

Determination of LEDs degradation with entropy generation rate

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(Received 18 July 2017; accepted 2 October 2017; published online 13 October 2017)

We propose a method to assess the degradation and aging of light emitting diodes (LEDs) based on irreversible entropy generation rate. We degraded several LEDs and monitored their entropy generation rate (\dot{S}) in accelerated tests. We compared the thermoelectrical results with the optical light emission evolution during degradation. We find a good relationship between aging and \dot{S} (t), because \dot{S} is both related to device parameters and optical performance. We propose a threshold of \dot{S} (t) as a reliable damage indicator of LED end-of-life that can avoid the need to perform optical measurements to assess optical aging. The method lays beyond the typical statistical laws for lifetime prediction provided by manufacturers. We tested different LED colors and electrical stresses to validate the electrical LED model and we analyzed the degradation mechanisms of the devices. Published by AIP Publishing. <https://doi.org/10.1063/1.4996629>

I. INTRODUCTION

Light emitting diodes (LEDs) as electroluminescence devices have been common in commercial electronics since the 1960s, as indicators or small screens, in red, yellow, and green colors. The invention of the high intensity blue LED in 1994 promoted the widespread use of LEDs in the illumination field as it was possible to design white lamps. Since then, there is a growing interest in LEDs for many applications due to its low power consumption and high efficiency in comparison to incandescent or gas bulbs.

Of particular interest is the study of LEDs' aging to predict its lifetime. LEDs' aging is manifested in the decrease of light intensity. Following the standards provided by the Alliance for Solid-State Illumination Systems and Technologies, ASSIST,¹ the commonly accepted thresholds in the optical intensity decrease are established at 70% (L70) or 50% (L50) of the nominal intensity. L70 is the most common threshold; although for non-critical areas, L50 is also considered. Expected operating hours inferred from statistical distributions range between 50 000 and 60 000 and can eventually reach 100 000.

Aging causes a decrease in light intensity and color offset.² This is attributed to the fact that semiconductor bands change with aging, and as a consequence, optical performance worsens. Aging is commonly studied with accelerated tests in the scientific literature,^{3,4} although long-term reliability tests are also undertaken.^{5,6} Accelerated tests may consist in testing the LEDs at high currents⁷ or at high temperatures,⁸ and their results are extrapolated to normal operation conditions. The advantage is that experiments are faster; the drawbacks are that aging physical mechanisms can be different or that

extrapolation can be misinterpreted. At the industrial level, accelerated tests have to be validated with specific operation standards.^{1,9}

Several issues affecting aging have been reported: the increase in non-radiative recombination centers,^{10,11} temperature junction changes,^{3,12} discoloring or cracking of the encapsulating lens,¹³ crystal imperfections and structure defect generation,¹⁴ changes in the tunneling current and series resistance,⁸ or variations of the thermal resistance in the chip and package.⁸ When the density of a particular degradation mechanism or the combination of some of them increases in a particular area of the LED, dark spots (DSD) and dark lines (DLD) can appear.^{15–17} Moreover, the junction temperature is also critical in device degradation, which is enhanced with high currents.⁷ Finally, electrostatic discharges have also shown important effects on LEDs' aging.¹⁸

To explain these degradation effects, theoretical models have been proposed, based on diffusion,¹⁹ kinetic (based on the carrier-recombination enhanced defect motion),¹⁶ or dopant activation and changes of defects in the semiconductor junction.⁸

A general classification of LEDs' failures describes three main factors: supply and assembly faults, overstress faults, and wear out faults (or aging). These failures depict the typical bathtub profile.²⁰ Reliability studies were performed on the statistical distribution of these failures,^{21,22} but these do not consider the processes leading to failure. Because of this, we propose an approach based on entropy generation. Failures are undoubtedly irreversible processes which, according to the second law of thermodynamics, imply an entropy increase. In fact, entropy has already been applied to mechanical^{23–26} and electrical²⁷ damage characterization. It has also been suggested as a valuable parameter for instrumentation and measurement.²⁸ Theoretical validation of these experimental approaches have also been

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proposed^{29–31} along with a relationship between entropy and defect concentration in semiconductors.³² We have already proven entropy increase in resistors³³ and capacitors³⁴ during aging and degradation.

In this contribution, we expand entropy framework to semiconductors, in particular, to LEDs' failure description. Changes in the electrical, optical, and thermal characteristics were found to depend on and affect each other.⁸ We aim to correlate optical degradation to thermodynamic entropy because the present reliability models have not established a clear connection between the aging parameters of electrical LEDs and their optical performance evolution. Moreover, this is a suggestive approach because LEDs are semiconductor diodes, and thus, their performance is strongly dependent on operating temperature. Entropy simultaneously takes into account the input electrical power, the temperature, and the optical efficiency.

