Increasing the reliability of solid state lighting systems via self-healing approaches: A review

Ugo Lafont a,c,*, Henk van Zeijl b, Sybrand van der Zwaag a

a Novel Aerospace Material, Faculty of Aerospace and Engineering, Kluyverweg 1, 2629 HS, Delft, The Netherlands
b DIMES, Delft University of Technology, P.O. Box 5053, 2600 GB, Delft, The Netherlands
c Corresponding author at: Novel Aerospace Material, Faculty of Aerospace and Engineering, Kluyverweg 1, 2629 HS, Delft, The Netherlands

Abstract

Reliability issues in solid state lighting (SSL) devices based on light emitting diodes (LED) is of major concern as it is a limiting factor to promote these optoelectronic devices for general lighting purposes. This postulate is even truer for high power devices in which high current and thus high thermal load are involved. In order to increase reliability and lighting efficacy, LED designs related to thermal management are evolving parallel to LED research and development. However there are still some issues mainly related to the degradation of LED's constituents with time involving a faster decay of the lightning efficacy. In order to increase reliability of SSL devices, components presenting self-repairing properties could be implemented. In this review we will first briefly expose the state of the art on inorganic semiconductor based LED research and development, trends and challenges that lead to an increase of lighting efficiency. In a second part the different failure mode occurring for SSL devices have been compiled highlighting what are the main mechanism influencing and limiting LED reliability. Strong from this knowledge, in the last part, self-healing concepts will be proposed to further improve LED’s reliability.

© 2011 Elsevier Ltd. All rights reserved.

Article info

Article history:
Received 19 April 2011
Received in revised form 22 August 2011
Accepted 22 August 2011
Available online 25 September 2011

Keywords

Self-healing, LED, Solid state lighting, Inorganic semiconductor, Reservoir based systems, Reversible chemistry, Thermoplastic–thermoset blend, Conductive polymer, Pending function/unreacted functions

Contents

1. Introduction ........................................................................................................... 72
2. LED development, trends and challenges .......................................................... 72
  2.1. The die ........................................................................................................... 72
  2.2. Challenges .................................................................................................... 74
  2.3. White LEDs ................................................................................................ 74
  2.4. LED packaging .............................................................................................. 75
  2.4.1. Level 1: die packaging ........................................................................... 75
  2.4.2. Level 2: LED on substrates ................................................................. 77
  2.4.3. Levels 3 and 4: LED modules and luminaire ........................................ 77
3. LEDs failure modes .............................................................................................. 77
  3.1. Failures related to electrical stress ................................................................. 78
  3.2. Failures related to thermal degradation ....................................................... 78
  3.3. Failures related to (thermo) mechanical stress ............................................ 80
  3.4. Failure related to chemical reactions ............................................................ 80
4. Self-repairing approach to enhance LED reliability ............................................. 80
  4.1. Semiconductor damages-healing ................................................................. 80
  4.2. Packaging damages-healing (cracks and delamination) .............................. 81
  4.2.1. Reservoir based systems ....................................................................... 81
  4.2.2. Reversible chemistry ........................................................................... 82
  4.2.3. Thermoplastic–thermoset blend .......................................................... 82
  4.2.4. Reversible physical network (ionomers) ............................................... 82
  4.2.5. Conductive polymer ............................................................................ 82
  4.2.6. Pending function/unreacted functions .................................................. 83

* Corresponding author at: Novel Aerospace Material, Faculty of Aerospace and Engineering, Kluyverweg 1, 2629 HS, Delft, The Netherlands.
E-mail address: U.Lafont@TUDelft.nl (U. Lafont).

0026-2714/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
1. Introduction

Since the development of the monochromatic red LED using GaAsP semiconductor in the early sixties, the efficiency of light emitting device based on p-n junction has hugely increased. In 1993, researchers at Nicha Chemical Industries using metal organic chemical vapor deposition were able to produce the first high brightness blue light-emitting diode based on p-GaN/n–InGaN/n–GaN double heterostructure [1]. Later on, the combination of a yellow phosphor with the blue emitting device gave birth to the first white LED. Nowadays, advances in development of groups III–V semiconductor allow a fine tuning of the semiconductor band gap leading to wavelength emission from UV to Infra-Red. Besides, the phosphor conversion based white LEDs have also greatly improved during the last 10 years presenting high luminous flux and efficacy. Recently, researchers at Cree Inc. have claimed a luminous efficacy for a white power LED above 200 lm/W (4579 K) [2].

LEDs are small, present a high luminous efficacy, exhibit a long lifetime and low energy consumption compared to usual lighting devices. It is certain that these types of solid state lighting will be of major interest worldwide from an economic and environmental point of view. Efficacy (~150 lm/W) and lifetime (~50,000 h) of solid state lighting devices are the two main factors that are usually highlighted as main advantages. However, as with many electronic devices, pushing the limit of LED devices to increase efficiency using higher current combined with multiple thermal cycling in harsh environment (moisture) involves reliability issues that need to be solved to guarantee optimal light emission over long periods of time. An alternative approach to the classical reliability improvement strategies is the use of materials or component with self-healing or self-repairing capabilities, such that small scale defects do not grow into catastrophic defects but disappear more or less autonomously. Of course, for such self-healing strategies to work, detailed knowledge of the prevailing materials and operating conditions as well as the resulting damage mechanisms is required.

Hence, in this review we first briefly present the state of the art in inorganic semiconductor based LED research and the developments, trends and challenges that lead to an increase of lighting efficiency. In the second part the different failure modes occurring for SSL devices have been compiled, highlighting the main mechanisms influencing and limiting LED reliability. In the last part, we look at using self-healing concepts potentially relevant to further improve the reliability of SSL devices.

2. LED development, trends and challenges

LEDs are optoelectronic devices consisting of multiple components. A LED is made of two distinct parts, namely the die and the packaging. The die is composed of a thin monocrystalline layer of semiconductor presenting a p-n junction and responsible for the photon (light) emission upon electronic stimulation. The packaging brings electrical contacts with the electrodes, thermal dissipation, mechanical resistance, optical properties (lens, reflector), chemical protection and phosphors encapsulation (for white LEDs). In the SSL value chain “packaging” is used at different level from the initial bare semiconductor die to the final commercial product (Luminaire or “Ledinaire”). We can distinguish five different valorization levels (Table 1):

- Level 0 related to the bare die.
- Level 1 related to the packaged die (LED).
- Level 2 related to LEDs on substrate (printed circuit board – PCB).
- Level 3 related to LED modules (optics, remote phosphors, electrical modules, drivers ...).
- Level 4 related to luminaire housing and design incorporating cooling and reflector.

So, parallel to progress in die development and manufacturing to increase conversion efficiency there is a huge effort made on packaging design to optimize the overall luminous efficacy and reliability of LEDs. The LEDs’ luminous efficacy is expressed in terms of external quantum efficiency (EQE):

\[ \text{EQE} = \text{IQE} + \text{EXE} \]  

where IQE is the internal quantum efficiency and EXE is the extraction efficiency related to intrinsic properties of the die and the packaging, respectively.

2.1. The die

In a LED, the die is composed of a monocrystalline semiconductor. This semiconductor can be doped to increase either the amount of negative charge (electrons) or positive charge (holes) carriers becoming an n-type or p-type semiconductor, respectively. When a p- and n-type semiconductor are in contact, the recombination of the electron and the hole at the junction leads to the production of a photon. The photon energy and thus its wavelength is directly proportional to the band-gap of the semiconductor used. In this respect, it is theoretically possible to produce radiation from UV to infrared using a suitable semiconductor with suitable band gap. The band gaps of the main semiconductors used in LEDs are presented as function of the lattice constant in Fig. 1. In principle, it is now possible to tune the emitted wavelength energy from 0.6 (Ge) to 6.28 eV (AlN).

