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LEDs: the new revolution in lighting / Les LED : la nouvelle révolution de l'éclairage

Historical perspective on the physics of artificial lighting

Perspective historique sur la physique de l'éclairage

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ABSTRACT

We describe the evolution of lighting technologies used throughout the ages, and how the need for improvements was such that any new technology giving better and cheaper lighting was immediately implemented. Thus, every revolution in energy sources – gas, petrol electricity – was first put to large-scale use in lighting. We describe in some detail several "ancient" techniques of scientific interest, along with their physical limitations. Electroluminescence – the phenomenon by which LEDs directly convert electricity into light – was long thought to only be of use for indicators or flat panel displays supposed to replace the bulky cathode-ray tubes. The more recent uses of LEDs were mainly for street traffic lights, car indicators, small phone displays, followed by backlighting of TV screens. LED lamps for general lighting only emerged recently as the dominant application of LEDs thanks to dramatic decrease in cost, and continuous improvements of color quality and energy conversion efficiency.

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RÉSUMÉ

Nous décrivons l'évolution des technologies d'éclairage utilisées à travers les âges, et comment le besoin d'améliorations était tel que toute nouvelle technologie donnant un éclairage meilleur et moins cher a été immédiatement mise en œuvre. Ainsi, chaque révolution en matière de sources d'énergie – gaz, pétrole, électricité – a été dans un premier temps utilisée à grande échelle dans l'éclairage. Nous décrivons en détail plusieurs techniques anciennes présentant un intérêt scientifique, ainsi que leurs limites physiques. L'électroluminescence – le phénomène par lequel les LED convertissent directement l'électricité en lumière – a longtemps été considérée comme étant uniquement utile pour les indicateurs ou les écrans plats censés remplacer les tubes cathodiques volumineux. Les utilisations les plus récentes des LED concernaient principalement les feux de signalisation, les indicateurs pour voitures, les écrans de téléphone, suivies par le rétroéclairage des écrans de télévision. Les lampes LED pour l'éclairage général ne sont apparues que récemment, comme leur application dominante grâce à une réduction spectaculaire des

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coûts et à des améliorations continues de la qualité des couleurs et de l'efficacité de la conversion d'énergie.

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1. Historical perspective up to the 20th century – Lighting through ages: a major human need and energy use

Artificial lighting has always been a fundamental human need that has continuously mobilized a significant share of resources, right now 15 to 20% of electricity in developed countries. This may sound like a lot, but it reflects the need for lighting. Despite numerous improvements through new emerging technologies, lighting has always exercised and is still exerting a major drain on energy resources. Any progress in chemical resources, physical phenomena has been put to good use throughout centuries to increase efficiency, improve light quality and decrease costs.

1.1. Early lighting systems [1,2]

Lighting methods have changed from burning wood in fireplaces or torches to oil lamps (vegetable or animal, which includes whale oil from the 16th to 19th century, which almost led to extinction) with wicks, and then to candles (based on oil, tallow, or wax) from 1200 onwards. There were continuous improvements: for instance, beeswax-based candles were producing less smoke and smell, and better light, but were more expensive. Depending on technological advances, availability and cost, sources for candles material evolved from animal to plant to whales to paraffin (extracted from minerals like coal or petrol), and often coexisted. Oil lamps also evolved from wicks placed directly in the oil reservoir to advanced designs where the wick is fed with air through a chimney to ensure a fuller oil combustion (Argand lamp, 1783, equivalent to 6–8 candles), much resembling the later petrol/kerosene lamps that displaced the oil lamps from the 1850s on.

Lighting remained a luxury for a long time: between 1 and 2% of the average income was spent until 1950 in Europe (1% in the UK) with a very limited individual lighting consumption until 1800, which then increased by a factor of 1500 between 1800 and 1950 (Fig. 1b, c). For a long time, until 1800, the cost of lighting hardly decreased, but between 1800 and 1950 it decreased by 600 times. Between 1950 and 2000, the cost further decreased by a factor of 6, consumption increased by 5X times as well as GDP per capita, reducing the cost of lighting to 0.17% of income [3].

As of today, there were at all times many different needs (or markets) for lighting: private individual house, palaces or temples, streets, lighthouses, which required different solutions.

As an example of the development of one key need, public lighting was a critical demand for safe walking in streets at night. Before its implementation, the only way to find one's way was to have a lantern or rent the service. For a very long time, the public service was minimal: ancient Romans used oil lamps filled with vegetable oil in front of their houses and had special slaves whose only duty was to take care of those lamps, to light them, extinguish them, and make sure that they always had oil. First organized public lighting was done on 1417 in London with the mayor ordering owners to hang lanterns in the early night hours during the winter months. Paris followed in 1524 with an order to put lights in windows facing streets [4].

As is evident from Fig. 1b, while lighting generation remained stagnant during many centuries, things changed dramatically in the 19th century, with three revolutions in lighting, successively due to gas, kerosene, and electricity. The main factor for the jump in individual light consumption are the increase in light source efficiency (Fig. 1a) and the decrease in lighting fuel cost by a factor of 10 between 1700 and 2000, as GDP per capita "only" increases by a factor 20 between 1700 and 2000 [3].[1] At the appearance of each new source of energy capable of producing light, most of that new energy production was consumed by lighting, so critical was the demand for better light (Fig. 1d).

1.2. Gas lighting

Efficient lightning only started with the demonstration of gas lighting fueled with coal gas (produced by the distillation of coal, a by-product of coke fabrication for the steel industry, up to then rejected in the atmosphere). Efficient gas production appeared at the beginning of the 19th century. The cost of gas lighting was only 25% that of oil lighting, and thus it grew rapidly [2]. Local gas production and distribution companies quickly developed: in 1860, there were more than 400 gas companies in the US, 900 in Britain, and 266 in Germany [2]. London got its first gas streetlight in 1807. Other cities followed, with Paris starting gas lighting in 1820. Gas was supplied to lantern poles through pipes running in the cities.

The light-emitting species in gas flames is due to de-excitation of the heated carbon species originating in hydrocarbons ("illuminants") dissolved in coal gas, producing a bright yellow color, but also soot. The initial coke production process produced such illumination gas by partial pyrolysis of coal in air, but it produced poor coke for metallurgy. The process was refined in the 1850s by coal burning in air and steam cycles, producing gas containing only H_2 and CO after elimination of

[1] For a discussion of the relation between GDP and lighting consumption, see [7].

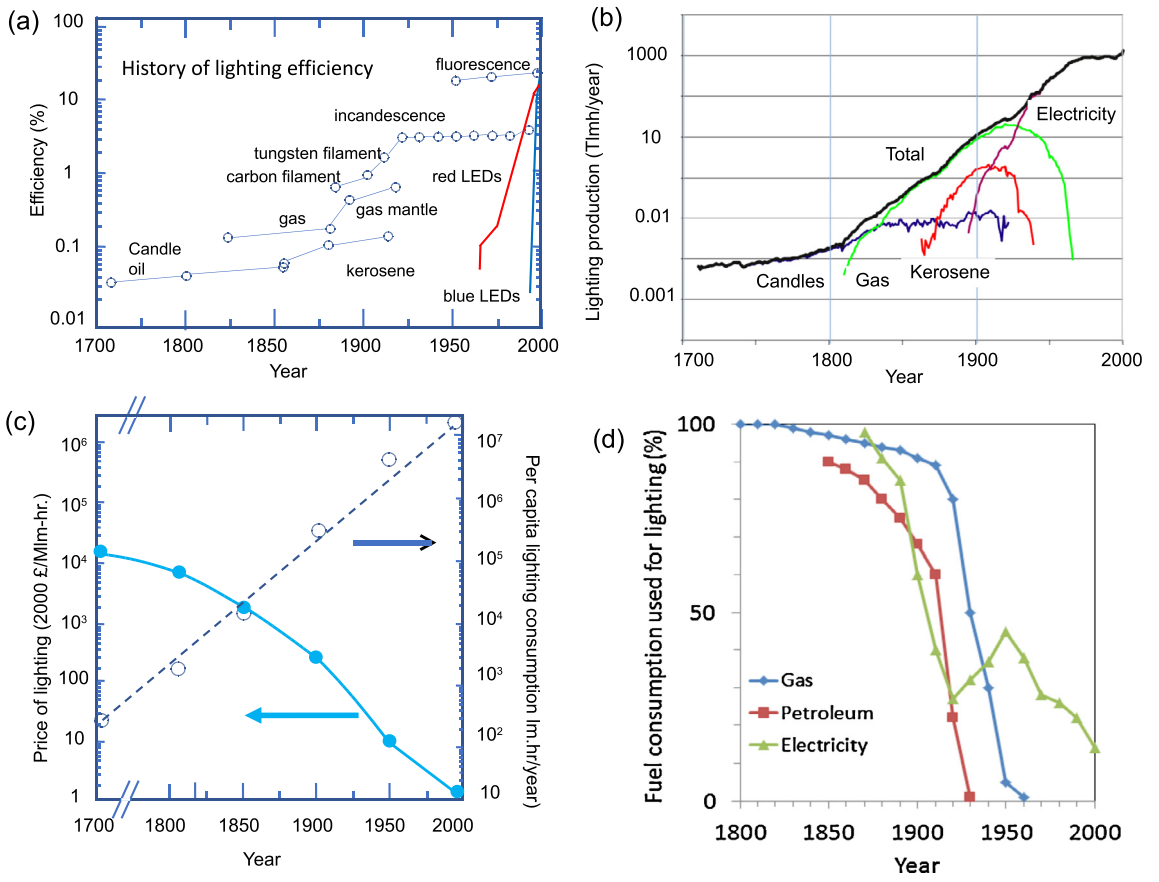

Fig. 1. Time evolution of lighting: (a) evolution of light source efficiency [5,6]; (b) evolution of yearly light production (Tlm·h) (from [3]); (c) evolution of lighting prices (in £ 2000 and lighting consumption per capita, UK (after [3]); (d) evolution of the share for lighting of new lighting energy sources (after [3]).

A word on units

Lighting units are not connected to the MKS system as they deal with physiological properties of light.

The basic units are lumens, candela, lux representing respectively the luminous flux (a source property), the luminous intensity (a source property), the source luminance, the illuminance (the result of illumination of an area).

The relation between lumens and watts depends on the light wavelength. For monochromatic light, it is given by the photopic response curve of the eye at normal light illuminations (under low light, the response curve is the scotopic one). The maximum efficacy of the eye response defines the lumen; 1 W of light at 555 nm gives a luminous flux of 683 lm. The candela, unit of luminous intensity, gives the luminous flux per steradian. Therefore, the light of a candle (the definition of the candela) represents a luminous flux of $4\pi \times 1$ lm $\approx$12.6 lm. Luminance is the luminous intensity per unit area (cd/m^2). One lux is the illuminance provided by one lumen per unit area (1 lm/m^2).

Modern candles typically produce 80 W of heat and light, 13 lumens of light, thus operate at 0.16 lm/W efficacy.

The Internal Quantum Efficiency of an LED (IQE) is the ratio of photons emitted inside the LED to the number of electrically-injected electron–hole pairs; the Light-Extraction Efficiency (LEE) is the ratio of photons emitted outside the LED to those emitted inside; the Wall-Plug Efficiency (WPE) is the ratio of the optical power emitted by the LED to the electrical power supplied.

The efficiency of an electrical light source is then defined by three numbers, WPE (conversion of electrical watts to optical watts), the luminous efficacy of radiation (number of lumens per optical watts for the emitted spectrum), LER, and the luminous efficacy (lm/electrical watts). The LER illustrates the distribution of the optical power among the visible spectrum weighted by the eye response curve. The luminous efficacy is then the product of the WPE of a light source by the luminous efficacy of its spectrum, the LER (Fig. 2).