II. THEORETICAL APPROACH

LEDs are modeled from optical and electrical perspectives. We also include here a thermodynamical model.

The optical model of the LED aging^{20,35} establishes that the luminous flux decreases exponentially as

$$\Phi_t = \Phi_0 e^{-\beta t}, \quad (1)$$

where Φ_t represents the luminous flux, Φ_0 is the initial flux, β is the degradation coefficient corresponding to a junction temperature, and t is the working time. The relationship between the degradation coefficient and the junction temperature is expressed by the Arrhenius equation

$$\beta = \beta_0 e^{\frac{E_a}{kT_j}}, \quad (2)$$

where β_0 is a constant, E_a is activation energy, k is Boltzmann constant, and T_j is the junction temperature (absolute temperature). The junction temperature is calculated by

$$T_j = T_a + V_{LED} I_{LED} R_{j-a}, \quad (3)$$

where T_a is the ambient temperature, V_{LED} and I_{LED} are the voltage drop and the current in the LED, and R_{j-a} is the thermal resistance junction-ambient.

A typical model of a LED is illustrated in Fig. 1. The ideal diodes represent the diffusion (I_d) and the nonradiative recombination (I_r^{nr}). R_s and R_p are the dissipative elements, and I_{light} stands for light emission.³² If diffusion and non-radiative terms can be discriminated with two different ideality factors, electrical current is written as

$$I_{LED} = I_{s,diff}^{n=1} \exp \left[\frac{e(V_{LED} - R_s I_{LED})}{kT} \right] + I_{s,nr}^{n=2} \exp \left[\frac{e(V_{LED} - R_s I_{LED})}{2kT} \right] + \frac{(V_{LED} - R_s I_{LED})}{R_p} + I_{light}. \quad (4)$$

Otherwise, current is simplified to

$$I_{LED} = I_s \left\{ \exp \left[\frac{e(V_{LED} - R_s I_{LED})}{nkT} \right] - 1 \right\} + \frac{(V_{LED} - R_s I_{LED})}{R_p} + I_{light}. \quad (5)$$

R_p is related to surface conduction between contacts. At large injection currents, the injected minority-carrier density can become comparable with the majority-carrier density.³² However, aging is not strictly considered in the model. It is assumed that either the diffusion and non-radiative currents or internal resistances will intrinsically change with aging.

We perform now a thermodynamic approach of the LEDs' failure. We write the first and second laws of thermodynamics³⁶ as

$$dE_{in} = dW + dQ + dE_{irr}, \quad (6)$$

$$\dot{S} = \dot{S}_e + \dot{S}_i, \quad (7)$$

with

$$\dot{S}_i \geq 0 \quad (8)$$

in a non-equilibrium system considering the approximation of local equilibrium. The dot over the variable represents a time derivative, i.e., $\dot{S} = dS/dt$. In (6), E_{in} is the electrical input energy delivered to the LED; W is the light emitted energy; Q the dissipated heat; and E_{irr} the energy devoted to cause irreversible damage. In (7), subindices e and i refer to external (entropy exchange) and internal entropy (entropy generation), respectively.³⁷ We are interested in \dot{S} , which includes the thermal dissipation and aging and must be positive.

Input energy E_{in} is usually expressed in terms of the total input injected power P

$$E_{in} = \int P dt = \int V_{LED} I_{LED} dt, \quad (9)$$

where I_{LED} and V_{LED} are the current and voltage drop between the external terminals, as shown in Fig. 1. Input power is split into light emission and dissipative terms.

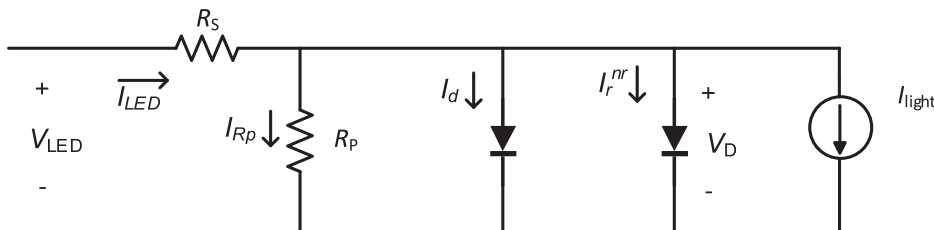


FIG. 1. LED electrical model.