However, there is one restriction to this postulate being the possibility making of the semiconductor to be p- or n-doped. The production of LED dies is mainly achieved by means of epitaxial growth using Molecular Beam Epitaxy (MBE), Chemical Vapor Deposition (CVD) and Metal Organic Chemical Vapor Deposition (MOCVD) techniques. In order to control the crystal orientation of the as-grown layers, the use of a growth substrate is needed. These substrates are generally made of SiC, Si, GaAs, ZnO or Al₂O₃ (sapphire) presenting a particular crystallographic orientation. The initial substrate crystallographic orientation will determine the orientation of as-grown layers. Moreover, in case of a multiple layer die, the crystal structures of the different epitaxially grown semiconductor films should fit each other to avoid huge lattice mismatch, interfacial dislocations and even debonding. We can distinguish three main crystal families used in LED die production: cubic diamond structure (Si, Ge, C), cubic zincblende structure (III-Phosphides and III-Arsenides) or hexagonal wurtzite structure (III-Nitrides). This last class of material (III-Nitrides) is the most...
important semiconductor since silicon. As shown in Fig. 2 it is possible to tune the band gap from 0.7 to 6.28 eV alloying $\text{Al}_x\text{Ga}_y\text{In}_z\text{N}$ ($0 < x, y, z < 1$), making this class of material to the best theoretical candidate for optoelectronic application. Moreover, the lattice changes between the different alloys are quite small, minimizing the interfacial dislocations density.

LED internal quantum efficiency has tremendously improved since the 1960s due to the use of quantum-well structures (Fig. 3). The construction of a quantum well implies that the hetero junction of two semiconductor presents a straddling gap. The injection of the free carriers in the quantum well increases their concentration and thus the radiative efficiency. The completed filling of the well by the free carrier leads to luminescence saturation. In order to increase the optical power at higher current densities, multiple quantum well based LEDs nowadays are the most commonly used structures.

LED dies are 2D layered vertically structured systems (Fig. 4). This morphology implies that the light extraction will occur on the side of the die and the light will encounter several reflecting interfaces in the epilayer. Reflectors are used to improve the extraction efficiency of LED and light emitted downward toward the substrate is reflected upward in order to contribute to useable light output. High refractive metallic mirrors like Ag or Al are commonly used. Those metallic mirrors can efficiently reflect light at
arbitrary angles and polarizations, however they are somewhat less efficient in the visible regime and have reliability problems at the interface with semiconductor due to chemical degradation or electro-migration. These problems can be overcome by replacing metallic mirrors by a distributed Bragg reflector [4] or an omni-directional reflector [5] in the die bottom part. Beside this mirror approach, die surface roughening has also improved light extraction in flip-chip mounted type LEDs [5]. Finally, the use of 3D LED architectures has recently proved to be one of the best solutions to drastically increase the effective area and thus the light extraction efficiency [5,6]. Moreover, the 3D die architecture will limit the dislocations densities. These 3D structures can be achieved by patterning the initial substrate or by using nanorod-like structure of semiconductor. Recently, a luminous efficacy of 249 lm/W for white LEDs has been made possible using ITO transparent p-electrode instead of Ni/Au based translucent one in combination with a patterned die architecture [6–12].

2.2. Challenges

LED systems based on III-phosphide semiconductor exhibit high efficiency for the emission of red light. However these systems become less efficient at shorter wavelength (green and yellow) due to weak carrier confinement and indirect minima in the conduction band. Similarly, III-nitrides systems (AlGaN) present high internal quantum efficiency for emission of near UV and blue wavelength but suffer from loss of efficiency for longer wavelength (green, yellow and red). Recent research has related this phenomenon to the increase of threading dislocations [9] and fluctuation in the alloy composition for InGaN quantum well system at high indium content [13]. These structural defects negatively affect the emitting efficiency of LEDs by increasing leakage current [14] and Auger recombination [15]. As can be seen on Fig. 5, both III-Nitride and III-phosphide systems are not efficient to produce wavelength shorter than 550 nm leading to the so-called “green gap”.

In order to fill this “gap” the III-Nitride material is the most promising system at this moment. The efficient production of green light is indeed the limiting factor for warm white light production using tri-chromatic (red green blue) systems. To reach this goal, efforts to avoid structural defect [16] as well as minimizing piezoelectric polarization using non- or semi-polar structure [17] need to be done to emit green light as efficiently as the existing red and blue LEDs system. Threading dislocations in the GaN structure induce the generation of V-shape defects during the growth of GaInN quantum well layer. These defects drastically limit the internal quantum efficiency of LEDs. Hydride Vapor Phase Epitaxy (HVPE) [18] has been used to reduce the threading dislocation density from $10^9$–$10^{10}$ cm$^{-2}$ to $10^6$ cm$^{-2}$ during the growth process of GaN-based structures and thus consequently the V-defects formation. Using more common epitaxial growth techniques, a reduction of the threading dislocation density can be achieved by selective defect passivation using SiO$_2$ followed by epitaxial re-growth. The threading dislocation density in the re-grown epilayer is reduced from $1 \times 10^7$ to $4 \times 10^7$ cm$^{-2}$ resulting in LED output power increase of 45% [18]. Recently, the incorporation of micrometer voids close to the sapphire substrate has led to a reduction of the defect density by two orders of magnitude [19]. These voids act as termination sites or “sinks” for the dislocations generated as a result of the sapphire/GaN lattice mismatch. Beside initial defect reduction, another way to improve internal quantum efficiency of III-Nitride based green LEDs consist of using a structure that does not present any piezoelectric properties. Indeed, all commercially available LED structures are grown along the c-axis of the hexagonal wurzite structure as most of the supports (i.e. sapphire) are oriented along the [0001] direction. III-nitrides materials present piezoelectric and spontaneous polarization properties perpendicular to the c-axis inducing the generation of electric fields. These electric fields negatively affect the electron–hole recombination limiting the overall efficiency. In order to overcome this problem, the use of structures without any polarization is of great interest (Fig. 6). Such structures will allow higher In uptake, allow the electron capture, reduce the electron overflow and finally, minimize the blue shift at high injection current. Many recent works have been devoted to the growth of structures along semi-polar (1013, 10 bar11, 1122) or non-polar (m-plane and a-plane) GaN planes [18,20–31]. As a result, non-polar structures lead to high power violet and blue LEDs whereas semi-polar structures generate green LEDs with reasonably high power and yellow LEDs with the same efficiency as AlInGaP systems.

2.3. White LEDs

Whereas LEDs emit monochromatic light, white light for many applications related to human everyday life is needed. There are multiple ways to produce white light using LEDs. However, it should be kept in mind that development of White LED (WLED) is intimately related to the progress of UV and blue LEDs performances as long as the “green gap” is not filled. One of the most trivial ways to create white light is to mix red, green and blue light. As discussed in the previous paragraph, the lack of efficient green LED limits this approach. Moreover, the red and blue LEDs are also not equal regarding their efficiency in time. Hence over time an initially perfect white light source will drift into a colored direction. Finally, because of the intrinsic narrow emission peak of LEDs, the color mixing will exhibit a poor color rendering and bad coverage of the visible spectrum. This last problem can be solved by using more than three colors to produce white light like in the red, green, yellow and blue systems.

Alternatively white light can also be produced starting with monochromatic light using phosphors. The first commercially available white LED was manufactured by coating a blue emitting InGaN die with a yellow cerium-doped yttrium aluminum garnet (YAG) phosphor [18]. In the same way, it is possible to combine red, green and blue phosphors to produce a warmer white light [32] that is more desirable for home lighting. Due to the low excitation of red phosphors by blue light, the use of near-UV LEDs is more suitable for multi phosphors approaches.