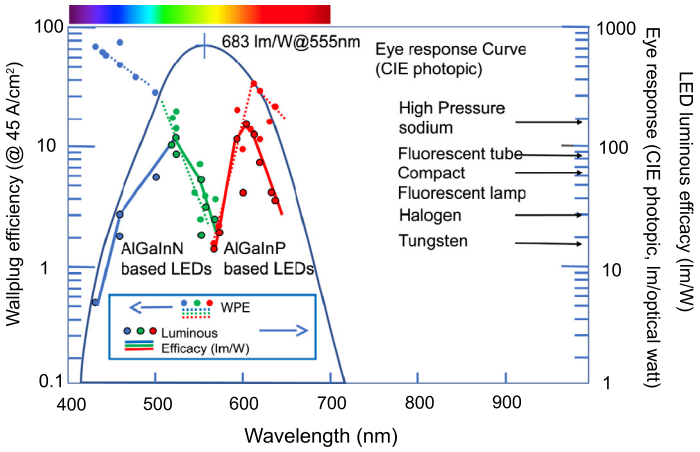

Fig. 2. Wallplug efficiency (WPE), luminous efficacy, and eye response curve (full line curve). Note that the luminous efficacy (lm/W) is the product of the WPE and the eye response, hence violet LEDs have a poor luminous efficacy in spite of their excellent WPE.

nitrogen.[2] The produced coke had metallurgical quality, but it burned with a blue flame due to the absence of hydrocarbons, as well as does gas from oil or natural gas. Thus, gas lighting would have had a short lifetime, had it not been for the use of other schemes to improve light emission from materials heated by a blue flame, lime rods, and incandescent mantles.

A first specific lighting need requiring gas lighting was that of directed lighting such as in lighthouses, theaters, or long-range communications such as for ships or land surveying. Projectors first relied on oil lamps flames associated with parabolic reflectors or Fresnel lenses. For theaters, the limelight, discovered in the 1820s, was a major advance once gas became available in cities: heated by a gas flame, a piece of lime (CaO) – hence the name limelight for theater lighting – produces a bright source of light, ideal for producing a sharp beam of light in compact projector systems [1,8]. This is due to the low IR emission from the heated material, which leads to an enhanced visible light emission relative to a blackbody heated with the same power (see below the extended discussion of the better solution, the Welsbach mantle). Limelight was from the middle of the 19th century on the major stage source until the advent of the electric arc. Other oxides also display high brightness when heated. The use of limelight was limited to large lighting systems as supervision was necessary.

A major and much more widely used advance in gas lighting came with the rare-earth-doped mantles, consisting in oxides doped with rare earths (variably called Auer or Welsbach mantles, from the name of their inventor, Carl Auer von Welsbach) – for an early and detailed history of the Auer mantle, see the report leading to the attribution of the Elliott Cresson medal in 1900 to Auer [9]. Such doped ceramics have weak absorption in the whole infrared region due to their transparent ceramic, but have significant absorption in the green or the blue due to the rare earths. Conversely, they have significant emission in the visible without radiating much infrared according to Kirchhoff's radiation law. The mantle reaches the flame temperature, hence high visible emission due to the Cerium with little gas consumption due to the weak infrared emission. Heated at the flame temperature of 700–900 °C, it radiates like a source at 1700–1900 °C (Fig. 3). The mantle is a mixture of thorium oxide with 1–2% of rare earth oxides, at the beginning cerium oxide. The latter is the main visible emitting species (it is noteworthy that Ce in YAG is today the main ingredient for high-efficiency phosphors in LED lamps). The mantles are produced by dipping a meshed fabric (e.g., cotton, silk, nylon...) into a solution of thorium and rare earth nitrates. Upon the operation at high temperature, the fabric is calcinated and what remains is a mesh of the metal oxide ceramic. The success of Auer mantles was in great part due to the simplicity of their fabrication.

The first Auer lamps were installed in 1891 at the Vienna opera house. This was the first large-scale use of rare earths [10]. In 1893 43,000 lamps were produced [11], and by 1913 worldwide annual production reached 300 million units. The gas lamp with Auer mantle remained competitive with the electric lamps because of its much lower initial and operating costs. The gas mantle invention stretched the actual use of gas lighting well into the era of the first 50 years of electrical lighting, due to their high efficiency, 2.2 lm/W, increasing gas lighting efficiency by a factor of five. They are still used for portable white lighting for camping, where gas bottles are also used for cooking, and are thus readily available. They are presently a source of concern: thorium is naturally radioactive and it is a major environmental issue in the extraction of rare earth ores as these always contain thorium. Mantles are often now using yttrium oxide in place of thorium [12].

Auer-like mantles were also used in electrically-driven lamps, from visible to infrared, where both gas and electrical heating are used, or with only electrical heating, such as in the Nernst lamp or todays' globar lamp, where a SiC filament is used to obtain a high-brightness IR source. Mantles were and are still used today to enhance the efficiency of kerosene lamps, which are still widely used in developing countries where they are the major lighting sources [14].

[2] It should be noted that the distribution network of such gas constituted a first case of hydrogen distribution, showing that large-scale distribution of hydrogen (considered to be a major future energy vector of renewable energy) is quite possible.

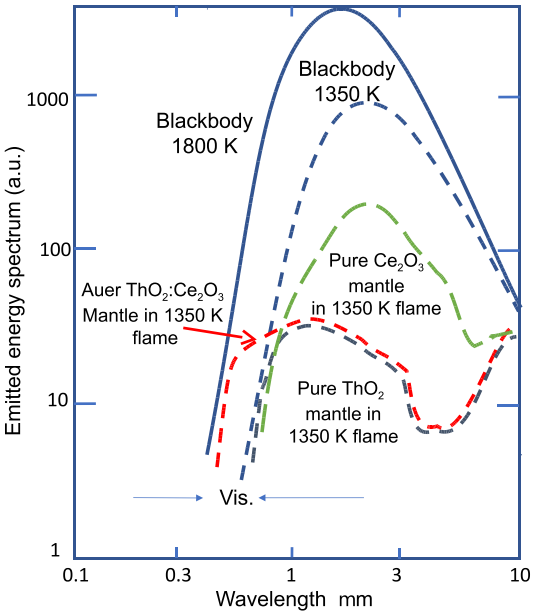

Fig. 3. Emission spectra of blackbodies at 1800 K and 1350 K, and of gas-heated mantles with either pure ThO_2 (green), Ce_2O_3 (blue) or Auer mantle, TiO_2/Ce_2O_3 (red) (after [13]).

The use of heat-converting mantles is having a renaissance, at the research level at least, in the field of thermophotovoltaics [15], converting heat into electricity by first converting heat into light with wavelengths potentially adapted to solar cells bandgaps, first proposed by Aigrain [16–18]. Such systems would be particularly interesting for heat recuperation, for instance in power plants or cars. They also can be operated day and night at short notice. The overall efficiency is then the product of the conversion efficiency of heat into useful light by the mantle times the solar cell efficiency under the mantle illumination. The Welsbach mantle is of course a choice converter of heat to visible light. Competing implementations rely on using selective filters to extract visible light from a heated source to power the solar cell while recycling the infrared light with heat mirrors. Such solutions are seeing a large research effort with the availability of nanostructured optical systems (plasmonic or photonic crystals), which in principle allow a 3D spatial and spectral control of light propagation. Such selective filter and mirror systems are also now contemplated to improve the incandescent lamp efficiency [19], but the performance required to compete with other visible light sources seems out of reach [20]. This conversion scheme of heat to electricity is of course in competition with thermoelectrics.

1.3. Kerosene lighting systems

Gas lighting in the 19th century was not a general solution for home lighting as widespread gas distribution to homes took a long time to develop, even in densely populated cities. For the countryside, gas distribution was not expected because of cost. The next generation of energy for home lighting replacing oil was then kerosene, first extracted from coal, a few years later from petrol in the mid-1850s, achieving a major revolution for domestic lighting. The kerosene lamp allowed a huge increase in lighting quality and intensity when compared to candles or oil lamps, and it produced less smoke and soot. When Auer mantles became available, they were of course adapted to the kerosene lamps, whose efficiency they increased. Due to their low cost and versatility, gas and kerosene lamps remained long in competition with electric lighting. Kerosene lighting is still today the only available source in the vast regions of the world where no electricity is available, providing lighting at a very high relative cost, however now being rapidly replaced by solar-powered LED systems [14].

1.4. The prehistory of electrical lighting [1,2,21]

Bright light was produced from electric arcs as early as 1800, but electrical lighting had to wait for the availability of electrical production facilities allowed by the discovery of electric induction by Faraday. As soon as electricity generation from dynamos became available in the mid-1860s, electrical lighting developed rapidly (Fig. 1b). It was the origin of many local electricity plants and companies, as electricity was to be used in the vicinity of the production plant. Electricity was first used in specialty lighting such as in theaters, etc. to replace the limelight with its obvious hazards. They first relied on electric arc lamps from 1846 on, which however required monitoring or complex machinery to take care of the consumption of electrodes. They allowed spectacular (for the epoch) spotlight lighting. Early electric streetlight using arc lamps was first used in 1878 in Paris, where the latter progressively replaced gas lanterns. Arc lights however produced cold light and had severe lifetime problems. In time, they were replaced with incandescent lamps (see the change in slope for the lumen·h

production in Fig. 1c) that were cheaper and lasted longer, while arc lamps remained useful on industrial sites or theaters. Today, legacy streetlights use high-intensity discharge lamps, the modern version of the arc lamp where light is produced by excitation of atoms into plasma species, most often high-pressure sodium lamps.

2. Historical perspective 2 – 20th-century electric lighting, pre-LED technologies

A variety of electrical lighting sources were invented due to the many physical phenomena leading to light emission allowed by electricity excitation (Table 1). They are often used in different markets due their vastly different performance, particularly power, color temperature, and color rendering. They are being progressively replaced by LED lamps that outperform them in any specification (see, e.g., the document produced by the Department of Energy on energy savings by LED adoption [22]).

The first practical electric lamp was the filament incandescent lamp as soon as it appeared in the 1880s. It took more than 30 years to develop from the heated carbon filament by Edison to tungsten filaments in inert atmosphere (1913), raising the efficiency by about 10-fold to nearly 10 lm/W in the 1920s [2,21,23]. Their performance is limited by two main factors: their blackbody emission concept, which leads to a large fraction of the emitted spectrum in the infrared; the limited filament temperature, which leads to a maximum of the emitted spectrum in the infrared. The tungsten filament is quite optimum as tungsten is refractory with a melting temperature of 3422 °C. In addition, tungsten has a strongly decreasing emissivity in the infrared, which somewhat improves its visible emission relative to the infrared loss [23].

A remarkable progress in incandescent lamps was reached in the 1960–1970s with the advent of the quartz halogen lamp. It relies on a self-repair process to operate at 200 °C hotter temperatures than usual incandescent lamps; these usually break down by developing a hot point where the filament is thinnest (highest resistance), which will vaporize the whole filament. Conversely, the tungsten halide gas present in the halogen bulb decomposes into metal and pure halogen gas at the point of the filament with highest temperature. This is the region of the filament which is the thinnest and it is thus regenerated to a thickness comparable to the rest of the filament. Due to their higher operating temperature leading to their better efficiency, these lamps had to originally use quartz bulbs, now high-temperature glass, to avoid glass softening.

Further progress occurred with the various discharge lamps (mercury vapor, sodium, or metal halides, fluorescent tubes, or lamps) [24].

Gas discharge lamps (so-called fluorescent lamps) rely on the UV light generated by excited atoms which is down-converted to visible light by phosphors placed on the glass envelope of the lamp. They appeared in the 1930s with efficiencies in the 35 lm/W range. The next step was the sodium low- and high-pressure discharge lamps, which have an efficiency of 150 and 80 lm/W respectively, however with a yellowish color that makes them only acceptable for outdoors lighting, with the benefit of reducing light pollution to a narrow spectral range, but at the cost of reduced color rendering.