TABLE I. Characteristics of studied LEDs, measured at 25 °C and at 20 mA. The emission angle is 60° for all except for Red800, that is 30°.

Model	Color	Material	λ (nm)	FWHM (nm)	I (mcd)	V_d (V)	P_{\max} (mW)	I_{\max_pulsed} (mA)
L-53LSRD	Red20	AlGaAs	660	20	20	1.85	100	155
L-1503SRC-D	Red800	AlGaAs	655	20	800	1.85	75	185
L-7083SURDK	Red200	AlGaInP-GaAs	645	28	200	1.95	75	185
L-7083CGDK	Green	AlGaInP-GaAs	574	20	100	2.1	75	150
L-7083SYDK	Yellow	AlGaInP-GaAs	590	20	450	2	75	175

The energy converted to light, dW , is related to I_{light} according to

$$W = \int_0^\infty I_{\text{light}}(\lambda) d\lambda. \quad (10)$$

This energy is related to input electrical energy through the LEDs' efficiency. For commercial display LEDs, wall-plug efficiency in terms of input energy (in W) to output energy (in W) is small, no larger than 0.1%.

Heat is dissipated as depicted in the model of Fig. 1 at the resistances due to the Joule effect

$$Q_d = R_s I_{\text{LED}}^2 + \frac{V_D^2}{R_p}. \quad (11)$$

No literature about E_{irr} was found, so its form is unknown at present. In terms of entropy generation rate $\dot{S} = dS/dt$, for electrical systems, it is commonly written as³⁶

$$\dot{S} = \frac{P}{T} = \frac{V_{\text{LED}} I_{\text{LED}}}{T}. \quad (12)$$

III. MATERIALS AND METHODS

Commercial LEDs manufactured by Kingbright (listed in Table I) were investigated as a function of color and current. Their maximum operating current and temperature in the DC mode are 30 mA and 85 °C, respectively.

LEDs were biased with a voltage source V in the setup illustrated in Fig. 2. Currents were measured with a series shunt resistor R_c (10 Ω and 25 W). Investigated currents were around absolute pulsed currents. Thermal sensors (PT1000) were thermally connected to the metal terminals with a heat sink compound (Dow Corning 340). LEDs were operated under free convection at room temperature. Voltages, currents, and temperatures were collected with a microcontroller based data acquisition system and transferred to a computer. The list of tested LEDs is given in Table II.

Optical measurements were performed with a spectrometer Avantes 2048. The LED and the optical detector were aligned through their vertical axis. Light intensity as a function of wavelength was monitored, along with the peak shift and its Full Width at Half Maximum (FWHM).

IV. RESULTS

We summarize the results obtained from electrically stressed LEDs under various experimental conditions, in order to determine the relationship between damage and entropy generation.

LEDs were supplied with a constant current until total light fade due to electrical open or short circuit. Time evolution of electrical and optical properties was monitored and compared for several situations, as illustrated in Fig. 3. LEDs' voltage drop and temperature were monitored. We observed that both voltage and temperature increased in steps. Delivered power to LEDs was estimated as the product of its voltage drop and current $P = V_{\text{LED}} \cdot I_{\text{LED}}$. Entropy rate, \dot{S} , was then obtained from (12), dividing the power by the absolute temperature. The temperature increased with power dissipation and time.

Optical properties were studied until LED failure in order to correlate them with electrical performance. Luminous spectra, relative intensity evolution, maximum peak shift, and FWHM evolution are depicted in Figs. 4 and 5. In Fig. 4, we observe that the emission peak shows a clear decrease in intensity with degradation time. Emission spectra were deconvolved in two peaks, one centered at around 624 nm and the other at around 650 nm. Both peaks show a red shift and an increase in their FWHM with degradation time. Light intensity shows a monotonous decrease down to 10%. In Fig. 5, we compare LED performance for different bias currents. Light intensity decreases faster with the increase in current bias. The light spectrum shows a