The last and most recent approach implies the use of semiconductors nanocrystals like “quantum dots” as blue or UV light converter [33]. This approach is closely linked to the research and development of semiconductor nanocrystals. Nowadays it is possible to produce highly monodisperse and tunable quantum dots of a

![Fig. 5. External quantum efficiency vs. peak wavelength for high-power LEDs based on the III-nitride and III-phosphide material system (reproduced from Ref. [16]).](image-url)
A wide range of materials (CdSe, CdS, CdTe, ZnS, ZnSe, ZnTe, ZnO) presenting pure or core–shell structures. Depending on their size and composition, these quantum dots present photoluminescent properties converting UV/blue light into visible radiation. A coating of a blend of different quantum dots (red, green and blue) on a commercial UV LED successfully produced white light.[34–48]. It is important to mention that this last approach involves the production of quantum dots with narrow size distribution in order to control the color mixing.[37,49,50]. Recently, some researches have aimed at producing direct white light-emitter nanocrystals for solid state lighting. The main advantage of this last approach is to eliminate the need of complex color mixing or conversion techniques. Several groups have reported the generation of direct white emission using ZnSe nanocrystals [34], ZnO–SiO2 nanocomposites [51], ultrasmall CdSe nanocrystals [52] or 5 nm ZnO nanocrystals [53]. Some other materials like Pb2+ doped ZnS [54], Mn2+ doped ZnS [55], Mn2+ doped CdS [56] and ZnS doped silicon [57] are being considered as potential direct white light emitter.

It is certain that white light production based on LED is the driving force of all solid state lighting research and development. From the state of art, the white light production can be done by mixing three or more color sources, by converting and mixing blue radiation, by converting blue/UV radiation into three or more color and by converting UV radiation directly into white light (Fig. 7).

### 2.4. LED packaging

The technology related to the bare die (level 0) has been presented in the previous paragraph. In this section, developments in LED packaging covering levels 1–4 will be discussed. In this respect, research and development on LED packaging, assembly and design play a major role in the luminescent device efficacy and reliability by increasing the efficiency of light extraction. Currently internal quantum efficiency (IQE) can reach 80% for blue based LEDs however the external quantum efficiency is only of 70% for the best end-user products.

#### 2.4.1. Level 1: die packaging

"If one considers the die as the LEDs heart, the packaging is the body." The die packaging is one of the most important parameters in the value chain as it is the warrant of the usability of the LED the device’s reliability and luminous efficacy, since:

- It provides the electrical contact to the die.
- It manages the heat dissipation.
- It mechanically protects the die.
- It preserves the die from external chemical aggression (moisture for example).
- It drives the light extraction.
- It can incorporate the phosphors for light conversion.

First of all, once the die has been produced and sliced into a suitable shape and size, it needs to be paced on a support and the cathode and anode need to be connected. There are different ways to connect electrodes to the die depending on the die architecture and design used. Two main designs are those where one electrode is on the top and the second one is located at the bottom of the die or those where both anode and cathode are located on the same side of the die. The first design involves the use of at least one bonding wire for anode connection; the cathode being directly connected to the other side of the die using conductive glue or solder (Fig. 8a).

With the development of high power LED, the classical design used for the so called “signalization” LEDs (Fig. 8a) is not suitable due to its poor heat transfer capabilities. In high power LEDs, a drive current of 1A can be used and the junction temperature can reach values >150 °C. It is generally accepted that good reliability
performance will only come from fine thermal design of the chip as well as the package when it comes to power application. In this respect new designs have been implemented to enhance heat transfer during LED operation. These surface mount packages include a heat-sink directly connected to the die (Fig. 8b). The thermal transfer between the die and the heat sink is achieved by direct soldering (Fig. 9a) or by using a thermal conductive adhesive/resin (Fig. 9b) that can also present electric conductivity properties (epoxy composite filled with Ag or Al particles). Recently, electroless and electroplating techniques of Au/Ni electrodes have been used to embrace and directly bond the die to the heat sink [56]. As a result the thermal resistance has decreased and the luminous intensity has increased compared to LEDs with a resin-bonded die. To further enhance the thermal transfer from chip to heat sink, diamond filled AgSnCu solder has been used showing an output power of 350 mA enhanced by 22% compared to silver paste mounted chip [59].

In order to further maximize heat transfer flip-chip technology has been developed for InGaN based LED. Indeed, most of III-nitrides are grown on sapphire. Sapphire has a low thermal conductivity of about 30 W/m K. In a conventional face-up surface mount LED, the sapphire induces a larger thermal resistance on the thermal conduction path to the heat sink. Thus a huge amount of heat will be transferred from the front of the die via the encapsulant and then dissipated in the air (Fig. 10). In a flip-chip configuration, the sapphire is on the top and a thermally conductive substrate/submount is used with metal interconnect to the die for a better thermal pathway.

As we just saw in face up and flip-chip technology, LED submounts are not just simple carriers of the semiconductor but should exhibit good thermal conductivity. Moreover, the coefficient of thermal expansion (CTE) of the submount is another important parameter to take into account in LED packaging. In order to avoid CTE mismatch between the die and the carrier and to improve heat dissipation, silicon and ceramic substrate like Al2O3 or AlN are preferred to classical lead frame. The heat transfers efficiency can be enhanced using AlN instead of Al2O3 [60], as the intrinsic thermal conductivity values for Al2O3 and AlN are 20 and 230 W/m K, respectively.

To protect the die from the external environment (dust and moisture) and to provide mechanical strength to the LED package, encapsulants are used. Beside they protective function, encapsulants have an optical function: they act as focusing lens and thus improve the light extraction efficiency. The most commonly used encapsulants are organic thermosets resin (i.e. epoxy, polycarbonates or polymethyl methacrylate). Epoxies have been used for decades in small LEDs packaging as they are easy to process and present high light transmission, high refractive index and high glass transition temperature. However, several degradation problems occur when using epoxies encapsulant in high power LEDs.
that are mainly caused by the high amount of heat together with the UV/blue light of these systems (these problems will be discussed in the next chapter). Nowadays, optical grade silicone is preferred over organic based encapsulant due to its high refractive index (1.38–1.58), good UV and thermal resistance [61,62], high optical clarity and low modulus [63]. Silicone chemical structure consists of Si and O bonded together via an inorganic siloxane (Si–O) bond (444 kJ/mol). Compared to carbon–oxygen (C–O) bonds (339 kJ/mol) and carbon–carbon (C–C) bonds (356 kJ/mol), siloxane bonds exhibit a better chemical stability and therefore a higher reliability. On the other hand hybrid encapsulant are also widely investigated to enhance refractive index [64,65] and thus the performance of light extraction. Dispersion of nanosized particles (SiO₂ [66,67], TiO₂ [68], ZrO₂ [69–71], ZnO [72]) in the organic matrix has proven to be a suitable way to increase refractive index of encapsulant. The incorporation of nanosized particles can also bring other properties to the encapsulant: a nanosized ZnO/silicone encapsulant has recently shown to be an efficient way to shield undesirable UV radiation emitted from the die [73]. Finally, hybrid encapsulants can also directly incorporate phosphors [74] or quantum dots [75,76] for light conversion purpose.

For white light production, placement of phosphors in LED is of great importance. In classical LEDs the phosphors are simply dispersed in the encapsulant. Due to phosphor particle settlement and agglomeration during curing process of the encapsulant there is a significant variation in correlated color temperature (CCT) of white LEDs made this way. Moreover there is a huge CCT variation depending on the angle of the light emission and whether it is emitted from the top or side of the die. To increase CCT uniformity conformal coating of phosphors on LED die have been developed and patented [77]. By controlling the thickness and distribution of phosphor coating over the entire die, the emitted light does not present any CCT variation whatever the LED viewing angle. However it has been proved that using this phosphor configuration some part of the emitted light travels back to the die. The light could be re-absorbed by all LED constituents (reflector, LED chip, encapsulant, adhesive . . .) adding additional thermal loading and loss in extraction efficiency. Remote phosphor technique also called “scattered photon extraction” has been developed to minimize absorption loss and improve light extraction [78]. In this configuration the phosphor is moved away from the die resulting in a 60% increase in luminous efficacy compared with traditional white LED packages where the phosphor is placed close to the die.

It is well established that external quantum efficiency of LEDs as well as luminous efficacy and reliability is highly related to packaging and encapsulation development. Nowadays, a better thermal management, light extraction and reliability are achieved in high power LEDs thanks to the packaging improvement/development using flip-chip technology on ceramic substrate with silicon based encapsulant.

