since the city was founded in the year AD 179 (Osram Opto Semiconductors, 2004). Figure 1.19 shows the accent-lighted entrance of the Science Based Industrial Park located in Hsin Chu, Taiwan, an industrial park housing numerous companies active in semiconductor technology.



Fig. 1.16. LED display consisting of 18 million LEDs covering front of building, located in New York City.



Fig. 1.17. Pedestrian sign indicating number of seconds left to cross street, located in Taipei, Taiwan.



Fig. 1.18. Stone Bridge located in Regensburg, Germany, illuminated by LEDs (after *Focus Magazine*, 2004).



Fig. 1.19. Artistic accent lighting at the main gate of the Science Based Industrial Park located in Hsin Chu, Taiwan (courtesy of K. R. Wang and L.-W. Tu, 2005).

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2

Radiative and non-radiative recombination

Electrons and holes in semiconductors recombine either radiatively, i.e. accompanied by the emission of a photon, or non-radiatively. In light-emitting devices, the former is clearly the preferred process. However, non-radiative recombination can, under practical conditions, never be reduced to zero. Thus, there is competition between radiative and non-radiative recombination. Maximization of the radiative process and minimization of the non-radiative process can be attained in a number of ways which will be discussed below.

2.1 Radiative electron-hole recombination

Any undoped or doped semiconductor has two types of free carriers, electrons and holes. Under equilibrium conditions, i.e. without external stimuli such as light or current, the law of mass action teaches that the product of the electron and hole concentrations is, at a given temperature, a constant, i.e.

$$n_0 p_0 = n_i^2 (2.1)$$

where n_0 and p_0 are the equilibrium electron and hole concentrations and n_i is the intrinsic carrier concentration. The validity of the law of mass action is limited to non-degenerately doped semiconductors (see, for example, Schubert, 1993).

Excess carriers in semiconductors can be generated either by absorption of light or by an injection current. The total carrier concentration is then given by the sum of equilibrium and excess carrier concentrations, i.e.

$$n = n_0 + \Delta n$$
 and $p = p_0 + \Delta p$ (2.2)

where Δn and Δp are the excess electron and hole concentrations, respectively.

Next, we consider recombination of carriers. The band diagram of a semiconductor with

electrons and holes is shown in Fig. 2.1. We are interested in the rate at which the carrier concentration decreases and denote the recombination rate as *R*. Consider a free electron in the conduction band. The probability that the electron recombines with a hole is proportional to the hole concentration, that is, $R \propto p$. The number of recombination events will also be proportional to the concentration of electrons, as indicated in Fig. 2.1. Thus the recombination rate is proportional to the product of electron and hole concentrations, that is, $R \propto n p$. Using a proportionality constant, the recombination rate per unit time per unit volume can be written as

$$R = -\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{\mathrm{d}p}{\mathrm{d}t} = Bnp \qquad (2.3)$$

This equation is the *bimolecular rate equation* and the proportionality constant *B* is called the *bimolecular recombination coefficient*. It has typical values of 10^{-11} – 10^{-9} cm³/s for direct-gap III–V semiconductors. The bimolecular recombination coefficient will be calculated in a subsequent section using the van Roosbroeck–Shockley model.



Fig. 2.1. Illustration of electron-hole recombination. The number of recombination events per unit time per unit volume is proportional to the product of electron and hole concentrations, i.e. $R \propto np$.

2.2 Radiative recombination for low-level excitation

Next, we discuss the recombination dynamics as a function of time. Consider a semiconductor subjected to photoexcitation. The equilibrium and excess electron and hole concentrations are n_0 , p_0 , Δn , and Δp , respectively. Since electrons and holes are generated and annihilated (by recombination) in pairs, the steady-state electron and hole excess concentrations are equal,

$$\Delta n(t) = \Delta p(t) . \tag{2.4}$$

Using the bimolecular rate equation, the recombination rate is given by

$$R = B \left[n_0 + \Delta n(t) \right] \left[p_0 + \Delta p(t) \right].$$
(2.5)

For the case of *low-level excitation*, the photogenerated carrier concentration is much smaller than the majority carrier concentration, i.e. $\Delta n \ll (n_0 + p_0)$. Using $\Delta n(t) = \Delta p(t)$ one obtains from Eq. (2.5)

$$R = B n_i^2 + B (n_0 + p_0) \Delta n(t)$$

= $R_0 + R_{\text{excess}}$. (2.6)

The first summand on the right-hand side of the equation can be identified as the *equilibrium recombination rate* (R_0) and the second term as the *excess recombination rate* (R_{excess}).

The time-dependent carrier concentration can be calculated from the rate equation

$$\frac{\mathrm{d}n(t)}{\mathrm{d}t} = G - R = \left(G_0 + G_{\mathrm{excess}}\right) - \left(R_0 + R_{\mathrm{excess}}\right)$$
(2.7)

where G_0 and R_0 are the equilibrium generation and recombination rates, respectively.