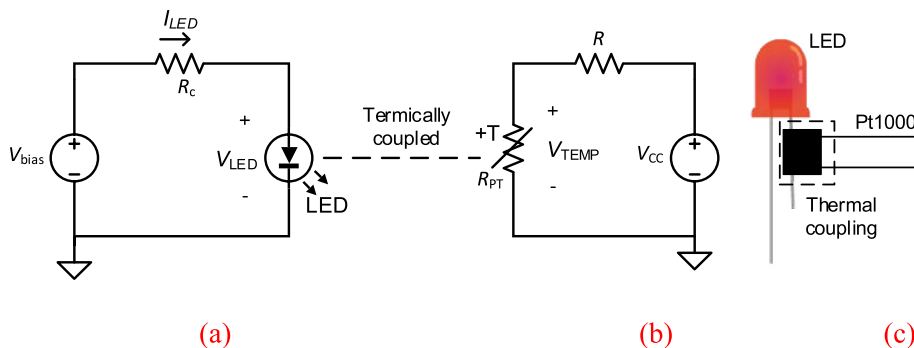


FIG. 2. (a) Electrical circuit to characterize LEDs. V_{bias} stands for bias source and R_c is used to fix current. The circuit is thermally coupled with the PT1000 sensor, attached to the LED terminal. (b) Electrical circuit to bias the PT1000 sensor and (c) illustration of the LED and PT1000 experimental implementation.

TABLE II. LEDs and currents tested.

Current (mA)	LED Red20	LED Red800	LED Red200	LED Green	LED Yellow
170	X		X		
180	X		X	X	X
190	X	X	X	X	X
200	X	X		X	X
210		X			X

slight wavelength shift and an increase in FWHM in all cases, in the range of light intensity above L50.

A close look at the light intensity and \dot{S} offers interesting details. First, entropy generation rate, as power, shows discrete increments. Also, the first increment is found in the range 50%–70%. Thus, optical intensity can be difficult to quantify in practical LED operation because an optical sensor is necessary, but this signature in \dot{S} could lead to a simple method to monitor LED's lifetime considering only electrical measurements. In Sec. V, we evaluate this approach in detail.

LED comparison for Red200, Yellow, and Green are presented in Fig. 6. \dot{S} increases in all cases, no significant differences are found, and thus LEDs' performance is mostly independent of colour. Apparently, AlGaAs degrade faster than AlGaInP LEDs, but as these are commercial devices and we do not have access to the fabrication details, we cannot extrapolate this particular case.

V. DISCUSSION

Experimental results illustrate that \dot{S} is a valuable magnitude to assess and monitor LEDs' aging. There are some issues to be discussed from the previous results, in particular, the effects of the accelerated tests, the temperature effect on LED performance, and its influence on the energy balance.

Accelerated tests are common in the literature^{3,4,7,8} as they save time at the cost of introducing different effects to regular aging. However, we have already shown that in resistors³³ \dot{S} increases regardless of the degradation mechanism. Thus, as we are only interested in finding the overall degradation of the LED that leads to the reduction of optical intensity emission, \dot{S} is able to become a reliable degradation tracker.

We evaluated the injected power in the LED as a function of its temperature, as depicted in Fig. 7. The slope of the curves is related to \dot{S} . We found that power dissipation slowly decreased until a temperature threshold, where we found a sudden increase in \dot{S} . In resistors³³ and capacitors,³⁴ we observed that power increased in all temperatures. A possible explanation is that LEDs are able to absorb the dissipated power as heat. Temperature rises due to power dissipation according to

$$Q = \int C_v dT, \quad (13)$$

where C_v is the heat capacity, which would not be a constant. This could be attributed to changes in the AlGaInP-GaAs semiconductor lattice structure. As long as the semiconductor is hotter, it could undergo small irreversible lattice