These “classical” lamps, however, reach their limits: the efficacy of converting electrical power into luminous power reaches to 150 lumens per watt for the best ones, but is most often in the 80–100 lm/W range. These lamps also have a number of possible intrinsic drawbacks, sometimes simultaneously: difficulty in modulating the luminous flux without losing on the conversion efficiency (the filament temperature of an incandescent lamp decreases when its wattage is decreased), emission in all directions that requires a reflector to redirect the emitted light and introduce at least 30% loss, wear (or even breakdown) during switching on/off, need for high voltage for starting, heating time of high efficiency lamps such as compact fluorescent lamps (CFLs), inability to restart certain lamps when hot, poor “quality” of the light emitted, toxic products in certain lamps (mercury in CFLs).

3. Historical perspective 3 – The prehistory of electroluminescence

The demand was thus great for a new lighting mechanism, more flexible, and more efficient than incandescence first, but also than fluorescent tubes and other discharge lamps.

Electroluminescence, the direct conversion of electricity into luminous energy, was not the result of a deliberate search, but was serendipitously discovered by Round in 1907 in studies of the rectifying effect for alternating currents by crystals of silicon carbide SiC (carborundum) [25]. It should be reminded that in the beginning of the 20th century, the major new “exciting” technology drivers were radio broadcast and communications. The emitter and receiver technologies were very poorly understood (to say the least of, for instance, the “coherer” emitter and receivers [26] consisting in changes of the electrical conduction of slightly oxidized metal particles in a glass tube under irradiation by an electromagnetic wave) and very erratic. Solid-state device solutions were actively pursued, and a leading technology was the metal point contact demodulator based on galena (PbS)-type materials, invented in 1898 by Braun, the basis of the most popular radio receiving systems until the mid-20ies when vacuum thermionic valves where found to be much more reproducible. During his rectifiers studies, Round (working on radio research at the Marconi company) observed in 1907 weak luminescence from SiC. His brief note of 21 lines describes the appearance of light emission when current is passed between two metallic tips through a SiC crystal, the color varying with the voltage applied, starting at 10 volts. However, this work was not continued (everyone was busy with radio technology) and had fallen into oblivion until Round’s letter to editor was retrieved in 1969 [27]. A soviet researcher, Losev (variably also spelled Lossev, Lossew, etc. in the literature), independently rediscovered the

Table 1
Performances and characteristics of various lighting sources.

Lamp type	Physical phenomenon	Luminous efficacy (Lm/W)	Power (W)	Lamp cost	Operating costs	Color temperature (K)	Averaged lifetime	Remarks
Oil lamp/candle	Light-emitting carbon-based plasma excited by flame	0.3	80	low	high	1700		Many sources: olive oil in the Mediterranean since 3000 BC, tallow, beeswax, whale oil...
Gas/kerosene mantle	Plasma created by flame	2	10–50	medium	high	1800		Highly used in developing countries without electricity
Incandescent	Blackbody by resistive heating; low-IR emissivity tungsten filament	10	3–500	low	high	2400	1000	Warm color temperature High electricity costs
Halogen	Blackbody by resistive heating with filament regeneration	15–20	5–500	medium	high	2700	3000	Warm color temperature High electricity costs
Fluorescent tube	Electrical gas discharge creates UV; phosphor-coating conversion	60–100	4–200	medium	medium	5000	20,000	Needs high-voltage power supply Contains Hg
Compact fluorescent lamp	Electrical gas discharge creates UV; phosphor-coating conversion	50–75	3–120	medium	medium	3500–5000	10,000	Need high-voltage power supply Needs warm-up Delay for restrike Contains Hg
High-intensity discharge metal halide	Electrical arc leading to gas discharge	60–115	30–2000	high	low	6500	15,000	Needs high voltage power supply Needs warm-up Dim with aging Delay for restrike
Low-pressure sodium	A gas discharge excites Na in states emitting at 589 nm	100–200	10–180	medium	low	1700–2200	15,000	Needs high-voltage power supply Needs warm-up Delay for restrike
High-pressure sodium	High-pressure Na emits broader, whiter light than low-pressure Na	100–150	35–1000	high	low	2200–2700	15,000	Needs high voltage power supply Needs warm-up Delay for restrike
LED lamps	Direct electricity-to-light conversion	80–200	2–20	medium	low	2700–6000	50,000	

phenomenon in 1922 [28,29] in his research on rectifiers and oscillators based on ZnO and SiC. Through his systematic studies, he discovered two mechanisms of electroluminescence, one by *direct bias* injection in the semiconductor, the one used today in LEDs (type-II luminescence in Losev's terms), the other by excitation of the semiconductor under *high reverse bias* voltage (called by him type-I luminescence) [30].[3] Amazingly, in 1928 he published an explanation of the emission by linking it with the theory of quanta, as he observed that under optimal observation conditions the emission of light quanta of energy $h\nu$ occurred when the applied voltage V was such that $eV \cong h\nu$ [32]. It should be noted that at the time the band theory of insulators and semiconductors did not exist (it only came in 1932 with the papers by Wilson [33]), thus he could not attribute the emission's origin to the transitions between the conduction and valence band quantum states of the semiconductors. He therefore relied on the interpretation of the spectral continuum of X-ray emission, due to the braking radiation (bremsstrahlung) of electrons *accelerated in vacuum* to a kinetic energy eV at a voltage V and penetrating a crystal: there, the electrons give up their energy when deflected by nuclei by emitting photons, the most energetic of which, corresponding to the loss of all kinetic energy in a single photon emission event, having an energy $h\nu = eV$. For Losev, the electrons would be accelerated *in the crystal* by the applied electric field, and their radiation would be due to their bremsstrahlung electrons in the crystal.

Today's explanations of Losev's observations in his single doping samples (either n type or p type, he seems to have had both) are based on the band structure of semiconductors, and on injection of minority carriers (type II), or creation by avalanching of electron–hole pairs (type I), through rectifying metal contacts (Fig. 4d or 4c, respectively): we know that it is very difficult to accelerate electrons (or holes) by an electric field to kinetic energies corresponding to visible photons in semiconductors or insulators crystals. At weak accelerating electric fields in homogeneous semiconductors, electron relaxation occurs by their interaction with the lattice by emitting phonons, and the maximum kinetic energy of the electrons is equal to the energy of the optical phonons, threshold for ultrafast phonon emission, far from the band-gap energy. Applying much higher electric fields and voltage is limited by the phenomenon of dielectric breakdown, which is, when intrinsic, due to hot carriers creating avalanche impact ionization. This is, however, the emission mechanism of Losev type-I luminescence. Applying in a controlled manner, thanks to an insulating depletion region, a high reverse bias (tens of volts) [30], electrons in the high electric field can gain kinetic energy faster than losing it by phonon emission and reach kinetic energies larger than the bandgap (Fig. 4c). They can then lose their excess energy by exciting e–h pairs by impact ionization, which can then recombine by emitting photons. Current through the device is limited by an injecting blocking contact to avoid breakdown. This is the effect rediscovered by Destriau (see below). The mechanism of type-II luminescence observed by Losev under forward bias at lower voltage is due to minority carrier injection in a homogeneously doped semiconductor through a metal-semiconductor contact (Fig. 4d).

Today, emission of light under an electric field occurs under situations where minority carriers such as electrons can be excited in the conduction band of a semiconductor in the presence of holes of a p-doped region (or vice-versa) by direct injection into a p–n junction (similarly to Losev type-II luminescence of a metal-semiconductor junction, Fig. 3d), which requires applied voltages such as $eV = E_g \approx h\nu$, of the order of volts. Actually, Losev also observed p–n junction electroluminescence for samples where he observed conducting regions separated by insulating regions [34], clearly samples with both types of dopants [35] separated by the depletion of a junction. Light emission was then due to the direct injection of minority carriers in p–n junctions, as described below in section 3.2 and Fig. 6.

It is difficult to overestimate the size and quality of Losev's discoveries, who, in addition to electroluminescence, discovered negative differential resistance, made full solid-state radio receivers, demonstrated solid-state optical transmission of signals, even apparently the transistor (for good introductions to his works in English, see [36–38]. Losev's studies were not taken up by others. (Losev died of hunger during the siege of Leningrad in 1942, and he had no followers, having worked alone without creating a "school".)

For the sake of completeness, it should be noted that the bremsstrahlung hypothesis of emission by accelerated electrons in solids was revived recently [39] as the source of EL for light emission energy below the bandgap energy, this excluding e–h pair recombination across the gap (see, e.g., [40,41]).

We also know today why there are no such light emission mechanisms in metals leading to electroluminescence: the electrons in metals have a continuum of energy in the conduction band, without a band gap, which cannot allow electrons to reach kinetic energies much different from the Fermi energy. Due to metal high electrical conductivity, electron velocities acquired under the allowable electric fields and current densities are far too low for direct light emission. On the other hand, the relaxation of the electrons accelerated by emission of phonons produces heating and they emit by incandescence, such as in incandescent filaments.

Electroluminescence developed from 1936 on another track, following the discovery by Destriau at University of Bordeaux of the effect named after him, the electroluminescence of zinc sulfide powder (ZnS) in an insulating matrix subjected to strong alternating electric field (applied voltage of the order of the kV at least in Destriau's original paper, later tens of volts) [42]. It should be noted that this discovery was also serendipitous: Destriau was looking for better scintillation

[3] While both effects were discovered by Losev, type I is *often* called the Destriau effect (see below) and type II *sometimes* the Losev effect, see, e.g., [31].

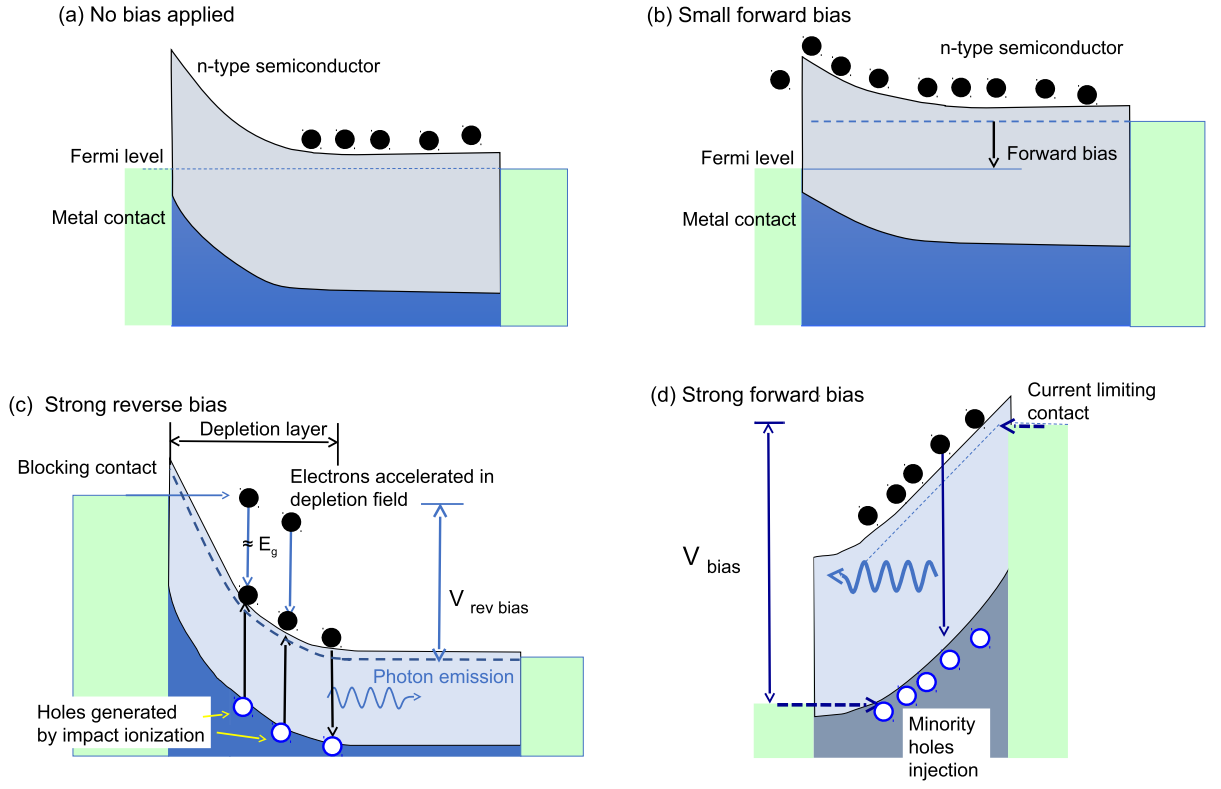

Fig. 4. Schematics of the modern explanation of Losev's type-I electroluminescence in case of an n-type semiconductor. (a) and (b): metal semiconductor rectifying contact, so-called Schottky contact (at the time, all metal-semiconductor were rectifying, as no such contact could be Ohmic because of the poor semiconductor doping). (a): no bias voltage applied; (b) small forward voltage applied (semiconductor negatively biased relative to the metal); a few electrons flow from the semiconductor into the metal; (c) strong negative bias applied through the contact, which acts as a blocking contact, regulating the injected current. Due to the high accelerating field in the depletion layer, electrons reach a kinetic energy larger than the bandgap, allowing electron–hole pairs to be generated by impact ionization. These electron–hole pairs with energies near the band edges can then recombine radiatively by emitting light; (d): under strong forward bias, minority holes are injected into the n-type semiconductor, recombining with electrons by emitting light. To avoid strong electron (majority carriers) current, electrons are injected by a current limiting contact, a Schottky contact.

