# HORIBA
## Scientific

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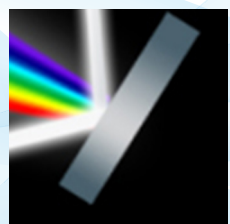PARTICLE CHARACTERIZATION
RAMAN
SPECTROSCOPIC ELLIPSOMETRY
SPR IMAGING

# Macro Photoluminescence and Electroluminescence    OSD-AN-116
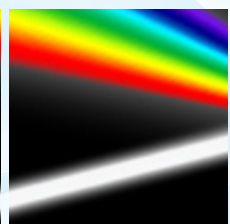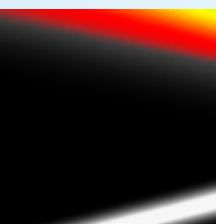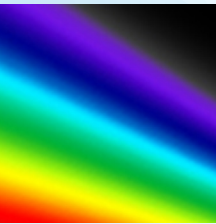
## Lifetime Measurements in PV Material Characterization

## Introduction

Time-resolved photoluminescence (TRPL) spectroscopy is an important tool which can be used to characterize optical materials such as LEDs and photovoltaic (PV) materials. Temporal information as well as spectral information can be used to understand the dynamics of excitonic transitions in such semiconductor materials. Analysis of TRPL contributes to understanding the competition between radiative and non-radiative energy transfer processes[1]. When steady state PL is not enough, PL lifetime can often provide the additional information to uniquely identify a material and may help distinguish isomers or very similar materials from one another. Furthermore PL lifetime measurements can provide information about the dynamics of a material process, information that is not readily obtained from steady state PL.

Electroluminescence (EL) measurements are complementary to PL measurements – the main difference being that the excitation is achieved by a current or voltage injection, instead of photons as in PL. Otherwise the emission part is similar to PL. When a current is applied to the material, electrons are injected into the material and carriers are generated leading to emission of light. Analysis of time-resolved EL measurements (TREL) can indicate fluctuations in the material structure, generating defects or irregularities in the material that may not be evident just from TRPL measurements, and thereby better predict the efficiency of the LED or PV device[2]. Based on the results of TRPL and TREL, improvements can be made to the manufacturing process of LEDs and PVs to make them more robust and efficient.

## Fundamental Principles of PL and EL

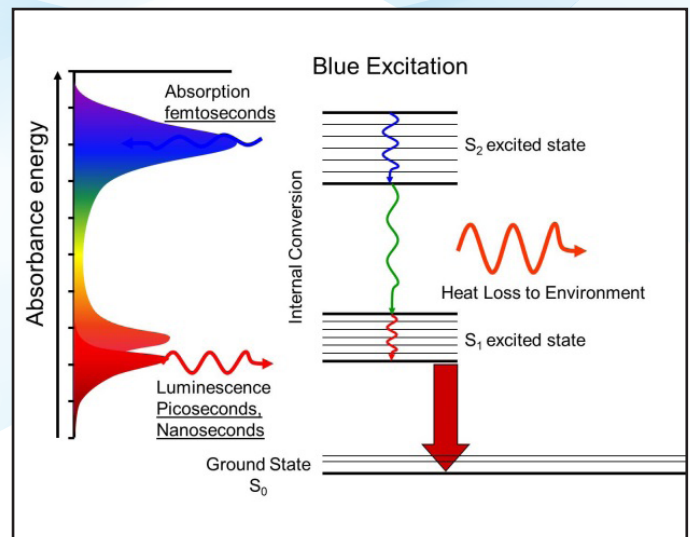In photoluminescence, light is emitted from a material



**Figure 1.** Typical photoluminescence, where blue photons are absorbed and red photons are emitted.

following the absorption of photons. As shown in Figure 1, light is absorbed by the molecule, which is excited to a higher electronic state ($S_2$), typically on a femtosecond timescale. Following a non-radiative energy transfer process, the molecule relaxes to a lower excited state ($S_1$), and photons are then emitted from an excited state also on a picosecond or nanosecond timescale[3]. For semiconductors, the process is slightly different; when light is absorbed, an electron-hole pair is generated (exciton), and photons are emitted upon recombination.