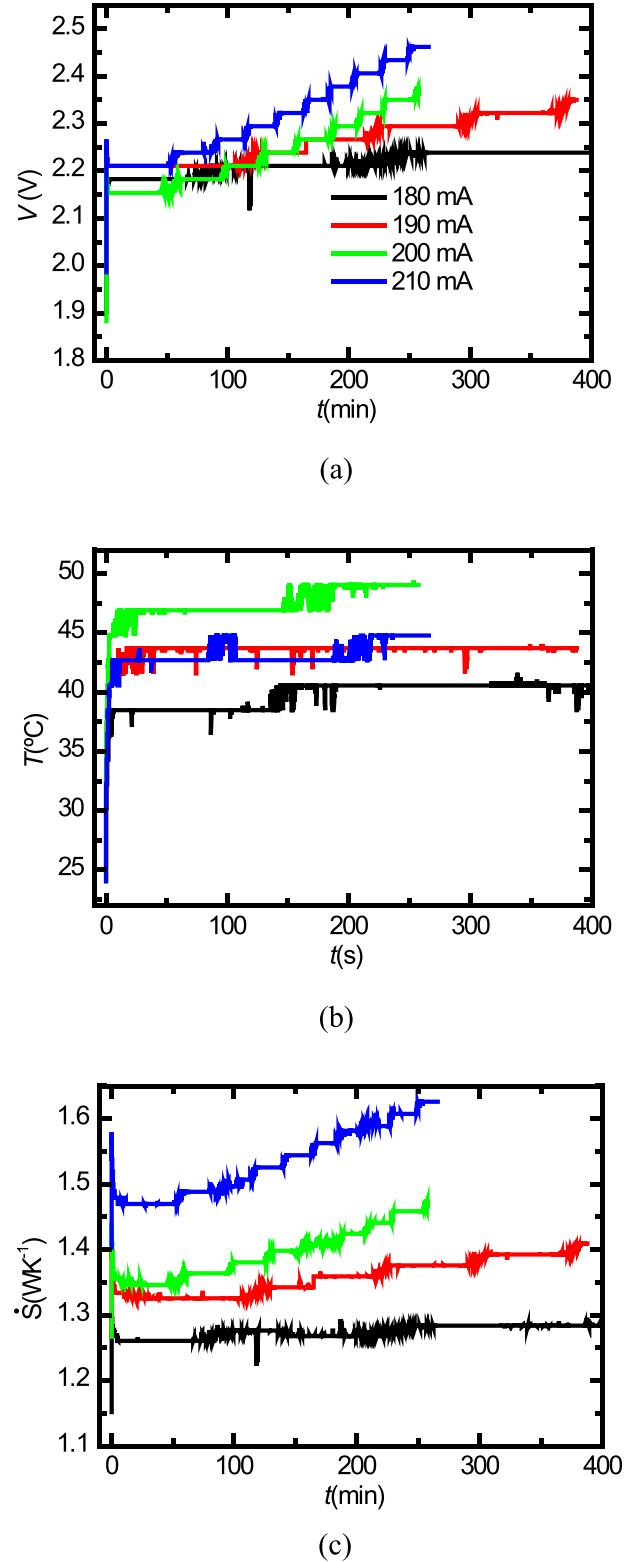


FIG. 3. Evolution of (a) voltage, (b) temperature, and (c) \dot{S} for yellow LED at different currents 180 mA, 190 mA, 200 mA, and 210 mA.

changes which, on one hand decreased its optical performance and, on the other hand, becomes less ordered and thus can generate more entropy. Also, in Fig. 7, we found two different behaviors: a decreasing region and a sudden increase. These results are different from entropy generation either in resistors,³³ where we found a positive slope, or in