materials for measurements of radioactive decay, hence the title and main focus of his paper (*Research on Scintillations of Zinc Sulphides under α-Rays*). His search for the possible excitation of luminescence by electric fields came from the possible explanation of the scintillation phenomenon as due to the excitation of ZnS by the intense electric fields produced by the ionization of light-emitting centers due to α particles. The phenomenon in powders is in principle that of the type I of Losev in crystals. Destriau later quoted Losev's work on silicon carbide as the first evidence of electroluminescence of solid bodies. The advantage of the "Destriau" effect lies in its simplicity of implementation, since it is sufficient to place the ZnS powder and a binder between two transparent conductive plates (Fig. 5). It has thus generated much research from the 1930s to the 1970s, and some had some beginnings of applications in electroluminescent screens [43,44].[4] The simplicity of manufacture, not requiring high-quality crystals, has however inherent drawbacks: the materials are poorly mastered, have random properties, do not age well, have a very low conversion efficiency, which will increase little with time, in spite of important research efforts [45,46]. Destriau himself will recognize in 1955 [47] that only the path of type-2 electroluminescence, i.e. direct injection in a semiconductor, could deliver the efficiency required for lighting applications. This was analyzed in detail by Fischer [48] and later by Dean [49].

[4] To emphasize the predominance of high-field electroluminescence in the post-war era, we can cite the remarkable introduction by Dean to his masterful 1969 review [50]: "Previous reviewers of electroluminescence have noted that it is a very complex phenomenon and have claimed [...] that the time was inopportune for a definitive survey of the fundamental mechanisms that take part in it. These remarks still apply in many examples of electroluminescence. Light can be generated in almost any material under the influence of sufficiently high electric fields. Unfortunately, it is often extremely difficult to define precisely the physical conditions that are necessary for the observed luminescence, which is an essential prerequisite to a detailed theoretical understanding of the effects. This is particularly so when materials are studied other than in macroscopic single-crystal form, and when exotic methods have to be used to overcome the electrical contact problems that plague the wider band gap materials.

The present reviewer has tried to focus attention upon those areas of the subject that seem to be least affected by the controversies of interpretation that inevitably arise in this type of situation. Thus, relatively little space has been devoted in this article to the extensive literature on ZnS-type phosphors... Following this prescription, it has been possible to present an account of relatively modest length that, it is hoped, is comparatively free of speculative material. With this objective, emphasis has been given to the electroluminescence of those materials within which p–n junctions can be prepared."

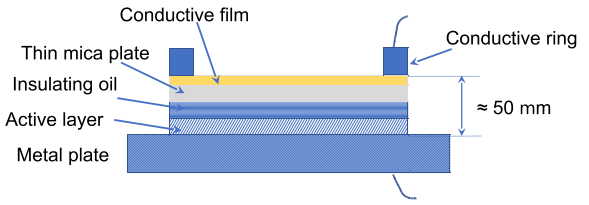

Fig. 5. Schematics of a Destriau cell (after Destriau [51]).

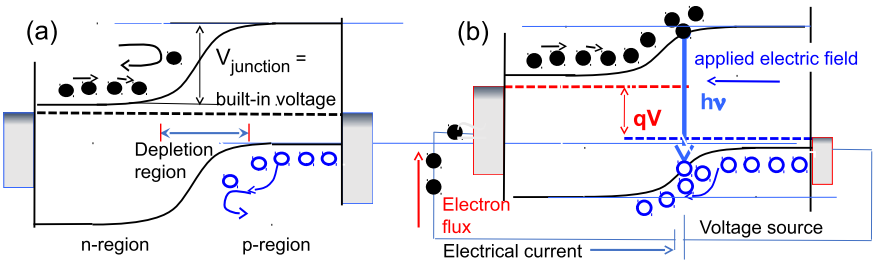

Fig. 6. Schematics of carrier injection in a forward biased p–n junction leading to light emission. (a) Junction with no applied bias. Carriers are repelled from the depletion region by the built-in potential. (b) Under forward bias, the repelling potential is reduced and both electrons and holes are injected in regions where they can recombine (after [54]).

4. The emergence of modern LEDs

4.1. Early LEDs, post-band theory

The realization of the potential of direct carrier injection in p–n semiconductor junctions for high-efficiency light emission came from the availability of high-purity crystalline semiconductor materials obtained by complex manufacturing processes, operating under conditions of high cleanliness and thus very reproducible. This was compounded by the detailed understanding of their operation derived from their fundamental properties, born from the quantum theory.

A major step in the mastering of semiconductors materials was the understanding of the doping effect of selected chemical impurities. Due to their shallow energy levels with respect to the conduction (donors) or valence (acceptors) bands, they release in that band their extra charge at room temperature, thus changing the conductivity [52]. It was this understanding that the semiconductor conductivity was controlled by impurities that led to the deterministic search for purification and controlled doping. Until then, researchers were confronted with the contradiction that when conductivity increased, it was due to poorer purity, whereas the comparison with metals behavior would lead them to believe the opposite. The further understanding of the physics of semiconductors (doping, defects, etc.), their purification and the advent of p–n junctions during the 1940s [53] led to the invention of the transistor at Bell Laboratories in 1947.[5] It quickly became clear that a p–n junction could be an interesting device for light emission. In 1951, Lehovec[6,7] [54] used p–n junction theory to explain the electroluminescence in p–n SiC junctions as resulting from the injection of carriers across a junction followed by radiative recombination of electrons and holes (Fig. 6). However, the observed photon energy was less than the energy gap of SiC, and he suggested that radiative recombination was likely to occur due to impurities or lattice defects. In some cases, it was observed that the emission occurred even when the energy supplied by the voltage source per electron–hole pair at 1.8 eV was smaller than the energy carried out by the emitted photons (2 eV).[8] This was correctly interpreted as due to carriers being supplied energy from the lattice by phonon absorption leading to cooling by radiation emission (see below the discussion on the ultimate efficiency of LEDs). The quantum efficiency (ratio of emitted quanta to number of e–h pairs injected) was $2{\cdot}10^{-6}$ [58].

4.2. Infrared LEDs

Due to the availability of better materials with bandgaps in the infrared, that spectral region was the one most investigated in the 1950s. Electroluminescence due to recombination of holes and electrons in p–n junctions was observed in 1952 in germanium and silicon [59]. However, these semiconductors have an indirect bandgap (for a thorough discussion

[5] As mentioned above, Losev might have had a working transistor in 1940 [38]. See also the parallel path to the transistor by German researchers in France after 1945 [55,56].

[6] It is noteworthy that [54] cites profusely Losev's work as the precursor to several effects.

[7] For a fascinating account of the genesis of Lehovec's LED work and his later achievements, see Lojek [57], pp. 195–207.

[8] The hexagonal SiC bandgap being in the 3.2-eV range, the observed luminescence is indeed due to recombination on impurities.

on indirect transitions, see Dupuis and Krames [60]). In 1955, injection electroluminescence was demonstrated in a number of infrared emitting III–V direct bandgap compounds (GaSb, GaAs, InP, and the Ge–Si alloys), at room temperature and 77 K, by metal contact injection [61].

The next few years were dominated by the search to make efficient p–n junctions with GaAs and its alloys towards infrared. GaAs was attractive because of its direct bandgap, enabling recombination of electrons and holes without involvement of phonons, and of the rapidly developing growth techniques for high-purity materials.[9] GaAs was also in high demand for the high-speed performance it allowed in electron devices. In the summer of 1962, the observation of light emission from p–n junctions was reported with outstanding efficiency [62]. An internal quantum efficiency (IQE) of 40% was calculated at room temperature, as well as a lower bound value of 48% at 77 K, the uncertainty coming from the lack of knowledge of the light extraction efficiency (see, e.g., [63,64]). In a fashion similar to the result of Lehovec [58], emission could be observed at electrical injection energies smaller than the energy of the emitted photon, with the mentioning of light emission possibly acting as a refrigerator [65] (see below, in section 6, the discussion of LED ultimate efficiency).

A few months later, laser emission in GaAs and GaAsP at liquid nitrogen temperature (77 K) was demonstrated independently and almost simultaneously by three research groups at General Electric, IBM, and Lincoln Laboratory at MIT (for an historical account see [67]). It would be a few years, however, before laser diodes became widely used. Thanks to the development of heterostructures, and later quantum wells, allowing for a better confinement of the carriers while reducing the losses, laser diodes could operate continuously at room temperature, with applications in a large variety of areas. The most important was the urgent needs of optical telecommunications, where the minimal losses in optical fibers in the 1.3- and 1.5-μm wavelength ranges called for lasers operating in the near IR.

4.3. Early visible-light LEDs

Following experiments in 1953 on blue and yellow emission in SiC [58], progress in visible light LEDs, mainly using GaP (indirect bandgap equal to 2.2 eV), was made in parallel by several groups (for the history of these early experiments, see the detailed accounts in references [68–70]). They had different objectives, ranging from communication, lighting, and television displays to indicator lamps for electronics and telephones (see, e.g., chapter 1 in Schubert [71]). Using different dopants (e.g., Zn–O or N) at various concentrations, different wavelengths were generated, ranging from red to green (see Fig. 8 below). From the early 1960s, many manufacturers in different countries were making red and green LEDs based on GaP [72,73].

Mixed GaP_xAs_{1-x} crystals were studied, since the emission wavelength can be shorter than for GaAs, reaching the visible range. Early experiments were reported in 1955 and 1956 by Wolff [74,75] with the growth of bulk crystals from solidification from a stoichiometric melt. Holonyak Jr. worked on GaP_xAs_{1-x} layers grown by vapor phase epitaxy [76] and succeeded in observing laser emission at 710 nm (red) in 1962 [77].[10,11]

However, in the beginning of the 1970s, almost all research efforts on visible LEDS were abandoned at the major industrial laboratories in favor of infrared lasers for telecom applications (in particular, at the laboratories that pioneered research on nitride semiconductors, Philips, RCA and Bell labs, see, e.g., [83]).