2.4.2. Level 2: LED on substrates
LEDs substrates are also expected to have a low CTE and good thermal conduction properties as they should act as a thermal bridge to the outside world. The technology used is similar to the one used in IC technology. Several types of submount/substrate material, such as PCB (printed circuit board), MC-PCB (metal core printed circuit board), ceramic substrate, direct copper bonded substrate and LTCC-M (low temperature co-fired ceramic on metal) substrate have been developed and employed as LED submount packages. The thermal conductivities of dielectric insulator materials such as PCB and MCPB are about 0.36 W/m K and about 2 W/m K, respectively. For LTCC-M substrate, the major compositions of dielectric material are SiO₂, MgO, CaO, B₂O₃, Al₂O₃, and the value of thermal conductivity is less than 20 W/m K. For ceramic substrate and direct copper bonded substrate, the most frequently used dielectric insulator materials are Al₂O₃ and AlN. These materials have a higher thermal conductivity, with typical values of 20–230 W/m K. Ceramic substrates also present CTE values that are compatible with those of the LED chip, Si substrate or sapphire. Metal composite presenting high thermal conductivity (Table 2) ranging from 200 to 1800 W/m K are also considered as substrates [79,80]. Generally it has been shown that the improvement of LED luminous efficacy using higher drive current is directly related to the lower thermal resistance of LEDs substrates [81].

### Table 2

<table>
<thead>
<tr>
<th>Materials</th>
<th>CTE (ppm K⁻¹)</th>
<th>Thermal conductivity (W m⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>4</td>
<td>150</td>
</tr>
<tr>
<td>SiC</td>
<td>4</td>
<td>120</td>
</tr>
<tr>
<td>GaAs</td>
<td>6.5</td>
<td>54</td>
</tr>
<tr>
<td>GaN</td>
<td>6</td>
<td>130</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.7</td>
<td>20</td>
</tr>
<tr>
<td>AlN</td>
<td>3.5–5.7</td>
<td>170–230</td>
</tr>
<tr>
<td>Al</td>
<td>23</td>
<td>150–230</td>
</tr>
<tr>
<td>Cu</td>
<td>18.5</td>
<td>398</td>
</tr>
<tr>
<td>AlSiC</td>
<td>8.4</td>
<td>200</td>
</tr>
<tr>
<td><strong>Substrates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB (FR4)</td>
<td>13–17</td>
<td>0.36</td>
</tr>
<tr>
<td>MC-PCB</td>
<td>4.8–8</td>
<td>24–170</td>
</tr>
<tr>
<td>Ceramic (Al₂O₃/AlN)</td>
<td>3.5–6.7</td>
<td>20–230</td>
</tr>
<tr>
<td>Cu–Mo–Cu</td>
<td>7</td>
<td>184</td>
</tr>
<tr>
<td>SiC/Al</td>
<td>8.75–11.5</td>
<td>170–220</td>
</tr>
<tr>
<td>Carbon fiber/Al</td>
<td>3.2–11</td>
<td>218–800</td>
</tr>
<tr>
<td>Carbon fiber/Cu</td>
<td>4.2–6.8</td>
<td>300–800</td>
</tr>
<tr>
<td>Graphite flake/Al</td>
<td>6–7</td>
<td>400–420</td>
</tr>
<tr>
<td>Diamond/Al</td>
<td>3.4</td>
<td>400–600</td>
</tr>
<tr>
<td>Diamond/Cu</td>
<td>5.8</td>
<td>600–1200</td>
</tr>
<tr>
<td>CVD diamond</td>
<td>1–2</td>
<td>1100–1800</td>
</tr>
</tbody>
</table>

2.4.3. Levels 3 and 4: LED modules and luminaire

The research and development at this value chain level is strongly related to solid state lighting manufacturer proprietary designs. Each company develops and assembles their own products with different level of reliability and performance according to their market targets. However, all efforts now focus on enhancing light extraction and color stability but also on better management of heat transfers to promote device reliability. These two targets are achieved by implementing in the device secondary optics as well as remote phosphors on one hand and heat sink and secondary active cooling system (synthetic jets, piezoelectric fans [82] or liquid cooling [83]) on the other hand. Finally, it is important to mention that power supplies and drivers that are part of the final product also present reliability issues and directly affect the solid state lighting device life time [84,85]. This topic will not be discussed in this review.

### 3. LEDs failure modes

The “aging” of SSL result in either a gradual lowering of light emission, or a complete and abrupt failure. In order to understand and optimize SSL reliability all the failure modes need to be known and understood. A LED can be said to have ‘failed’ when its light output falls below a threshold expressed as a percentage of peak output. According to the definition proposed by the Alliance for Solid-State Illumination System and Technology (ASSIT), failure is considered to have taken place when the luminosity decays to 70% of its initial value.

The failure is directly related to the properties of the SSL constituting components like:
– The precise chemical constituent of the semiconductor.
– The structure of the LED die.
– The chemical properties of the encapsulant.
– The chemical makeup and implementation of phosphor conversion.
– The bonding and interfacial component.
– The mechanical structure of the device.
– The materials used and device's thermal performance.
– The materials used and consistency and quality of the LED manufacturing process.

Basically, the mechanisms responsible for LED degradation are most of the time triggered and accelerated by the simple use of the device. They are related to the fact that a current is flowing in active region, that high temperature is reached during operation leading to thermo-mechanical stresses and that the device can be exposed to undesirable electrical events (reverse bias and electrostatic discharge). Moreover, environmental factors like moisture, volatile chemicals and heat will accelerate LED degradation. Recently, driven by the wish to enhance SSL devices reliability, many studies have been devoted to highlight, understand and predict LED failure modes [86]. Based on bibliographic study, in this chapter, we will review the causes and effects of the degradation mechanism involved in LED failure. Causes for failure are mainly related to electrical, thermal and mechanical stresses. It should be noted that electrical, thermal and mechanical stresses are, in part, interdependent.

3.1. Failures related to electrical stress

The exposure of LED to undesirable electric events has a non-negligible effect on the LED overall lifetime and luminous efficacy. The emission of photons in the active region of LED is the result of charges recombination. In this respect it is clear that all physical phenomena that are susceptible to slow down, interfere, disturb hole and electron recombination will negatively affect the LED internal quantum efficiency. Until now, there are no available systems showing 100% of internal quantum efficiency. One of the main reasons is that the monocrystalline structures used in LED die always present intrinsic defects. Add to their limiting factor in radiative charge recombination efficiency, these initial structural defects can be amplified during LED operation. For example, the growth and nucleation of dislocation in the active region can be triggered by the radiative recombination themselves. Moreover, this phenomenon is also amplified by high current density and resulting temperature rise [87–130]. Systems based on GaAs and AlGaAs are more sensitive to this type of failure compared to III-phosphide based material (GaAsP and InP). Detailed studies on GaN-based LEDs have shown the correlation between the optical degradation and the increase of non-radiative recombination rate in the active region [111]. This type of degradation has its origin in the modification of charge concentration in the active layer [128,129]. Propagation of defects from the p or n doped layer toward the active region, generation of nitrogen vacancies in the active layer and diffusion of doping/impurities (Mg, Si) via threading dislocation to quantum well region are responsible for the lowering of the internal quantum efficiency of the device [127]. High electrical currents or voltages can also involve metal diffusion between the electrodes and the active region [112]. The structural defects act as pathway for electromigrated metallic atoms. Increased leakage current, non-radiative recombination at the chip edges and shorts are the consequences of electromigration. Nowadays this problem is hindered using a metal barrier layer or by passivation of the edges of the die with SiO2 [131,132]. Reverse-bias also induce LED degradation mainly by increasing leakage current [132] and thus decreasing the breakdown voltage. Leakage occurs via a tunneling conduction mechanism through existing defects. The carriers accelerated by the presence of a strong electric field are injected in the active layer and can interact with structural defect. As we described in the previous paragraph, the propagation and generation of defect result in a gradual worsening of the device's properties affecting its luminous efficacy. Failures due to electrostatic discharge (ESD) are another type of electrical induced failure in LED [110,133,134]. ESD is problematic as it often results in catastrophic failure of the device. The presence of a structural defect is one of the main causes for ESD events. LEDs grown on SiC present a better stability against ESD compared to the one grown on sapphire [107,110] due to a better lattice matching of GaN with SiC rather than sapphire. To reduce the density of dislocation, the use of a SiN/GaN buffer layer has been proposed [127,135]. Another solution already adapted in most high power LED consists of including a protective silicon Zener diode directly on the chip [136]. The robustness of LED against ESD is greatly influenced by the quality of the manufacturing process of the die (mesa) contact and borders as well as its shape and design. Finally, electrical overloads, typically defined as an over-voltage or -current pulse durations exceeding 1 ms, can induce burning or breaking damage to the bonding wires [137].