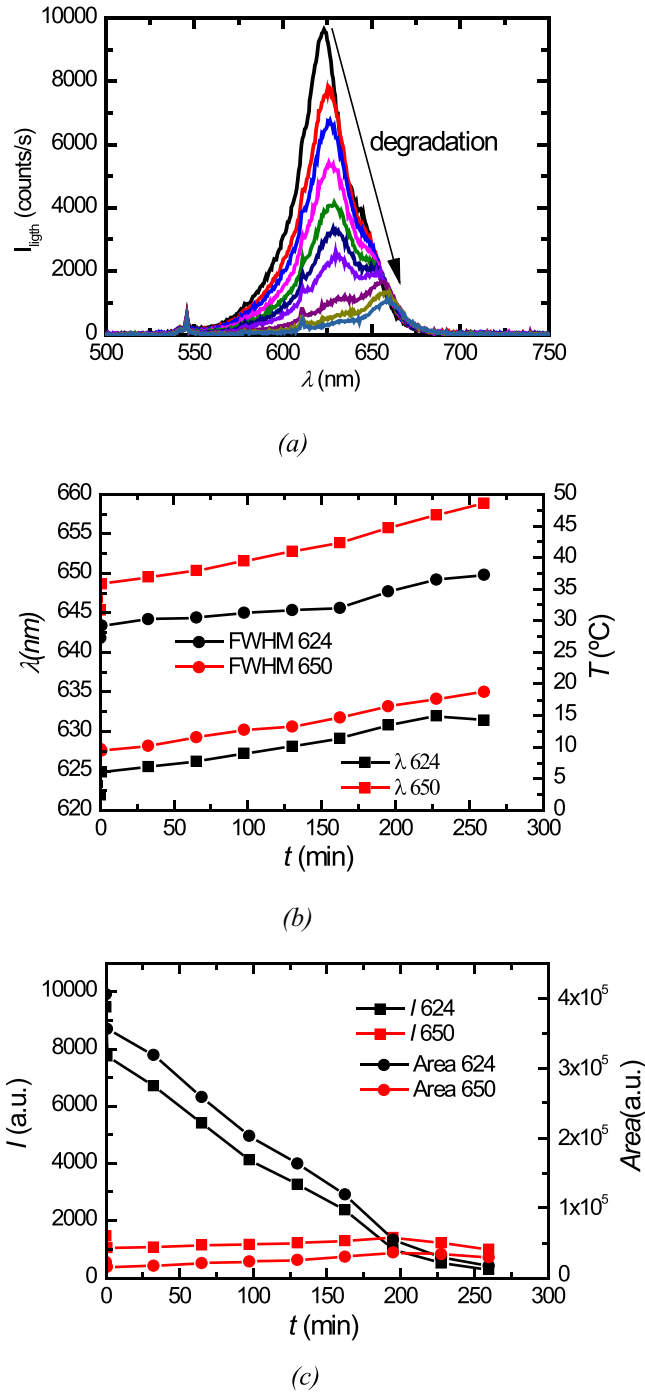


FIG. 4. Results for yellow LED for an input current of 210 mA. (a) Optical spectra measured at different aging stages. Two peaks are found around 624 nm and 650 nm; (b) peak position and FWHM evolution with aging; (c) intensity and area evolution with aging.

capacitors,³⁴ where we found four different behaviors, including a sudden increase that was attributed to gas generation inside the capacitors. These sudden increases might be a sign of a phase transition, as it is well established that phase transitions necessarily imply a discontinuity in entropy.

We now consider the general diode model described in Fig. 1 to interpret the experimental results. We observe that the output optical intensity has a smooth profile, while input electrical power has a quantized profile. The optical output is