The (early) competition between direct and indirect bandgap semiconductors for high-efficiency electroluminescence. Light emission from e–h recombination implies conservation of energy and momentum (for electrons in solids, this is the quasi-momentum k appearing in the Bloch wavefunction). The conservation equations read:

$$h\nu = E_c - -E_v = E_G$$

$$k_{phot.} = k_e - k_h$$

Compared to the usual electron and hole momenta for an average energy kT, the photon momentum is negligible, which leads to $k_e \approx k_h$, i.e. to vertical transitions between electron and hole states in the band diagram (Fig. 7a). In indirect bandgap semiconductors, momentum conservation is obtained through the simultaneous emission or absorption of a phonon (Fig. 7b), which makes emission or absorption of photons a second-order process, much less likely than the first-order process occurring in direct bandgap semiconductors. Thus, strong optical transitions only occur for direct bandgap semiconductors. It might seem that only direct bandgap semiconductors should be considered as candidates for high-efficiency light emitters. However, contrary to what is often said (*and taught*) this did not prove obvious in the early times [84]. While it is certainly true that the IQE is intrinsically higher for direct gap semiconductors, the intrinsically weak optical transition

[9] For an historical account, see, e.g., [66].

[10] Soon after that observation, Holonyak is quoted in a celebrated 1963 Reader's Digest article on lasers as saying "we believe that there is a strong possibility of developing the laser as a practical light source [...] Much more experimental work must be done, and it might be 10 years or more before such a lamp could be ready to use..." [5,78]. However, it is LEDs which are today used in lighting. This might come from the unforeseen improvement in LED efficiency (see, e.g., the discussion in Grimmeiss [79]). While still having an efficiency smaller than LEDs, there is recent interest in applying lasers to lighting, see [80–82] and section 4.8 below.

[11] An "interesting" viewpoint on the possibility LED lighting at the time is provided by Hilsum [66].

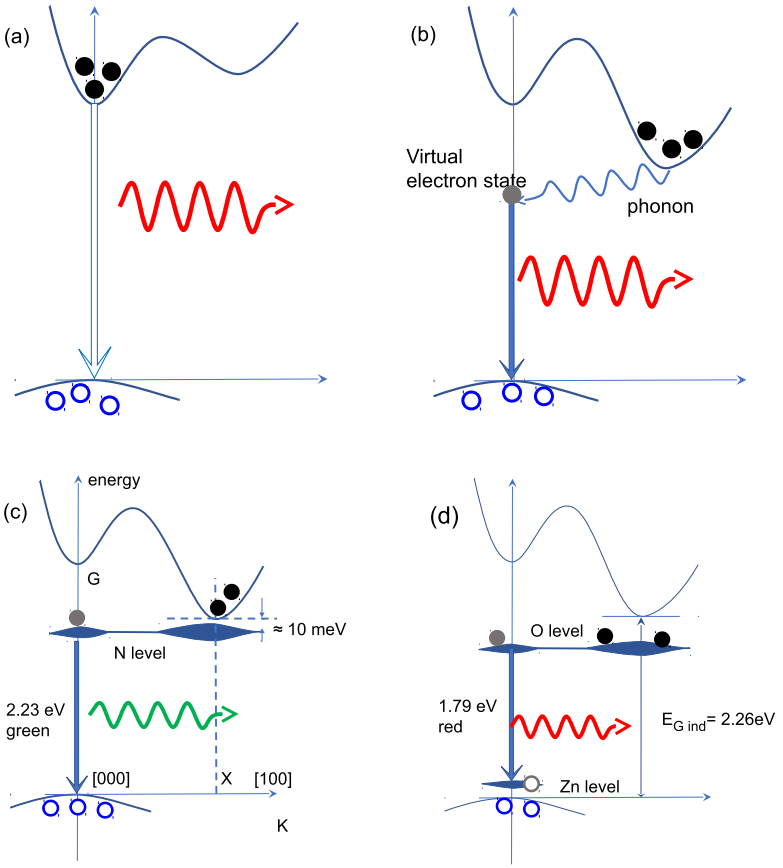

Fig. 7. Semiconductor optical transitions: (a) direct bandgap emission, (b) indirect bandgap phonon assisted emission, (c) indirect bandgap deep-donor assisted emission, (d) indirect bandgap deep acceptor assisted emission.

of indirect bandgap semiconductors can be increased significantly by materials engineering, and the weaker absorption of indirect bandgaps can turn into a blessing for the external quantum efficiency EQE:

(i) one can significantly improve the radiative recombination rate in indirect bandgap semiconductors by introducing deep impurities for which the extent of the highly localized wavefunction extends in k space (from the center of the Brillouin zone to the conduction band minimum for acceptor impurities, or from the conduction band minimum to the zone center for donors) (Fig. 7c, d). Then, the transitions between the impurity bound electrons or holes becomes quasi-direct with the complementary carrier as significant components of their wavefunctions extend throughout the Brillouin zone, matching the other carrier wavefunction (see, e.g., Nuese [85]);

(ii) beyond the IQE yielding photons within the semiconductor, the overall efficiency includes the light-extraction efficiency [86]. In the early direct bandgap semiconductor homostructure devices, a large fraction of the light emitted within the semiconductor was reabsorbed before reaching the surface both because of the large absorption coefficient (10^4 cm^{-1} and higher) and of the thick junction layers made unavoidable by the imprecise growth methods at the time. By contrast, very little reabsorption occurred in indirect bandgap LEDs due to the much weaker absorption coefficient (a few cm^{-1}). Therefore, for a long time, the performances of indirect gap green and red GaP LEDs were superior to those of direct gap GaAsP LEDs (Fig. 8 and Table 2). The latter become better when nitrogen doping was also introduced in the alloys, which shifted the emission energy below the bandgap thus diminishing reabsorption, in addition to reaching out to the compositions where the band gap was larger, hence allowing for shorter wavelength LEDs, but reaching a high alloying limit when the bandgap becomes indirect.

Table 2 shows the performances and market shares of these early technology LEDs, mainly used as luminous indicators. The major performance improvements later came with the advent of high-purity, high-precision growth methods that allowed fabrication of heterostructures where the active regions can have smaller bandgaps than surrounding materials, and therefore reabsorption can become negligible, even for the near edge emission of the direct band gap semiconductors of the active emitting region.

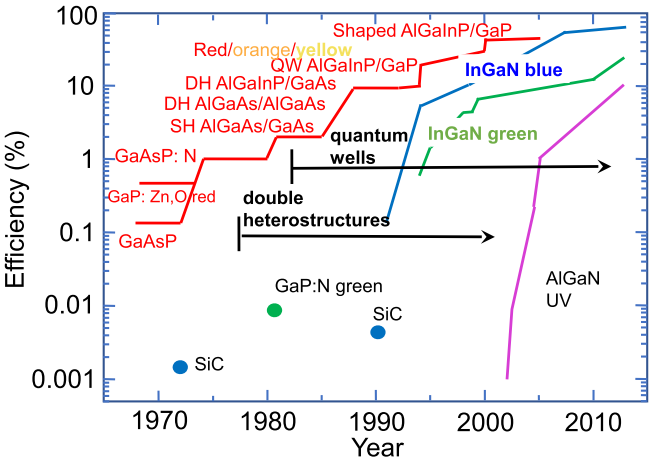

Fig. 8. Time evolution of the external quantum efficiency of visible and UV LEDs (after [87,88]).

Table 2
Performances of early (i.e. pre-nitride) visible LEDs (after [84,85,89], also table p. 185 of [90]).

LED material	Color wavelength	Internal quantum efficiency (%)	Light extraction efficiency (%)	External quantum efficiency (%)	Spectral efficiency of color (lm/W)	Luminous efficacy (lm/W)	Share of production in 1988
GaP:Zn, O	Red–orange	13–50	≈30	4–15	20	3	35–40%
$GaAsP_{0.4}$	Red	6–15	≈3	0.2–0.5	75	0.4	15–20%
$GaAsP_{0.65}$:N	Red–orange	1.2–3	≈30	0.4–1	190	1.2–2	40–45%
$GaAsP_{0.85}$:N	Yellow	0.6–0.9	≈30	0.2–0.3	400	1.4	
GaP:N	Yellow–green	0.3–2	≈30	0.1–0.7	610	4.5	
GaP:Zn	Blue	Not available	Not available	0.1	60	0.03	
ZnS:Al	Blue	Not available	Not available	0.05	200	0.05	
SiC:Al, N	Blue	Not available	Not available	0.004	150	0.01	

4.4. The modern semiconductor growth techniques

Progress in electronic devices is inseparable from progress in materials purity and control. Early semiconductors, Germanium, Silicon, Binary III–V have been grown in the bulk from melts. This usually resulted in materials with high impurities contents, poorly controlled dopant concentrations in addition to high defect densities. To purify the materials, extra steps had to be taken such as the zone melting method where a moving melted/solidified zone moves along the semiconductor ingot and segregates foreign atoms in the melting front. This was long the way to purify the first industrially produced Ge and Si, and was also used for GaAs. The wider used bulk growth technique is now the liquid encapsulated Czochralski growth: single crystals are pulled from the melt with a seed crystal [90]. While this technique produces high-quality substrates, two better growth techniques appeared in the late 1950s and early 1960s, liquid phase epitaxy (LPE) and vapor phase epitaxy (VPE) whereby crystal growths occurs over a crystalline substrate [60,91]. These techniques produced materials with very high quality, but the growth rates were rather high, only allowing layer thicknesses of at least 100 nm in multilayer structures, limited by the time required to change the liquid or vapor phase composition in the growth reactors.

In the 1970s, new crystal growth techniques, MBE (Molecular Beam Epitaxy) and MOVPE (Metalorganic Vapour Phase Epitaxy) were developed, allowing layer-by-layer growth epitaxial growth modes. Compared to VPE and LPE, they often lead to higher-quality crystals, but mainly provide better defined interfaces as these growth techniques grow much slower (typically 1 μm/h vs 10–50 μm/h), allowing growth of ultra-thin layers, quantum wells, by fast switching between different pure compounds, or between pure compounds and their alloys, most often in any composition [Stringfellow]. They also allow scaling up the growth area, with production reactors now treating at once several tens of wafers, leading to a total growth area in the square meter range. We note that very special designs of LPE reactors allowed for fast transfer of the growth substrate between different melts such that quantum wells could be grown, but these were extreme conditions (for a detailed review, see [92]).

A first major issue, a very important one, limiting the choices of possible semiconductor combinations, is the difference in lattice constants between the materials and the substrates (Fig. 9), and between the grown materials themselves, which creates strain in the layers, which can then lead to the creation of crystal defects such as dislocations and to accelerated material degradation (see, e.g., [93]. This is sometimes compounded by the differences in expansion coefficients of the materials, which adapt well at growth temperatures, but develop large strains when cooled down to room temperature. One therefore aims at using substrates whose lattice constants are well matched to the grown materials. One also limits designs to heterostructures with thin layers below a critical thickness defining the onset of dislocation creation [94].

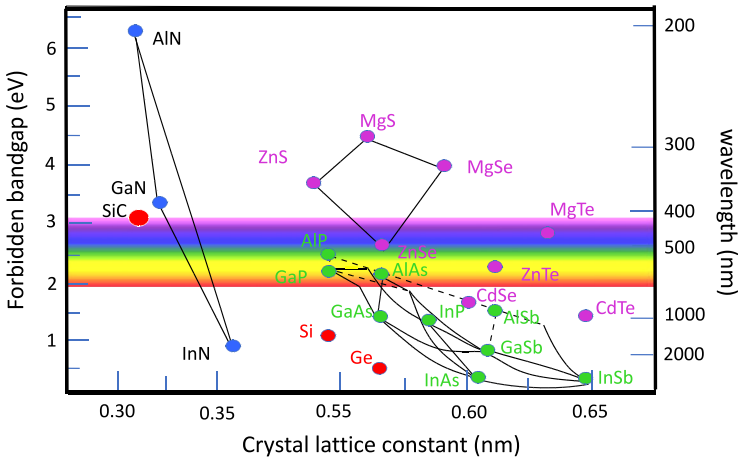

Fig. 9. Bandgap map (forbidden bandgap vs. crystal lattice constant) of major semiconductors and their alloys.