To conclude, all the failures occurring at the semiconductor level are related to the presence of intrinsic structural defects that are amplified by electrical stresses (Fig. 11). Manufacture of semiconductor p-n junction with the smallest amount of defects is the main technological challenge to increase both LED internal quantum efficiency and reliability. As such, no routes to self-healing of such defects beyond the level of thermal defect recovery have been identified up to now.

3.2. Failures related to thermal degradation

Notwithstanding the great progress made in thermal management of LEDs the generation of light as a result of the imperfect recombination process at the p-n junction and the absorption of light by the encapsulant leads to a temperature rise of the LED. It magnitude is determined by the balance between heat generation (which is coupled to the intended light intensity of the device) and the thermal conduction [135]. The increase of temperature will negatively affect all LED components: semiconductor, encapsulants, phosphors and interface materials (e.g. adhesives) (Fig. 12). In this respect it is not surprising that nowadays most of research and development efforts are conducted to efficiently manage the heat produced during LED operation. It is admitted that most of the failures occurring due to electrical stimulation/stress of the semiconductor are amplified by elevated temperatures. At the packaging level, thermal stress will mainly affect the encapsulant, die attach materials and other interfacial material worsening their intrinsic properties. However, the increased temperature affects in particular the polymeric encapsulant and the light converting phosphors.

Epoxy browning is a well know thermal-activated degradation resulting in light output decay and modifications of spectral properties. Darkening of reflective surface when used also contributes to reduce light extraction efficiency and thus the overall LED luminous efficacy. It has been shown that this degradation rate presents a linear dependence on the stress current level. Recently, it has been shown that silicone encapsulant also degrade leading to consequent optical losses implying wavelength shift and enlargement of the emission spectrum [138]. It has also been shown that high temperature will also directly affect the conversion efficiency of phosphors leading to a degradation of the LED’s spectral properties [16,87,91–94,96,100,101,105,107,113,115,116,118,119,126–129,139,140,171,141–145]. Moreover it has been demonstrated that with high power LED a high phosphor load in the encapsulant as well as thicker encapsulant layer will result in a higher lumen.
Fig. 11. Phenomena triggered by electrical stress leading to LED failure: (1) defect propagation, (2) defect creation, (3) migration of impurities, (4) metal electro migration and (5) leakage current and ESD.

Fig. 12. Different failure related to thermo-mechanical stress occurring in LED: (1) encapsulant browning and cracks formation, (2) phosphors degradation, (3) delamination of die/encapsulant interface, (4) cracks, delamination of die adhesive/bonding and its interface, (5) thermal interface material (TIM) degradation and (6) solder failure.

Fig. 13. Different failure related to chemical reactions occurring in LED: (1) phosphors degradation, (2) die surface corrosion, (3) moisture infiltration between at die/encapsulant interface, (4) electrode and copper on PCB corrosion.
loss upon thermal aging [146] as more light absorption occurs. Both degradation processes are related to oxidation of the base materials. The oxidation process of the organic compounds is effectively an irreversible process and hence no self-healing mechanisms have been identified or are likely to be found.

3.3. Failures related to (thermo) mechanical stress

Shocks and other related mechanical stresses can induce critical failure for SSL devices as with all electronic devices. Mechanical stress will be even more critical if the material already presents some weakness like solder fatigue, delamination or cracks in bonded contacts. Loss of electrical/thermal contacts is the resulting failure mechanism. Beside external mechanical stress, LED are invariably subjected to internal mechanical stresses which arise from thermal stress. Their main origins come from the fact that LEDs are multi-component-based devices presenting different CTE (coefficient of thermal expansion). CTE mismatch between all LED constituents will imply mechanical stress. As an example, if the temperature of the device is too high, the encapsulant can reach its glass transition temperature and start to expand whereas other components will be less sensitive to this thermal expansion resulting in high mechanical stress in the epilayer and electrode bonding solders [147] and possible delamination between the encapsulant and the die [101,135,148,149]. Delaminations and crack formation at the die attachment interface with the submount are also inevitable in this respect [106]. All LED’s interface worsening/degradation will result in an increase of thermal resistance that will amplify thermal stress and its related set of failures. This formation of cracks and delaminations, i.e. the generation of new interfaces, is a less irreversible process than the molecular chemical degradation and in principle strategies can be designed to restore the interfacial bond strength and structural and functional integrity across the two crack faces. It should be realized that self-healing of such damage may require well-timed temporary deviations from the steady state operation conditions, as crack formation and crack healing under exactly the same conditions is thermodynamically forbidden.

3.4. Failure related to chemical reactions

Moisture is one of the main concerns in SSL reliability. The simultaneous presence of moisture and heat leads to many corrosion problems [124] (Fig. 13). Corrosion of the copper-based electrical circuiting in the drivers or on the boards is common and often results in loss of electrical conductivity. It has been discussed that upon multiple thermal cycling, aging of the encapsulant occurs. It becomes more porous and looses its chemical barrier functionality and die protection ability allowing moisture to diffuse to the die/encapsulant and die/adhesive interfaces. This extra interface will drastically lower the light extraction efficiency as well as the thermal conduction properties. For white LEDs, remote and even encapsulated YAG:Ce phosphors are affected by humidity resulting in a gradual worsening of color rendering. Adhesion properties of YAG:Ce phosphor coating on the die are degraded leading to coating dissolution upon time involving migration of phosphors’ activator (e.g. Zn [89,96,98,150]) to the surface of the encapsulant via the moisture paths [151].

In order to further protect the phosphors against degradation occurring at high temperature and humidity a SiO2 coating of the phosphor particles has been reported to be efficient [104]. As such the thermal degradation due to the influence of oxygen or moisture is of a similar nature forbidding the occurrence of self-healing, however in the next chapter strategies will be presented to combat corrosive damage.

4. Self-repairing approach to enhance LED reliability

In order to enhance SSL reliability there are two main routes to follow. The first one consists of keeping the temperature of the LED at very low levels (typically <80 °C) by increasing the internal quantum efficiency of LED and/or by increasing the heat conduction to the surrounding atmosphere. The second approach focuses on selectively replacing existing materials that are more probable to fail by materials presenting “self-healing” or “self-repairing” properties.

Materials presenting self-healing or self-repairing properties have now been a reality for over a decade. This new field of material has already been successfully applied in many domains from aerospace to civil engineering. By mimicking what living organisms do, it is now possible to produce concrete, asphalts, ceramics, coatings and polymer composite presenting self-healing properties [152,153]. There are basically two approaches to develop self-repairing materials:

- The integration of small mono- bi- or tri-dimensional containers (layers, capsule, fibers or vascular network) loaded with active components into the matrix material. In this approach there is a physically separation between the material responsible for the healing action and the material responsible for the intended mechanical/thermal/electrical functionality.
- The development of intrinsically self-healing materials, i.e. materials which can restore their chemical or physical bonds via thermo-reversible bonds under the influence of a non-disruptive external stimulus. In this approach the material combines both the healing and the functional role.

As described in the previous section, LED failures are generally related to the degradation of the functionality of LED’s components, the alteration of the components’ intrinsic properties and or the loss of interfacial properties (adhesion, thermal and electrical conductivity). We will now address the options for healing of these damages in some more details.