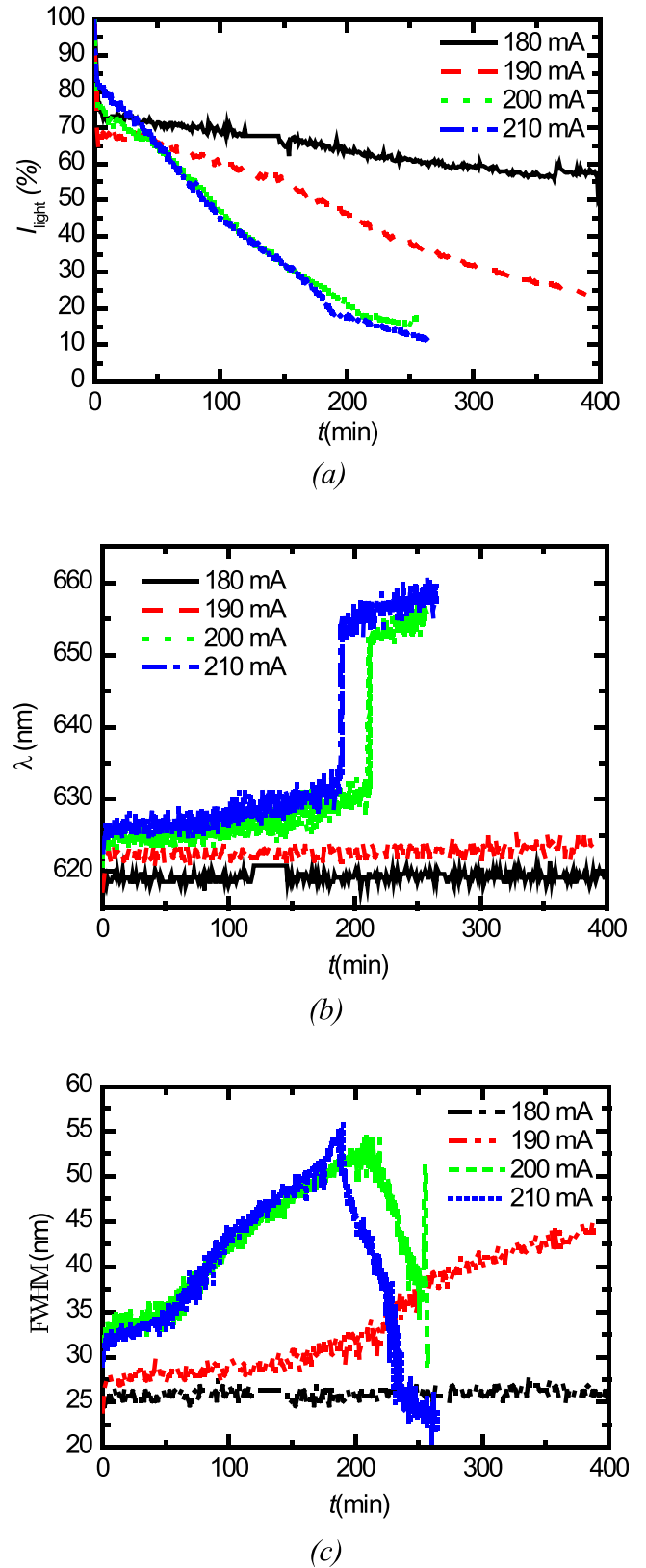


FIG. 5. Results for yellow LED considering the emission peak as the convolution of the peaks at 624 nm and 660 nm. (a) Relative intensity decrease for different bias conditions, (b) maximum peak shift evolution, and (c) FWHM evolution for different bias conditions. Relative intensity decreases monotonously with time and bias conditions. Peak shift is not significant in the expected LEDs' lifetime above L50. FWHM increases with aging. Notice that the anomalous change at around 200 min in either peak shift or FWHM is related to the intensity decrease of the 624 nm peak with respect to the 660 nm peak and it is found for optical intensity fade around 20%, so these changes will not be of interest.

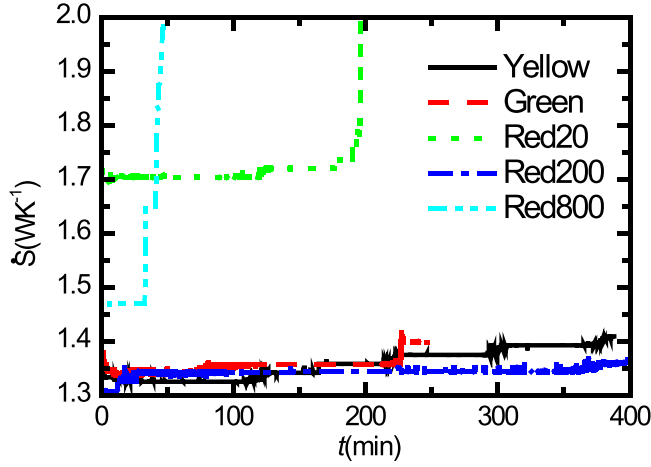


FIG. 6. \dot{S} evolution for green, yellow, and red LEDs for a bias current of 190 mA. Clearly, it increases in all cases.

related to I_{ph} , but the efficiency of these types of LEDs is small, below 0.1% in terms of W/W. This term can be neglected at this stage of accuracy. Non-radiative losses and diffusion losses are modeled by the two ideal diodes. Their I - V curves are exponential. The formation of non-radiative traps due to aging has been pointed out to create dark spots that decrease the optical emission,¹¹ as shown in Figs. 4 and 5. Also, the defect reactions are caused by the carrier-recombination-enhanced defect motion.¹⁶

The resistances take into account the leakage currents and heat dissipation, which describes the thermal heating of the LED. Yang *et al.* showed that these leakage currents were also related to a decrease in the optical performance.¹³ However, the simple model is insufficient to quantify the power dissipated in the material degradation; also, corrections due to band structure changes should probably be necessary.

The relationship between the optical intensity and temperature was also considered because LEDs' performance is sensitive to temperature. According to datasheets, LEDs' performance is given at room temperature while the

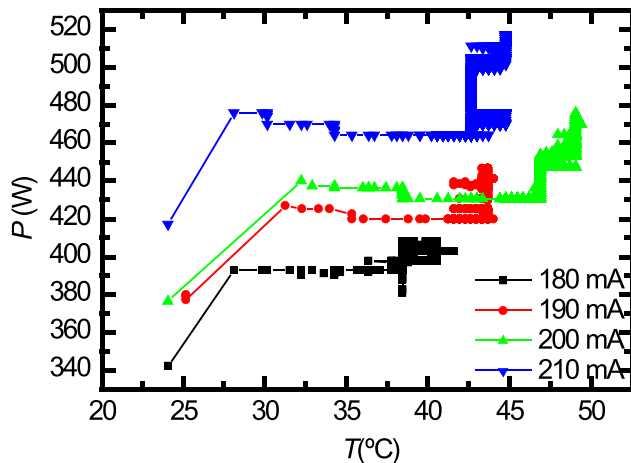


FIG. 7. Power as a function of temperature for yellow LED. The step between room temperature and the stationary regime is due to the transient regime, which was not particularly investigated.