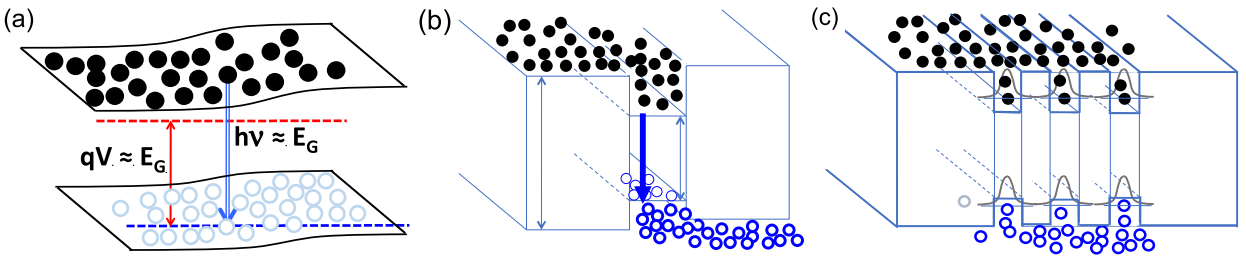

Fig. 10. Schematics of real-space band diagram and carrier diffusion in forward biased, from (a) p–n homostructure, (b) p–n double heterostructure, (c) p–n multi-quantum well structure.

The substrates are usually produced by the bulk growth methods, but when this is not possible another solution is to rely on epitaxially grown ultra-thick layers that are then cut at will along desired directions. This is presently done to obtain GaN with different planes from VPE grown thick layers, however at very high cost (∼100× more expensive compared to other substrates).

In the case of nitride materials, as a compromise between substrate lattice matching and cost, one has to use alternate substrates, such as sapphire (Al_2O_3) for the growth of nitrides, or GaAs for the growth of II–VIs. One selects crystal orientations for which the surface lattice is commensurate with the epitaxially grown material: Another critical item to obtain high-quality deposited layers is the quality of the substrate, which should have minimal crystal defect density as the substrate defects tend to replicate in the grown material.

A first effect of the new growth techniques was the possibility to have thinner layers between the emitting region of the LED and the surface. Therefore, much less reabsorption would occur, increasing the extraction efficiency. However, the constraints due to the formation of a good p–n junction with a controlled depletion layer did not allow one to take full advantage of the capacity to grow ultrathin top layers and reabsorption in direct gap materials remained an issue. The main improvement came from the use of heterostructures and quantum wells, where one can have a thick top layer which is quasi-transparent to emitted photons from the smaller bandgap material of the heterostructures.

4.5. Heterostructures and quantum wells

A major progress came from the use of heterostructures starting in the 1970s (see Fig. 8 to see the jump in performances). By using an active light-emitting region sandwiched between two higher bandgap materials regions, the emitted light is not reabsorbed on its path to the surface. An added benefit is that electrons and holes are concentrated in the small bandgap materials layer instead of being distributed over the diffusion lengths (Fig. 10), leading to the increase of the radiative recombination rate, which is a bimolecular process in terms of electron and hole densities [95]. Thus, both the IQE and the LEE were improved through the use of heterostructures. A further improvement is most often brought by the use of ultrathin heterostructure layers, the quantum wells (QWs). While the improvement of the IQE by the use of QWs is most universally observed, its origin is not fully understood for every materials system. For lattice mismatched materials pairs leading to strain, the use of QWs is however often required as it allows the system to remain below the critical thickness leading to dislocation formation and thus leads to better material crystalline quality. There is also certainly a clearly observable impurity and lattice defect gettering action at interfaces between materials, although this remains poorly understood.

A final beneficial effect of QWs could be the higher recombination mechanism induced by the 2-dimensional nature of excitons recombining in a 3-dimensional photon space. While clearly observed and explained at low temperatures [96–98], it is not clear whether this effect plays a role in device operation, as excitons are most probably thermally dissociated at room temperature, this however remaining subject to controversy [99–101].

4.6. Modern visible light LEDs: red

The red LEDs underwent a major breakthrough with the appearance of high-purity materials and heterostructures, and later of quantum wells.

The first material system for which this was possible was the AlGaAs/GaAs one, which has the peculiarity to be almost exactly lattice-matched for any alloy composition (Fig. 9), which easily leads to almost perfect epitaxy of high-quality heterostructures on the GaAs substrate. The effort was of course driven by the search for lower threshold, room-temperature CW lasers. This breakthrough moment was reached in 1969 [102–104]. For the invention of heterostructures which enabled this feat, Alferov and Kroemer were awarded the 2000 Nobel prize in physics. Red-emitting AlGaAs /AlGaAs developed rapidly in the late 1970s and became the dominant product in the early 1980s. However, the wavelength is confined to wavelengths above 650 nm (deep red) due to the insufficient bandgap of high Al content $Al_xGa_{1-x}As$ confining layers that retain carriers in the DH or QW active layers. Therefore, the need for larger bandgap materials system led to the development of the GaInAsP system as a first step, and then to the present GaInAlP system, which constitutes today the best source of materials for red, orange, and yellow LEDs [63].

As is clear from the previous discussion, getting to shorter wavelengths than those accessible by the GaInAlP materials system required emitting materials with larger gaps, and most importantly, heterostructure carrier confining materials with even larger gaps. From the band gap map in Fig. 8, II–VI and nitride materials were the obvious choices.

4.7. Modern visible light LEDs: blue and green

Although the concepts of heterostructures were well established, their extension to emission of blue light in wide-band-gap materials proved to be of considerable difficulty. Early attempts with II–VI materials (ZnS, ZnO, ZnSe) and SiC did not lead to stable efficient light emission [105], despite huge efforts. The material that enabled the development of blue LEDs was gallium nitride (GaN) and its alloys.

Already at the end of the 1950s, the possibility of light emitters based on GaN was foreseen by Grimmeiss [106,107] (see also [68,69]). Efficient *photoluminescence* from GaN over a wide spectral range was obtained using different impurities. Relying on small crystals obtained from powders, p–n junctions could not be produced at the time (it was however a much more fundamental problem, that of acceptor compensation, see below and [80]). Then the effort at Philips turned to GaP instead [68,68].

Later, GaN crystals were more efficiently produced at the end of the 1960s by growing GaN on a sapphire substrate using the Hydride Vapour Phase Epitaxy (HVPE technique). Several laboratories studied the growth and doping of GaN, mainly RCA [108] (for an history of GaN efforts at RCA, see [109] and Bell labs [110–112]). Basic electrical and optical properties were identified, GaN lasing was even observed under optical pumping at low temperature [111], but material problems were daunting. The surface roughness was not controlled, the HVPE-grown material was contaminated with oxygen and/or transition metal impurities, and p-doping seemed impossible, some theories claiming it to be (in a few other semiconductors indeed is doping of one type impossible). As mentioned above, the research effort stopped due to resource allocation to telecom lasers.

The story from then on leading to high-efficiency blue LEDs is reviewed in the companion article by Feezell and Nakamura in this issue [80] (see also [113,114]). Despite the reduced interest by major companies, efforts were made to improve the growth techniques for GaN. Akasaki began studying GaN as early as 1974, at the time at the Matsushita Corporation, then at Nagoya University in 1981. In 1986, high crystal quality and good optical properties could be produced with the MOVPE technique using a thin layer (30 nm) of highly defective AlN, first nucleated on a substrate of sapphire at low temperature (500 °C). Nakamura at Nichia later developed a similar method where AlN was replaced with a thin layer of GaN grown at low temperature (see [80] for a detailed account and references therein).

The challenge to obtain p–n junction LEDs was the difficulty to p-dope GaN in a controlled manner. At the end of the 1980s, Amano, Akasaki and co-workers made an important observation: when Zn-doped GaN or Mg-doped GaN was studied with a scanning electron microscope, it emitted more light, thus indicating better p-doping. This was an important breakthrough and opened the way to p–n junctions in GaN. The effect of electron irradiation was explained a few years later by Nakamura. Acceptors such as Mg or Zn form complexes with hydrogen and thus become passive. Electron beams dissociate these complexes and activate the acceptors. Nakamura showed that even a simple thermal treatment (annealing) leads to efficient activation of Mg acceptors. The effect of hydrogen on the neutralization of dopants was known from previous work in other materials (see, e.g., [115] and references therein). The next crucial step in developing efficient blue LEDs was the growth and p-doping of alloys (AlGaN, InGaN), which are necessary to produce heterojunctions. Such heterojunctions were realized in the early 90s, as well as MQWs [80].

Nitride LEDs have specific properties compared to other LED materials:

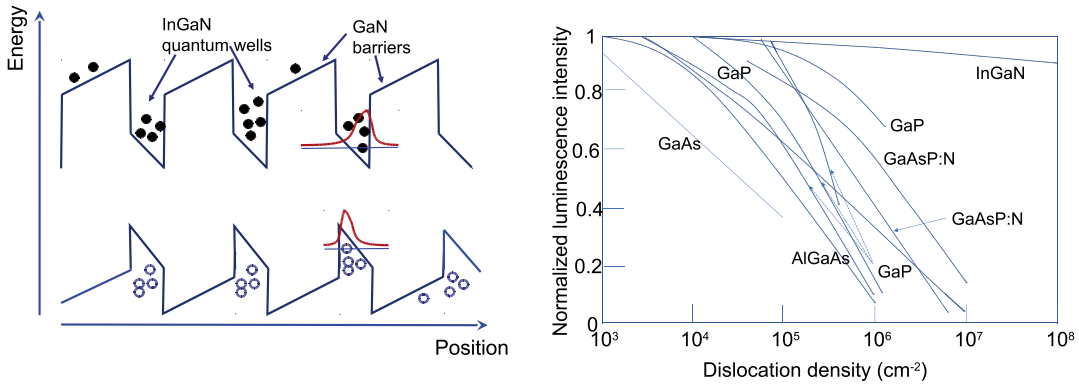

Fig. 11. Two specific aspects of nitride LEDs. Left: spontaneous polarization and strain induced piezo electric fields create strong internal fields in nitride heterostructures; right: despite the large dislocations densities in the 10^8–10^9 cm^{-2} range, InGaN materials exhibit high IQEs.

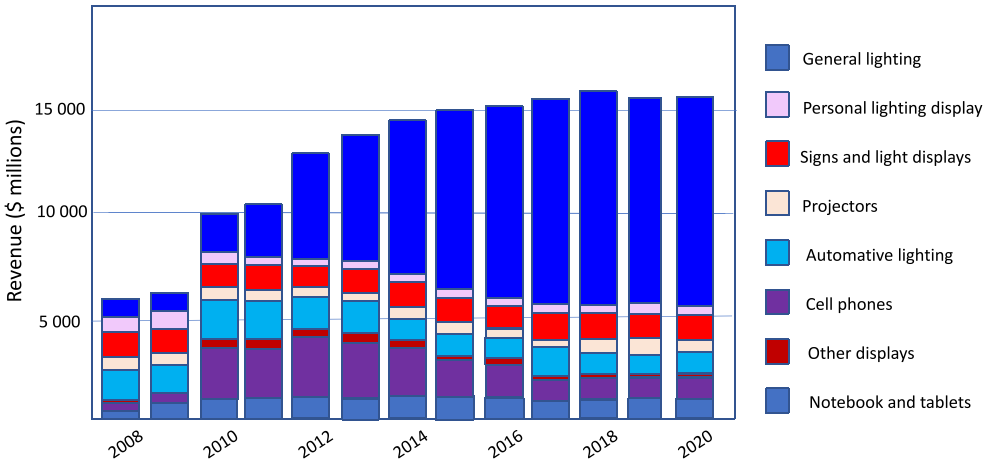

Fig. 12. Time evolution of LED markets (after Yole's development, 2014). Note that this is value of market, product of rapidly increasing number of devices and simultaneously rapidly decreasing unit costs.