4.1. Semiconductor damages-healing

As it was exposed in Section 3.1, most of the damages occurring at the die level are related to the loss of structural integrity at the atomic scale. In this respect, a self-repairing approach would imply to literally move atoms back to their original position to recover the initial crystalline structure. This dynamic recovery of crystalline defects could be done by submitting the die to heat pulses. Thermal annealing is a common technique used to reduce the amount of crystalline defects like threading dislocation in III-Nitrides, III-Phosphide semiconductors [154–156]. However the temperature involved in such process (~800 °C) is far above the range of temperature that a LED can tolerate. Thermal annealing can also be realized by increasing the current level for short time or by increasing the time if the temperature is lower. It is clear that the crystalline damages induced to the semiconductor during the life of the LED device are not yet conductive for a self-repairing approach. Failure related to electromigration of atoms from the solder to the die or within the solder/interconnect itself could be postponed by using reversed pulse current. This approach has been successfully applied to reverse electromigration induced damage in AlCu interconnects [157–159] or in Sn–Pb eutectic. Powering LEDs could be of interest to implement a periodical reverse current pulses to minimize electromigration and thus to enhance both the solder/interconnect and die life.
4.2. Packaging damages-healing (cracks and delamination)

As indicated in Section 3, cracks and delamination and more generally interfacial problems occurring in LED packaging are the most promising failure type to be cured using self-healing strategies. For the conditions relevant to LEDs the following routes are available.

4.2.1. Reservoir based systems

The main concept resides in the fact that storage vessels containing a liquid are dispersed into a hard matrix. Upon fracture, the containers are broken and literally bleed and fill the surrounding open space. This liquid that is mainly an un-cured matrix compatible resin is either mixed with a curing agent contained into adjacent vessels or come in contact with solid polymerization catalysts previously dispersed into the matrix. The solidification, re-bonding and thus fracture healing process occurs allowing the material to recover some of its mechanical properties, as the strength loss due to the emptying of discrete capsules or reservoirs is significantly less than that due to the presence of a microscopic/macscopic crack tip. Most of the research in this field has been devoted to find efficient ways to store and contain the liquid agent into a hard matrix. The use of capsules, wires, fibers and all types of reservoir presenting 1, 2 or 3-dimentional architecture have been implemented in many composites materials leading to the creation of materials with self-repairing properties [160]. The reactive species used can be epoxy resins [154,155] dicyclopentadiene monomer [161–164] and functionalized poly(dimethylsiloxane) [165–168]. The implementation of these strategies for LEDs is relatively straight forward as the die adhesives and the encapsulant itself are based on epoxy or silicon systems which are resin extensively used in self-healing composite development. However this concept based on the presence of containers in a matrix presents some disadvantages and limitations. First of all multiple healing is not possible in the same area. Once the capsules are broken in the vicinity of a crack, and their liquid content has polymerized in crack tip zone, locally the reservoir has lost its healing potential. In case the healing of the crack leads to later crack propagation in different directions, new containers may be intersected and become operational. The capsule-based approach is thus less suitable to allow multiple healing events regardless of the damage position in the matrix. A vascular based approach presenting a 3D interconnected network of circulating healing fluids would be more suitable in this respect. Another intrinsic limitation of this approach can be imputed to the fact that after fluid movement and healing, an empty space is left in the matrix and the overall matrix volume is increased. The presence of these empty spaces is not problematic if and only if recovery of mechanical properties is the main target of implementing self-healing concept. However, the presence of voids and healed area in the matrix in a self-healing adhesive for LEDs is problematic from a thermal and electrical conductivity perspective. Using a capsule-based approach for LEDs will be of interest if the free volume created during the liquid release is minimized or completely vanished. This means that for each healing event, the extra volume created by a fracture should be compensated by the diminution of space occupied by the used vessels. In this respect self-repairing capsules based material used in LED adhesives need to be implemented together with a system that will apply a sufficient pressure to close the gap left after the liquid release. This approach has recently been patented by Texas Instrument [164]. In this method, the die attach adhesive comprises metal particles, microcapsules containing a flowable polymerizable monomer and microcapsules containing a polymerization catalyst. All the system is kept under a compressive force that will first reduce the free volume and then rupture the vessels and force their liquid content to flow into the area to be healed while minimizing the loss of percolation based conductive paths.

Capable-based healing could be suitable for LED application in the perspective to create a material where only mechanical failure and bonding recovery is needed. A vascular based concept is more suitable compared to capsule-based healing in order to maximize the possible healing events and their location efficiency. When conduction properties as well as adhesives properties need to be maintained, the vessels-based approach is not the most suitable as it will require extra mechanical energy like pressure during the healing to keep the percolation paths intact. Furthermore, the dimensions of the crack sensitive LED components are such that the introduction of a microvascular network of some form may topologically be very hard to realize in practice.

4.2.2. Reversible chemistry

Material mending can also be achieved by reversible chemistry. Materials with intrinsic healing properties present advantages compared to systems based on encapsulated liquid healing agent [169]. First of all they are easier to process as there is no need to create a composite material in which a liquid phase need to be contained into a vessel. Secondly the mending and fracture healing do not create any voids in the matrix. Finally, multiple healing is possible. These advantages come along with fact that, in this approach, self-healing is not autonomous and need to be triggered by an external stimulus (thermal, mechanical, electric). For SSL applications, the reversible chemistry route to create a self-repairing material is of great interest due to intrinsic availability of heat, electric current in LED systems. Two elegant approaches are commonly used involving reversible covalent bonding like Diels–Alder based reactions [170] or cleavage of disulfide bonds or like hydrogen-bonded supramolecular network [171,172]. Several system based on Diels–Alder reaction, hydrogen bonding, molecules with disulfide bonds and covalent adaptable network can be used to create a material with reversible adhesive properties for LED application.

The implementation of Diels–Alder (DA) [173,174] and retro Diels–Alder (rDA) chemical reaction in a material has already proven successful for self-repairing purposes. For LED applications, the main advantage of a reversible adhesive based on Diels–Alder chemistry resides in the fact that thermal activation is needed. Several authors have shown that furan-maleimide polymers present a self-healing behavior upon thermal triggering [175]. “Mendomers” (mendable polymers) can also be produced using cyclopentadiene based polymer. Thermal mending can be achieved at 120 °C [171,172,176]. The dispersion of electrically conductive charges in such a mendomer will allow thermal activation of the DA and rDA reactions by electrical resistive heating. Incorporation and dispersion of thermally activated re-mendable polymer in an epoxy matrix could therefore lead to a thermally triggered self-healing non-fuly cured thermoset [177,178]. This last route is of great interest for LED application as the commonly epoxy based adhesive use could be modified in order to present self-repairing properties. More generally, regardless of already existing self-healing application, thermo-reversible chemical bonding can be achieved using multiple reaction [179,180] like nucleophilic addition between isocyane and imidazole, carbone dimerization, reversible radical coupling between 2,2,6,6-tetramethyl-1-piperidinyl-1-oxy and a styryl radical, DA cycloaddition between anthrancene and tricyanoacrylate, and fulvene and tricyanoacrylate. Reversible covalent bonding based on DA and rDA chemistry together with a fine tuning of the polymeric backbone will allow to design thermally activated mendable polymer for a wide range of temperature. While less relevant to LEDs, a room temperature transparent film presenting self-healing properties has been produced using dynamic polymers based on Diels–Alder chemistry of bis(fulvene) and bis(tricyanoacrylate) [181] with a reduced activation temperature.
Sulfur–sulfur bonds are also interesting for the development of self-repairing materials. A disulfide bond can be cleaved at moderate temperature. The resulting two thiol functions can further react to reform a disulfide bond by oxidation [182]. Epoxy resins [183] and polystyrene polymers [184,185] presenting reversible crosslinking properties can be achieved using this redox route. The use of trithiocarbonate crosslinker in a polymer has also shown self-healing properties under thermal and UV stimulation [186,187].