Next, we assume that the semiconductor has been illuminated with light and excess carriers are generated. At the time t = 0, the illumination is switched off (i.e. $G_{\text{excess}} = 0$) as indicated in Fig. 2.2. The recombination rate can then be calculated by insertion of Eq. (2.6) into Eq. (2.7) and using $G_0 = R_0$. This yields the differential equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\Delta n(t) = -B(n_0 + p_0)\Delta n(t) . \qquad (2.8)$$

The solution of the differential equation can be obtained by separation of variables. One obtains

$$\Delta n(t) = \Delta n_0 e^{-B(n_0 + p_0)t}$$
(2.9)

where $\Delta n_0 = \Delta n(t = 0)$. Rewriting the result as

$$\Delta n(t) = \Delta n_0 \, \mathrm{e}^{-t/\tau} \tag{2.10}$$

allows one to identify the *carrier lifetime* τ as

$$\tau = \frac{1}{B(n_0 + p_0)}$$
 (2.11)

For semiconductors with a specific doping type, Eq. (2.11) reduces to

2 Radiative and non-radiative recombination

$$\tau_{\rm n} = \frac{1}{B p_0} = \frac{1}{B N_{\rm A}}$$
 for p-type semiconductors (2.12)

and

$$\tau_{\rm p} = \frac{1}{B n_0} = \frac{1}{B N_{\rm D}}$$
 for n-type semiconductors (2.13)

where τ_n and τ_p are the electron and hole lifetimes, respectively. Using this result, the rate equation, Eq. (2.8), can be simplified for semiconductors of a specific conductivity type. One obtains the *monomolecular rate equations*:

$$\frac{d}{dt}\Delta n(t) = -\frac{\Delta n(t)}{\tau_n} \qquad \text{for p-type semiconductors} \qquad (2.14)$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\Delta p(t) = -\frac{\Delta p(t)}{\tau_{\mathrm{p}}} \qquad \text{for n-type semiconductors.} \qquad (2.15)$$



Fig. 2.2. Carrier concentration as a function of time before, during, and after an optical excitation pulse. The semiconductor is assumed to be p-type and thus $p_0 >> n_0$. Electrons and holes are generated in pairs, thus $\Delta p = \Delta n$. Under low-level excitation as shown here, it is $\Delta n \ll p_0$. In most practical cases the equilibrium minority carrier concentration is extremely small so that $n_0 \ll \Delta n$.

Figure 2.2 shows the majority and minority carrier concentrations in a p-type semiconductor as a function of time (similar considerations apply if an n-type semiconductor is chosen). Note that Fig. 2.2 shows the case of *low-level excitation* in which the photogenerated carrier

concentration is much smaller than the majority carrier concentration. However, the photogenerated carrier concentration is much larger than the minority carrier concentration.

Once photoexcitation is terminated, the minority carrier concentration decays exponentially with a characteristic time constant denoted as the *minority carrier lifetime* τ . It is the mean time between generation and recombination of a minority carrier.

Note that the majority carrier concentration also decays with the same time constant τ . However, only a very *small fraction* of the majority carriers disappear by recombination, as illustrated in Fig. 2.2. Thus, for low-level excitation, the average time it takes for a majority carrier to recombine is much longer than the minority carrier lifetime. For many practical purposes, the majority carrier lifetime can be assumed to be infinitely long.

Theoretical and experimental values for the minority carrier lifetime in GaAs as a function of the doping concentration are shown in Fig. 2.3 (Hwang, 1971; Nelson and Sobers, 1978a, 1978b; Ehrhardt *et al.*, 1991; Ahrenkiel, 1993). The theoretical line in the figure is calculated from Eq. (2.10) using $B = 10^{-10}$ cm³/s. In nominally undoped material, minority carrier lifetimes as long as 15 µs have been measured in GaAs at room temperature (Nelson and Sobers, 1978a, 1978b).



Exercise: *Minority carrier lifetimes.* Calculate the minority carrier lifetime in p-type GaAs at doping concentrations of 10^{15} and 10^{18} cm⁻³ using a bimolecular recombination coefficient of $B = 10^{-10}$ cm³/s. Assume that one could fabricate GaAs without any impurities. What would be the carrier lifetime in intrinsic GaAs with a carrier concentration of 2×10^6 cm⁻³?

Solution:	$\tau_n = 10 \ \mu s$	for $N_{\rm A} = 10^{15} {\rm ~cm}^{-3}$
	$\tau_n = 10 \text{ ns}$	for $N_{\rm A} = 10^{18} {\rm cm}^{-3}$
	$\tau = 2500 \text{ s}$	for undoped GaAs.

Discuss how the modulation speed of communication LEDs is affected by the radiative lifetime and the doping concentration.

2.3 Radiative recombination for high-level excitation

For the case of *high-level excitation*, the photogenerated carrier concentration is larger than the equilibrium carrier concentration, i.e. $\Delta n \gg (n_0 + p_0)$. The bimolecular rate equation (Eq. 2.3) is then given by

$$\frac{\mathrm{d}\Delta n(t)}{\mathrm{d}t} = -B\,\Delta n^2 \,. \tag{2.16}$$

Solving this differential equation by the separation-of-variables method and using the initial condition $\Delta n(0) = \Delta n_0$ yields the solution

$$\Delta n(t) = \frac{1}{Bt + \Delta n_0^{-1}} \qquad (2.17)$$

This solution represents, in contrast to the low-density approximation, a *non-exponential* carrier decay.

In an exponential decay, it takes the time constant τ for the carrier concentration to decrease from Δn_0 to $\Delta n_0 e^{-1}$. Using the same definition for the non-exponential decay given by Eq. (2.17), the "time constant" can be calculated from the slope of the decay by using the equation

$$\tau(t) = -\frac{\Delta n(t)}{\frac{\mathrm{d}\Delta n(t)}{\mathrm{d}t}} .$$
(2.18)

Using this definition for the non-exponential decay of Eq. (2.17), one obtains the "time constant"