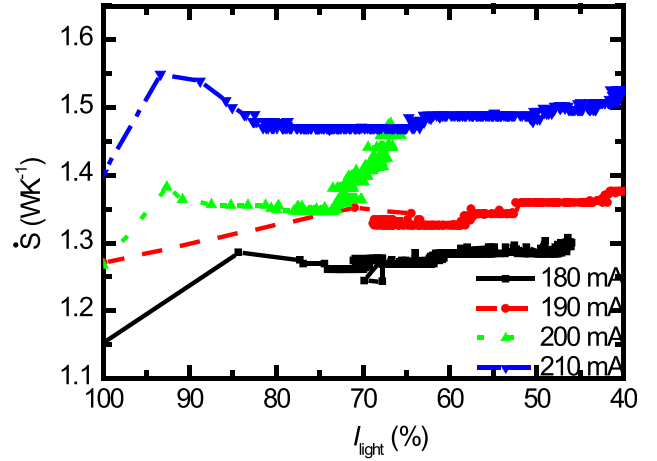


FIG. 8. \dot{S} as a function of light intensity decreases for yellow LEDs.

device is operating at its nominal current. In our case, the increase in temperature is a consequence of heat dissipation in the device and generates a reversible decrease in light intensity.³⁸

The main goal of this work was to describe the relationship between optical performance and LEDs' reliability (end-of-life) in terms of \dot{S} . In Fig. 8, we plot the \dot{S} as a function of optical intensity decrease. We found that \dot{S} decreases until a minimum and then increases. This minimum is in the range of 60% to 70% of optical performance, and it is characteristic of each of the LEDs and their history (bias

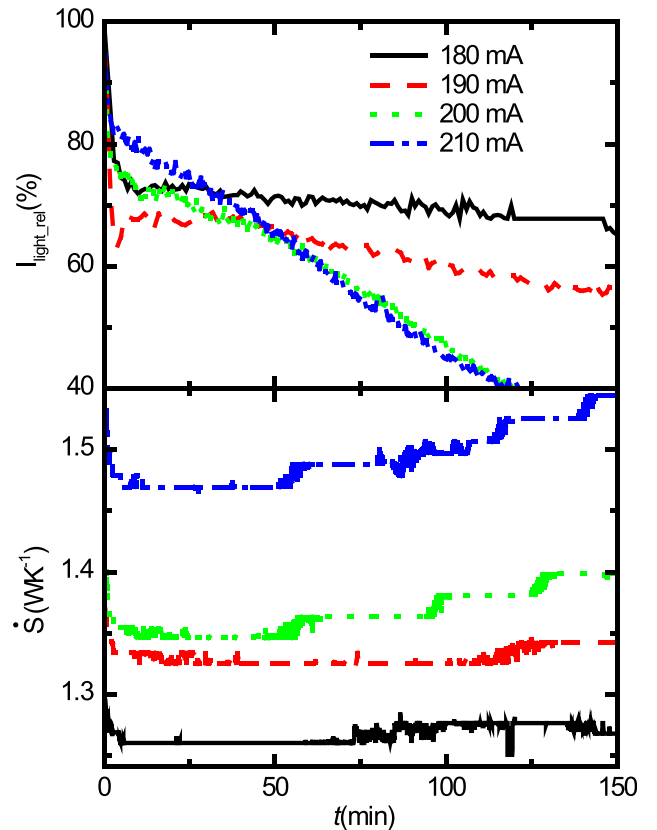


FIG. 9. Comparison between light intensity fade and \dot{S} evolution. A 60% light intensity corresponds to the first jump in the graph of \dot{S} .

conditions). This is in agreement with arbitrarily considered L70 and L50 thresholds in commercial LEDs.¹ Thus, we suggest that \dot{S} minimum can become an easy parameter to be electrically measured in order to predict optical performance without measuring optical irradiance. Similar results were found for all colors.

The method to obtain \dot{S} and correlate with optical performance is better illustrated in Fig. 9. Optical performance decreases monotonously as a function of time. \dot{S} shows increases in steps over time. The first step in \dot{S} can be established as a threshold for optical performance, obtained by measuring LED current, voltage, and temperature.

VI. CONCLUSIONS

We proposed a method to estimate the LEDs' reliability taking into consideration an operation threshold. It was based on their thermodynamics and consisted of measuring their entropy generation rate \dot{S} . \dot{S} could be easily obtained from voltage, current, and temperature measurements. A correlation between optical fade and \dot{S} was found. The threshold was found dependent on internal factors, i.e., colour, and on stress conditions, i.e., current bias. We believe that this approach confirms \dot{S} as a descriptive magnitude of material degradation once it has been assessed in resistors, capacitors, and LEDs.

ACKNOWLEDGMENTS

We would like to thank Professor Blas Garrido, University of Barcelona, for his discussions on LEDs' efficiencies, Ronan Doherty for his support in writing the manuscript, and Francis Lopez for technical support. This research has been partially supported by the Project No. TEC-2015-63899-C3-1-R (MINECO/FEDER).

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