Polymers having reversible hydrogen bonding are potentially useful as self-repairing adhesives. Contrary to material based on DA chemistry where self-repairing is only thermally activated, for supramolecular networks with reversible hydrogen bonding the self-repairing properties are also mechanically triggered. This supramolecular network contains molecules equipped with several different types of complementary and self-complementary H-bonding units: between 2-ureido-4-[1H]-pyrimidone molecules (Fig. 14) [188–191] or with amidoethylimidazolidone, di(amido-ethyl) urea and diamido-diethyl triurea [173,174,192–195]. The formation of such a supramolecular network leads to the development of elastomers presenting self-healing properties (SupraB® from SupraPolix BV) and reversible bonding at room temperature (Reverlink™ from Arkema). This class of material can be blended with other adhesives to increase its intrinsic mechanical properties. It has been shown that supramolecular networks can be used as adhesion enhancement of hot melt polyamides resulting in an increase by a factor 6 of the peeling force [196]. This type of chemistry is really promising for LED application due to the intrinsic self-healing properties of supramolecular network and also due to the possibility of tuning and improving properties of existing adhesives and their activation temperature. In order to enhance the thermal conductivity of these materials, dispersions of electrical charges in a supramolecular network could be of interest. Incorporation of charges in which the surface has been functionalized to present extra hydrogen bonds could without negatively affecting the self-repairing properties enhance the thermal conduction properties of the supramolecular network.

4.2.3. Thermoplastic–thermoset blend

Another approach to promote self-repairing of thermoset resin consists of including in its matrix a metastable thermoplastic. This approach stems from the realization that thermosets intrinsically have a highly restricted molecular mobility and a very limited maximum displacement range. Thermoplastic polymers on the other hand have a much increased mobility but much lower mechanical properties when tested over longer periods and at elevated temperatures. Upon thermal activation the more mobile thermoplastic phase is able to diffuse to the damage area of the harder thermoset matrix allowing chains re-entanglement and restoring mechanical properties. This thermally triggered healing has been achieved by dispersion of poly(BPA-co-epichlorohydrin) [197] or polycaprolactone [198] in epoxy matrix. This differential expansive bleeding can be tuned to be triggered over a wide range of temperature in order to induce reversible adhesion.

4.2.4. Reversible physical network (ionomers)

Ionomers are a class of material comprising ionic clusters that present reversible bonding properties that can be photo (UV) or thermally activated. The use of Surlyn 8940® (DuPont) a partially neutralized poly(ethylene-co-methacrylic acid) ionomer copolymer has proven to be efficient for thermally induced healing of punctures. The main parameter controlling the healing efficiency resides in a combination of a good mobility of the ionomer molecules upon disruption of the clusters [199,200] and the reversible clusters offering an additional driving force to restore the original topology as well as the mechanical properties after healing. In this respect, the ionomer route could provide self-repairing functionalities to existing thermosets.

4.2.5. Conductive polymer

All mechanical problems occurring in LED at different interface mainly result in loss of adhesion and deterioration of the interfacial material. These damages, depending of the interface function, can result in loss of thermal conductivity and in some cases loss of electrical conductivity. Typically, electrical conductivity is achieved by

![Fig. 14. Example of mechanism involved in reversible chemistry for self-healing material based on (a) Diels–Alder cycloaddition reactions and (b) redox reaction of disulfides bonds and (c) hydrogen bonding.](image-url)
dispersion of charges in a hard matrix. In order to implement self-healing, one approach could be to use polymer that present electronic conductivity as well as mechanical self-repairing properties. The use N-heterocyclic carbenes and transition metals salts result in the formation of electrically conductive organometallic polymers. Moreover this class of polymer presents a dynamic equilibrium between their monomer species and their polymeric form that is thermally dependent. The combination of these two intrinsic properties has been used to design electrically conductive self-healing materials [201]. When a crack or discontinuity occurs in the polymer, the electronic conductivity is locally disrupted. The resulting higher local resistivity generates heat that initiated the re-bonding. This interesting self-healing route is of great interest in LED application as it could bring to the system a fine medium to trigger the healing of interface materials. Indeed, controlling a current flow in a selected interface is easier than controlling the resulting heat produce due to the non-radiative charges recombination at the die level.

4.2.6. Pending function/unreacted functions

This approach is based the incorporation of unreacted chemical groups which can be activated and can lead to a volume change and has been demonstrated for silicone chemistry based polymers. Organosilanes Si(R)x(X)4−x where R is an organic group and X = Cl, Br, –OR are molecules that can be hydrolyzed and condensed in order to create a covalent network based on Si–O– and Si–R– bonds.

If the precursor used is not hydrolyze, the environmental presence of water can be used to initiate the hydrolysis reaction. This type of approach could act as water repellent as well as self-repairing material. In a second step a non-fully condensed silicone network will present pending hydroxyls (−OH functions) that can be thermally activated to create new covalent bonds with other pending −OH groups (Fig. 15). Some attempts have been made to use non-fully reacted organosilane to repair dielectric interface for advanced microelectronic applications [202]. Two surfaces presenting pending hydroxyl groups can be bonded by condensation reaction with a partially hydrolyze dipodal silane coupling agent. In a more general way, it is possible to design organosilane compounds where the organic part could:

- be active in a DA reaction,
- present possibility for hydrogen or ionic bonding,
- be compatible with a thermostet or thermoplastic,
- present a disulfide bond,
- be another organosilane (dipodal silane).

Surface functionalization of oxides can be achieved using organosilane but also by organophosphate chemistry [203]. Oxides are commonly dispersed into transparent matrix (epoxy, silicone...) to enhance their refractive index in LED application [63,66]. One possibility to couple refractive index enhancement with a self-repairing properties can be achieved by tuning the oxides’ surface with reactive species that can be condensed with other pending function as described earlier. Besides the enhancement of the refractive index of the encapsulant, the oxide will act as a carrier of the reactive species allowing network mending. Bringing together existing intrinsic self-healing routes with sol–gel chemistry and surface functionalization could lead to new horizons for composite material presenting self-repairing properties. The last route has great potential application to enhance both properties and reliability of LED transparent encapsulant.

4.2.7. Conclusion on self-healing route to solve physical problem in LED packaging

Most of the self-repairing routes already used to promote self-repairing properties in material could be implemented in LED system where physical contact needs to be guaranteed over long periods of time. As explained, self-repairing material based on the incorporation of reservoir into a matrix is less suitable for LED application because (1) multiple healing is not possible in the same area, (2) voids creation after healing will reduce thermal conductivity, (3) healing will induce an increase of overall matrix volume, and (4) damage volume needs to be sufficiently big >0.5 mm³ [154]. Material presenting intrinsic self-repairing properties are thus more favorable even if the healing events need to be triggered. Indeed, the damage volume where the healing is efficient spans from 0.05 to 1 mm³ which fits the mechanical failure occurring in LEDs. Moreover, all precursors and components that are presented as self-healing material for LEDs are already commercially available. From a manufacturer point of view they could be handle in the same way as it is done nowadays with epoxies and silicone derivatives. In this respect, manufacturer will not have any huge problems to implement or switch from one technology to another.

Thermal activation is the most trivial as heat is intrinsically available in LEDs. On one hand, the implementation of self-repairing systems should be done taking into account what is the energy needed to trigger the healing events and what is the energy that could be available in the LED device at a specific location. On the other hand, the implemented self-repairing material should present properties that meet as good as possible the required functional properties related to its use in the device. A good reversible adhesive with poor thermal conduction is therefore not suitable for thermal conduction purpose even if it presents very good self-repairing properties. Table 3 summarizes the possible chemistry that will present self-repairing properties, the temperature range that is needed to trigger the self-repairing events and finally where in the device they could be implemented.

![Fig. 15. (a) Hydrolysis reaction and (b) condensation reaction between −OH groups.](image-url)
4.3. Corrosion healing

Moisture is the principal environmental problem that limit LEDs’ reliability. However it should be kept in mind that if the protective function of the packaging is not damaged there is less probability for moisture or other type of chemicals to infiltrate and further degrade active components (phosphors or the die). In order to avoid moisture-related problems at the level 0 and 1 of the SSL value chain, the first action is to avoid packaging degradation. To prevent corrosion implementing self-healing many different routes have been compiled and described elsewhere in an extensive review paper [204]. All these routes implying smart coatings are susceptible to be applied at the levels 2, 3 and 4 of the SSL value chains.