- they have strong internal electric fields due to spontaneous electric polarization and piezo electric effects (Fig. 11 left). This leads, among other things, to charge separation in the active QWs, which diminishes radiative recombination rates and leads to increasing droop effect with In concentration, i.e. for long-wavelength alloys, as internal fields are increased [116];
- they operate at high efficiency despite having high threading dislocation densities, so high ($\sim 10^8$–10^9 cm^{-2}) that other semiconductors would have a negligible efficiency (Fig. 11, right). This has been linked to the localization of carriers by the intrinsic In alloy disorder which prevents carriers to reach non-radiative centers through very small diffusion lengths ($\approx$20 nm);
- degradation during operation is quite negligible: it was however well known for the usual semiconductors operating in the IR that the degradation of emitters originated from the generation of additional point defects (voids and interstitial atoms) or linear defects (dislocations) due to non-radiative recombination of e–h pars, or motion of pre-existing ones, in the active layer, during the operation of the infrared LEDs. This degradation mechanism should have been even more effective for visible or UV photon emitters because of the much higher energy of the recombining e–h pairs. In fact, nitrides, in contradiction with blue emitters based on II–VI materials, generate relatively few defects and dislocations during their operation: in particular, it seems that the usual nitride LEDs grown on sapphire, oriented along the *c*-axis of their hexagonal structure, have no shear stress along these planes and that the defects and dislocations have a very hindered slip motion [117].

The nitride progress from the breakthrough results in the early 1990s was very rapid and is described in the companion papers Feezell [80] and Pattison [118]. Let us only remark that LEDs only appeared recently as a major source of lighting: a 1998 report by the US National Research Council committee barely mentions the long-term hypothetic possibility of LED lighting [119]; for many years, LEDs were confined to specialty uses, from light indicators, traffic lights, etc. to phone and TV backlights, car lights and projectors. As can be seen in Fig. 12, LED lighting only developed into the major market for LEDs from 2012 on, when efficiency and cost made them competitive with the mainstream lighting solutions.

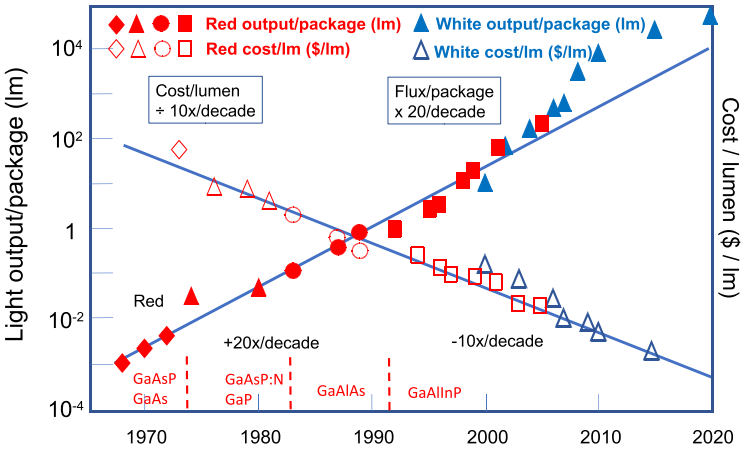

Fig. 13. Time evolution of light output and cost per LED lamp package, for red and white lamps [after 120].

This late, rather unexpected spectacular development results from both the exponential increase in light output per LED chip, described as Haitz's law, which is similar to Moore's law in microelectronics, and the simultaneous decrease in lumen cost (Fig. 13) [120].

It should be noted that the lamp cost is not the correct measure of lighting costs: besides luminaire, installation and maintenance costs, a major cost component is electricity costs. Therefore, the correct metrics should be $/klm·h. Looking back at Fig. 1c, which provides the historical price trend, today's best LED lamps with a luminous efficacy of 150 lm/W would deliver a Mlm·h for an electricity cost of US$0,66 for a 10 c kWh.

4.8. Further approaches to solid state lighting

Organic LEDs (OLEDs). Electroluminescence should happen in any material where carriers can be electrically injected in a metastable state from which they can recombine into a ground state. It is therefore no surprise that this can be achieved in molecular materials where such states exist, called HUMOs and LOMOs for, respectively, Highest Unoccupied or Lowest Occupied Molecular Orbitals. EL was first generated in organic materials along the "brute force" technique of type-I EL reported by Losev, i.e. with high electric field, high-voltage injection [121,122]. Electrons and holes are both injected with voltages in the range of a few hundreds of volts. While the quantum efficiency could be quite high, the WPE was low due to the energy loss per injected e–h pair.

Major breakthroughs, in the late 1980s, of Tang [123] and Burroughes [124] led to renewed interest in the field thanks to the EL at much lower voltage, replicating the injection scheme of semiconductor p–n junctions, from thin organic films made either of small molecules ("OLEDs") [123] or of conducting polymers [124] (sometimes alternatively called "PLEDs", although we will use the term OLEDs throughout indistinctively of the nature of the emitting species).

The IQE of OLEDs mainly requires mastering two properties: first, creating of a balanced flow of electrons and holes into the emission layer; second, efficient radiative recombination of these electron–hole pairs to the produce photons. Obtaining high radiative efficiency is hampered by an intrinsic property of molecular excitations: e–h pairs form correlated species, excitons, where electron and hole spins create singlet and triplet states in proportions of 25 and 75%, respectively. The selection rule of conservation of spin angular momentum could lead to a maximum quantum efficiency of 25% for organic materials if only singlet states contribute to radiative recombination. Remedial actions in the past few years have solved the issue to a large extent [125].

Besides the issues to obtain high IQE, OLEDs offer a specific challenge to obtain high extraction efficiencies [126]. A large fraction of the light generated within the device cannot escape the thin-film layer structure as it is guided between the electrodes, or emitted in the substrate, with the added issue of light absorption by the surface plasmons of the metal electrodes due to their proximity to the emitting layers. This results in low light-outcoupling efficiencies, typically on the order of 20%. Present light extraction techniques are quite similar to those of inorganic LEDs with the use of patterning of substrates, corrugated substrate surfaces, low-index diffractive intermediate layers, etc., see, e.g., the reviews [125,127].

OLEDs for lighting are still in a less mature state than inorganic semiconductor LEDs. While the difference in performance should diminish with time, the specific properties of OLEDs materials and architecture should make the injection and light extraction efficiencies still lower than those of inorganic LEDs. Cost-wise, as OLEDs operate at quite smaller current densities than inorganic LEDs, their cost expressed in klm/$ seems to always be at a disadvantage, compounded by their lower ultimate expected power efficacy (190 vs. 255 lm/W) [128]. It is thus foreseen today that inorganic LEDs should take the bulk of the lighting market while OLEDs, besides their display applications, will have applications in the decorative lighting market, where their large area can enable designers to achieve remarkable realizations.

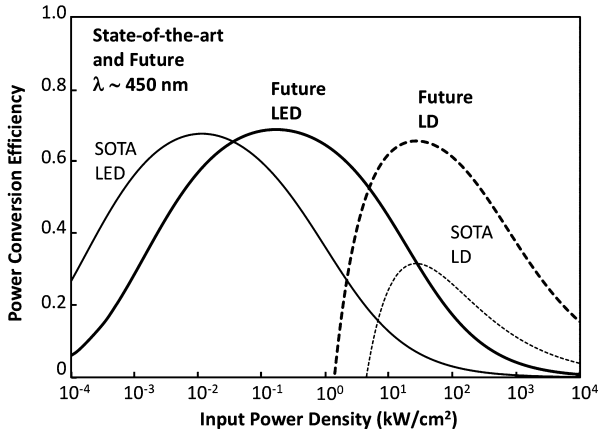

Fig. 14. Comparison of state of the art (SOTA) and expected future performance of blue LEDs and laser light sources (LDs). Lasers are expected to have a larger efficiency at high currents, because carrier densities and droop are clamped at their values at the laser threshold (from [81]).

Laser-based lighting. As mentioned above (Section 4.3), soon after his invention of the red laser [77], Holonyak mentioned the possibility to use lasers as a lighting source [5,78]. In spite of their present efficiency, smaller than that of LEDs, there is renewed interest in laser lighting [80–82]. Three advantages of laser lighting are put forward:

(i) nitride based LED are subject to the efficiency droop limiting their operation at high currents densities if one wishes to maintain high efficiency. Lasers are also subject to droop below threshold current, but the droop is clamped at higher currents as is carrier density when stimulated emission sets in. Then, as the *differential* efficiency can be very high above the threshold (even unity), the overall efficiency can be very high, until new dissipating mechanisms set in at higher currents (Fig. 14);
(ii) lasers have a much smaller source *étendue* than that of LEDs. They can therefore lead to much better shaped light beams. This property is already exploited in laser car headlights, for which the more controlled beam shape leads to a doubling of the useful range, while emitting the same amount of lumens as other headlights (imposed by regulations) and avoiding as much the blinding of opposite drivers. In general lighting, there are many situations where directional lighting is desired;
(iii) a strongly researched feature of lighting is its capacity to carry information through the so-called LIFI (for light fidelity) concept, in the same manner as high-frequency electromagnetic waves carry information in WIFI. The data rate is limited in LED lighting by the small bandwidth of LEDs due to their long recombination time. Thanks to the fast-stimulated emission mechanism, lasers have much larger bandwidths; therefore, laser-based lamps would have internally the device allowing high data rates in LIFI.

A topic under heavy discussion is the color rendering of laser lamps where white light is generated as the sum of three or four monochromatic beams [80,82,129].

While laser lighting can progress in these special markets, it is still too early to decide what share of the general lighting market laser lighting could reach.

5. Physical limits of LED efficiency: a brief historical note

The direct conversion of electricity into light has attracted early on interest in sorting out the limit efficiency of the process. One should first define the components of efficiency in LEDs. There is first the device efficiency, usually expressed as its electrical efficiency, the wallplug efficiency WPE, ratio of emitted power to injected power:

$$\mathrm{WPE} = P_{\mathrm{opt}}/V_{\mathrm{bias}}I$$

where V_{bias} is the applied voltage and I the current through the LED.

Expressed *per injected e–h pair*, WPE is the product of the internal quantum efficiency IQE, which is the fraction of emitted photon per injected electron–hole pair in the active layer, the light extraction efficiency LEE, the fraction of emitted photons that escape the LED chip, and the electrical efficiency EE per electron–hole pair, which is the ratio of the energy of the emitted photon (written as $h\nu = eV_{\mathrm{p}}$) to the energy supplied per e–h pair in the LED (eV_{bias}):

$$\mathrm{WPE} = \mathrm{IQE} \times \mathrm{LEE} \times \mathrm{EE} = \mathrm{IQE} \times \mathrm{LEE} \times \frac{V_{\mathrm{p}}}{V_{\mathrm{bias}}}$$

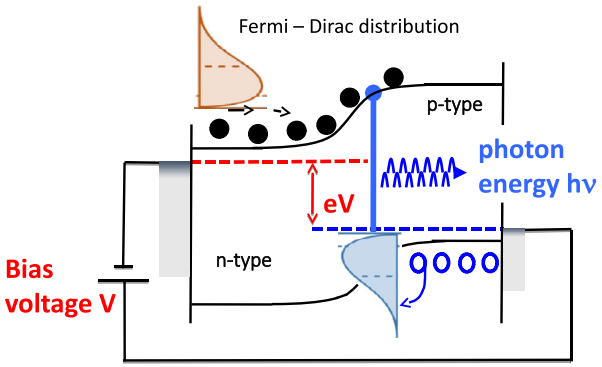

Fig. 15. Illustration of light emission at the bandgap energy for a LED electrically injected at an electron–hole pair energy lower than the bandgap: electrons and holes are "boosted" to energies higher than their injected energies thanks to the high-energy thermal tail of e–h distributions created by the thermal phonons of the lattice at finite temperature.