4.4. Analysis and recommendations of the effect of self-healing on the effective lifetime of LEDs

In the previous chapters the routes towards self-healing behavior have been identified. Some of them seem very promising but dedicated work is yet to be done to show the potential and quantify the life extension. However, without specifying the precise nature of the healing event, one can already simulate the effect of various scenarios, which may be helpful in the selection process of the system as well as the test protocols to evaluate the improvement.

As mentioned earlier, LED is considered to have failed when its luminosity reaches 70% of its initial value. This commercial definition of failure implies that triggering of self-healing could be done in two different ways:

- In a curative manner: when the luminosity reaches 70% of its initial value and if the related failure presents self-repairing capabilities, self-healing should be triggered.
- In a preventive manner: self-healing is triggered at regular time period before the luminosity decay reaches 70% of its initial value.

It has been shown that the light output degradation rate of LED is exponential in nature. In this respect, the light output can be expressed as follow:

\[ L = L_0 \cdot e^{-\alpha t} \]

where \( L_0 \) is the initial light output, \( t \) the operating time and \( \alpha \) the degradation coefficient or decay constant. Fig. 16a represents the light output degradation of a 5 mm signalization type white LED operated with a 15 mA current and 65 °C junction temperature. Self-repairing events (red curves and circles) are triggered at 70% of the initial light output. (b) For high power LED operated with a 350 mA drive current at 35 °C (red) and 60 °C (black) ambient temperature. The values between brackets are related to the junction temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Stimulus</th>
<th>Temperature range</th>
<th>Potential application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diels–Alder</td>
<td>Thermal/electrothermal</td>
<td>25–170</td>
<td>Die adhesive</td>
</tr>
<tr>
<td>Disulfide</td>
<td>Thermal</td>
<td>60–100</td>
<td>TIM</td>
</tr>
<tr>
<td>Trithiocarbonate</td>
<td>UV/thermal</td>
<td>–</td>
<td>Die adhesive</td>
</tr>
<tr>
<td>Supramolecular network</td>
<td>Thermal/mechanical</td>
<td>25–80</td>
<td>TIM</td>
</tr>
<tr>
<td>Epoxy/poly(BPA-co-epichlorohydrin)</td>
<td>Thermal</td>
<td>100–140</td>
<td>TIM</td>
</tr>
<tr>
<td>Epoxy/polyacrylate</td>
<td>Thermal</td>
<td>60–200</td>
<td>TIM</td>
</tr>
<tr>
<td>Modified Ionomers</td>
<td>Thermal</td>
<td>–</td>
<td>TIM encapsulants</td>
</tr>
<tr>
<td>Conductive polymers</td>
<td>Electrothermal</td>
<td>150–200</td>
<td>Die adhesive TIM</td>
</tr>
<tr>
<td>Organosilane</td>
<td>Thermal</td>
<td>25–100</td>
<td>Adhesive, TIM encapsulants</td>
</tr>
</tbody>
</table>

TIM = thermal interface material.

Table 3

Dif
dent chemical route for self-repairing application in LED.

Fig. 16. Light output degradation as function of time for a degradation factor \( \alpha = 1.5e^{-4} \) (data extracted from Ref. [205]) (a) for a 5 mm signalization type LED operated at 15 mA current and 65 °C junction temperature. Self-repairing events (red curves and circles) are triggered at 70% of the initial light output. (b) For high power LED operated with a 350 mA drive current at 35 °C (red) and 60 °C (black) ambient temperature. The values between brackets are related to the junction temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
failure point. The same study has been done for high power LEDs operated with a drive current of 350 mA. The light output plots as function of the operation time are presented in Fig. 16b. High power LEDs have an intrinsic life time longer than the 5 mm LED. However, they are more sensitive to degradation induced by ambient temperature rather than current. For this type of device a perfect self-repairing event occurring at the failure point is highly desirable as it has the potential to increase the LED operation life of 40,590 h. In this respect if one would like to implement self-repairing material in LEDs, it is better to focus on high power devices (surface mount LED) as the potential operation life gain is far greater than for a 5 mm signalization type LED.

In the previous scenario, the self-repairing process is expected to recover the entire initial properties of the luminous device. However, as it was described earlier, most of the failure mode occurring at the die level in LED are not (yet) conductive to be healed which mean that they will act as irreversible damage. In this respect, a full recovery of the initial device properties is highly improbable in this case. If the healing process is triggered at the failure point it is expected that the life time increase will be minimal compared to a self-healing event occurring before the apparition of irreversible damage at the die level. Curative healing will be in this case less efficient compare to a preventive healing where the packaging components will recover their functionality before their intrinsic failure bring irreversible damage to the die. Thus, in order to maximize the recovery by preventive healing one should take into account the degradation rate of the die.

For LEDs and microelectronics in general, thermal interface reliability are the most critical. A better efficiency in thermal management is a very known concept for lifetime improvement. However the current available techniques and strategies suffer from a self-degradation in time of the main components presenting these thermal functionalities (e.g. drying out and pumping out of TIMs). To overcome these problems, self-healing material should be implement at the most sensitive point of the system (packaging) in order to maximize its efficiency regarding life increase of the overall system. We expect that if the thermal stress could be manage in time with the same efficiency due to the presence of self-repairing materials, the LED reliability will be greatly enhanced as the thermal function of the components used will exhibit a better stability in time.

As promote in this review, implementing self-healing concept in SSL devices can be done following many routes to circumvent several critical failures. However, the most promising results on SSL device reliability could be achieved working in the area of auto-recovery of interfacial properties. For example, new materials that present both self-repairing adhesive property and self-repairing conductivity property (thermal and/or electronic) will help to overcome most of the thermal related failures that result in the loss of contact between interfaces. These new class of material presenting multifunctional self-healing behavior are currently under development in our group.

5. General conclusion

LED’s have a very bright future as they already offer a high energy-light conversion efficiency and a wide range of strategies to improve their properties well beyond their current level. Despite the extensive efforts made to improve packaging and thermal management, LEDs’ reliability in high power devices is still an issue that slows down the market penetration. The heat generated due to the presence of non-radiative charge recombination at the die level is the main cause of LED failure resulting in the decrease of luminous efficacy or in the worst case in the death of the device. While not all forms of damage are amenable to self-healing strategies, damage resulting in cracks, delaminations or loss of adhesion can potentially be well addressed using one of the several routes for self-healing polymer based systems currently under development.

Self-healing polymer systems based on molecular or intrinsic self-healing principles offer significant advantages over encapsulated self-healing systems. Their potential for multiple healing, the ease for processing and the availability of external stimuli to trigger the healing are the clear advantages. Bonding recovery can be promoted using different mechanisms that involve reversible cleavage of covalent bonds (e.g. Diels–Alder, redox of disulfide), hydrogen bonds (supramolecular networks) or physical networks (ionomers). Reversible adhesion can also be achieved by a “bricks and mortar” approach where a soft flowable thermoplastic is included in a hard thermoset. All these approaches are thermally triggered and the thermal healing response can be tuned playing with the chemistry of the chosen system. Thus it is virtually possible to create reversible adhesive that can be activated from room temperature to 190 °C. The implementation of conductive species in the thermally induced reversible adhesives could allow electrical triggering of the self-repairing process. Last but not least, the incorporation of unreacted organosilane species in an existing network allows mending due to the condensation reaction between hydroxyl group and/or due to a reactive organic function carried by the organosilane itself or by functionalized inorganic particles.

As most of the self-repairing routes identified as potentially attractive are thermally triggered, a smart electronic system could be incorporated at no cost in solid state lighting devices to activate at regular interval the self-healing processes by increasing for a short period the current in the system and to aim for preemptive healing rather than truly autonomous healing.

Acknowledgment

This research was carried out under Project Number M71.9.10381 in the framework of the Research Program of the Material innovation institute (M2i) (www.m2i.nl).

References


Lane MW, Roush A, Callahan SE. Repair of dielectric interfaces with chemistry specific coupling agents. In: All conference proceedings, Austin, TX; 2009. p. 71–86.