Classically, one expects the maximum WPE to be somewhat below unity, as the three factors entering the equation will each be below unity: the IQE is limited by non-radiative recombination, the LEE suffers from the various loss mechanisms that light undergoes before leaving the device, and the EE has limitations coming from resistive losses of the LED current and carrier leakage mechanisms.

However, this analysis relies on considering the *LED as an isolated system*, whereas it interacts thermally with its environment. It is generally considered that the only pathway for energy exchange through this interaction is the release of the heat generated by the LED through various loss mechanisms. But through the same interaction, the LED could gain energy from its environment. At the quantum level, one can expect power efficiency larger than unity *for emitted photons* if injected electron–hole pairs get an energy boost from the lattice thermal energy. Already in 1953, Lehovec et al. [58] remarked that the emitted photon could have an energy larger than that of the energy of electrically injected electron–hole pair, i.e. eV_{bias}. The energy gain was attributed to the energy drawn from the lattice thermal energy. Bradley applied already in 1956 for a quite complete patent on cooling from a high efficiency light emitting p–n junction [130]. He discusses at length Ge and Si, and ways to improve their efficiency by doping, but he also mentions that direct-gap semiconductors might have higher recombination efficiency. The issue of reabsorption is to be solved by placing the emitting volume near the surface of the device. More experimental data came in 1962 when Keyes and Quist [62] remarked that in GaAs "*the above results indicate that it may possible to fabricate diodes in which for every injected hole a photon of energy close to the band-gap is emitted from the diode. If such diodes are possible, they will, when forward-biased, extract heat from the surroundings. This is because the holes that are injected are from the high-energy tail of the Fermi distribution, and the full band-gap energy is not necessary to inject them into the n-region. The heat extracted per unit time will be* $-\mathrm{dQ}/\mathrm{dt} = I[(h\nu/q) - V]$, *where V is the applied voltage in volts and hν/q is the average photon energy also in volts. It is evident from the above equation and Fig. I that diodes in which each injected carrier produces a photon of energy close to the band-gap can act as refrigerators.*" The first evidence that the *average* photon energy could be larger than the supplied energy came in 1964 [131] who attempted to cool a GaAs LED through light emission. However, the IQE was too small to prevent the overall heating of the diode. The fact that the LED can overall act as a refrigerator conversely meant that the overall electrical energy efficiency (wallplug efficiency) could be higher than unity by drawing thermal energy from the surroundings. See Fig. 15.

It should be noted that, due to the need to have alternatives to the existing cooling techniques in microelectronics (thermoelectrics, cryogenerators, cryofluids), the search for photoluminescence or electroluminescence cooling has attracted much more efforts than increasing LED WPE by thermoelectric carrier pumping.

The possibility of increasing light emission at the quantum level by drawing energy from the thermal energy of the surroundings has given rise to debates that can be traced back well before the appearance of the LEDs in the 1950s. It is at first look surprising that a "degraded" form of energy such as heat could be transformed into "good" energy such as light. It started with the discussion on the issue of the Stokes and anti-Stokes fluorescence in atomic vapors in the article by Lenard et al. in *Handbuch der Physik* [132], where it was claimed that the observation of anti-Stokes emission in vapors, i.e. with emitted photon energies higher than the exciting photon energies was contradicting the second thermodynamics principle, as one would convert heat (energy with high entropy) into radiative energy (energy with a lower entropy). Pringsheim [133] noted that energy conservation could be fulfilled by collisions that would cool down the atom vapor. He described a gedanken experiment where one would cool the vapor in an isolated vessel by exciting it with the lower of the two yellow Na lines, i.e. in the ground state while through collisions that vapor would emit from the excited state, thus cooling down. Exciting with this light a second Na-containing vapor would heat the latter compared to the first vessel. While this is true only in a transient situation if the two vessels were completely isolated, Pringsheim argued that the system could not be isolated as it required an external light source, thus could operate cw.

This discussion was revived in 1945 by Vavilov [134], who insisted that the second law was violated as one could establish a *reversible* cycle from excitation to emission back to excitation, where one would have gained energy through the

anti-Stokes emission. In the first of a series of three papers in the same issue of the *Journal of Physics of the USSR* in 1946, Pringsheim [135] doubted the feasibility of such a reversible cycle, however still being evoked by Vavilov [136] in a rebuttal of the response by Pringsheim in the next paper of the issue. In particular, he discards the argument by Pringsheim that the transformation of an incident directional beam into scattered fluorescence emission is an irreversible process. For this, he relies on a drawing by Lomonosov in 1743 claiming an optical mirror system transforming a point source emission in all directions into a directional beam, which would then be able to re-excite the vapor (obviously disregarding the issue of the beam *étendue*)! This argument is the more surprising as in a paper following that containing Vavilov's response, the issue is settled by Landau in the third paper [137] who showed that the light emitted in random directions carries out a much larger entropy than the incoming exciting beam, which leads the anti-Stokes process to obey both first and second principles. Interestingly, Landau remarked that if light is emitted in a narrow frequency range and is directional, which appeared 15 years later as a laser, that light would have a negligible entropy and would not then lead to cooling.[12] Vavilov had triggered the paper by Landau (paper which Pringsheim apparently did not know) and used it as a support of his views "An insignificant entropy increase during photoluminescence processes for the case of non-chromatic light is discussed in the paper by Landau". Indeed, Landau mentions "Thus the relative luminescence yield, even when capable thermodynamically to exceed unity, does so by an insignificant quantity." Landau reaches this conclusion by an overestimate of the luminescence effective temperature. In any case, it is puzzling that Vavilov uses the argument that the effect is small to continue to claim that Pringsheim is wrong. He, however, concludes that more efforts should be devoted to study photoluminescence yields.

We of course now know how to realize Vavilov's objective of reversible light emission: this is the regime of strong light–matter coupling, where the selective coupling of the emitting species to a *single, lossless photon* mode leads to the Rabi oscillation of the coupled system between the emitting system state and the photon mode state. In the bulk solid state, this was identified as phonon or exciton polaritons [138,139] and in multilayered microcavity structures as cavity polaritons [98,140]. It should be however emphasized that under the strong coupling conditions, the emitter efficiency is poor as light modes are to be confined and photons undergo many absorption/emission cycles with some dissipation setting in [141].

The tackling of cooling by light emission has since drawn huge efforts, the most well-known being that of laser cooling of atoms. A pioneering analysis was given by Kastler in the context of optical pumping, which could be used to cool down the internal degrees of freedom of optically pumped atoms and cool down by collisions atoms of a buffer gas, an effect that he calls "lumino frigorifique". He extended his concept so far applied to magnetic sublevels of atomic vapors to the Stokes and anti-Stokes lines due to crystal fields in rare-earth ions in a crystalline matrix, reviving the concepts of Pringsheim. He was however carefully optimistic in his prediction of cooling in the solid state: "*It therefore does not seem impossible to obtain at low temperatures a cooling by irradiation leading to anti-Stokes re-emission if the fluorescence yield of the illuminated crystal is near unity*" [142]. As we know, optical pumping quickly developed into a major tool for the study of atomic spectroscopy, for which Kastler received the Nobel prize in 1966. The other major cooling method in atomic physics, for which Chu, Cohen-Tannoudji and Phillips received the Nobel prize in 1997, was the use of detuned laser excitation for atomic vapors leading to the progressive slowing down of the translational motion.

In solids, *net* radiative cooling was much more difficult to observe, because of the parasitic effect of non-radiative recombination mechanisms that instead lead to lattice heating. The first demonstration of cooling of a solid was performed in 1995 on a Yb^{+3}-doped heavy-metal fluoride glass (ZBLANP) [143], where the needed power conversion efficiency is reduced through laser optical excitation, avoiding the losses associated with electrical carrier injection. As for semiconductor LEDs, it is interesting to note that, while lattice cooling was invoked as early as 1953 [58], the first demonstration of *overall LED* cooling was very recently done indirectly by observing a LED power efficiency larger than unity, which by difference implies that energy has been taken from the surroundings [144]. The demonstration relies on a detailed analysis of the above equation for WPE: V_p/V_{bias} can be made arbitrarily large by diminishing V_{bias}. Of course, the price to pay is a vastly diminishing current density, roughly exponentially according to Shockley's diode equation. Also, the EQE diminishes according to the diminished bi-molecular radiative emission rate which scales as Bn^2. Then, in the simple ABC model of radiative efficiency where A, B, and C are respectively the non-radiative recombination coefficient, the radiative recombination coefficient, and the non-linear non-radiative recombination coefficient, usually an Auger coefficient, the radiative efficiency as a function of the carrier density n is given by

$$IQE = \frac{Bn^2}{An + Bn^2 + Cn^3}$$

It would seem that the radiative efficiency would diminish to zero with voltage as the carrier density would vanish, but at extremely low bias such that $V < k_B T/q$, the active region excess carrier concentrations become negligible compared to the equilibrium carrier concentrations n_0 and p_0, i.e. $\Delta n \ll n_0$, $\Delta p \ll p_0$, and the IQE

$$IQE = \frac{Bn_0^2}{An_0 + Bn_0^2 + Cn_0^3}$$

[12] This remark by Landau is not emphasized by him as proving that the re-directionality of the emitted light by Vavilov's scheme would be the one violating the second principle!

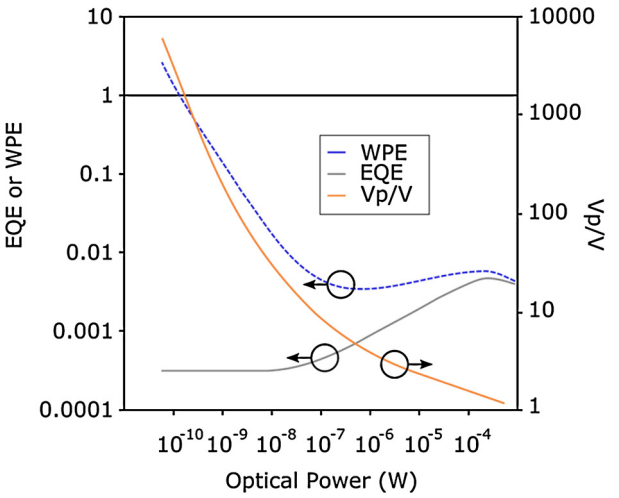

Fig. 16. Relationship for EQE, WPE, and electrical efficiency V_p/V on emitted optical power for the mid-IR LED reported in [144]. The WPE curve has two peaks, the conventional peak near the EQE peak, and the other at low bias, where the EQE saturates as V_p/V continues to rise. At low bias, the WPE exceeds 100% at an EQE of just 0.03% and V_p/V of ∼700%. The plot is based on 135 °C measurement data [from 144,145].

becomes independent of voltage [144]. Then, as the LEE is independent of voltage, WPE will vary as $1/V$ and can reach values above unity (Fig. 16).

From this discussion, it would seem that WPE larger than 100% can only be reached at vanishingly small, useless currents. There is however another operating point with $V < V_p$ for which WPE might be larger than unity provided the EQE is large enough [146–149]. This would occur at voltages nearby V_{phot}, detuned enough to have a sizable thermal energy pumping from the lattice $V_{phot} - V$, but with not too large a detuning, so that IQE is large enough and the radiative recombination term Bn^2 is much larger than the SRH recombination An.

6. Summary

Lighting has seen many revolutionary changes in history, each driven by improvements in light quality or cost, or both. Due to the importance of the lighting needs, most of a new energy source for lighting was used for that application. LEDs are the latest of many such revolutions, however still relying on electricity. It consists in the direct conversion of electricity in light by radiative recombination of electrically inject electron–hole pairs in semiconductor heterostructure p–n junctions. Thanks to the versatility of this concept, it seems that LED solid-state lighting might supply all characteristics of lighting in view of its quality, ease of use, reliability, and its reaching of the physical limits of electricity-to-light conversion.

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