In electroluminescence, an electric current is applied to a semiconductor material, and photons are emitted. The process is called radiative recombination and is a type of spontaneous emission.

## Methods

A popular technique first developed in the 1980's for measuring TRPL is called Time-Correlated Single Photon Counting (TCSPC). The TCSPC method is based on the assumption that the probability of detecting a single photon at time t (after an excitation pulse) is proportional to the photoluminescence intensity at that time. The luminescence decay is reconstructed after timing and recording the single photon signals following a large number of excitation pulses. Figure 2 shows a luminescence decay curve; after a population of molecules is excited with an instantaneous flash from a pulsed source (LED or laser) the molecules randomly decay back to the ground state with each molecule emitting one photon[4]. The lifetime, $\tau$, is defined as the 1/e point, or the amount of time it takes for the population in the excited state to be reduced to 37% of its initial value.
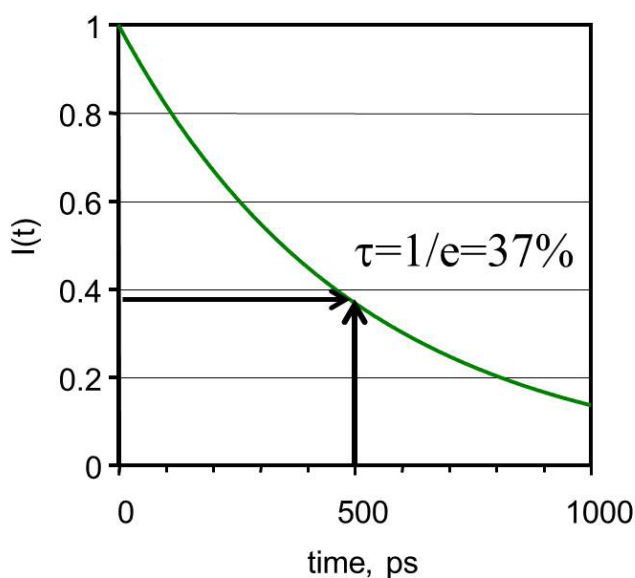


**Figure 3:** Modular HORIBA lifetime system with components (left to right): ASC-RSC-01, iHR320, PPD-850 and DeltaHub.

A typical experimental setup is shown schematically in Fig. 4. Production of an excitation light pulse "starts" the timer. The sample is excited by this pulse and it proceeds to emit fluorescence photons. As described above, emission process is probabilistic in nature and the probability of detecting a single photon at time t (after an excitation pulse) is proportional to the photoluminescence intensity at that time. Detection of the first emission photon "stops" the timer. The difference in time between these two signals (creation of the excitation pulse and detection of one emission photon) is output to a histogram, consisting of time bins, each with fixed time width ($\Delta_t$). Signals arriving within $t+\Delta_t$ go into one specific bin. The width of the bins will influence the measurable time resolution of the system, allowing measurement of the time a molecule stays in the excited state following excitation.



**Figure 2.** Representation of a photoluminescence lifetime.

### Advantages of TCSPC:

a. High sensitivity allows measurements of weakly emitting samples;
b. Wide temporal measurement range is possible (10's of picoseconds to seconds) depending on combination of excitation source and detector;
c. Rapid data acquisition is possible (usually within a few seconds) including single and multiple exponential fits.

## Measurement Setup

The modular, compact HORIBA system used for lifetime measurements (Figure 3) consists of the following components: (a) ASC-RSC-01 sample compartment with reflective optics, (b) iHR320 spectrometer, (c) PPD-850 fast PMT with built-in amplifier-discriminator electronics, (d) DeltaHub TCSPC electronics, and (e) DeltaDiode pulsed ps source (not shown).
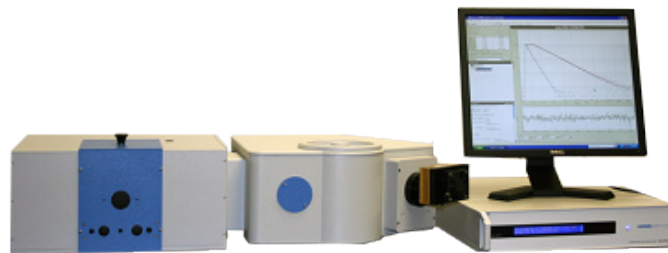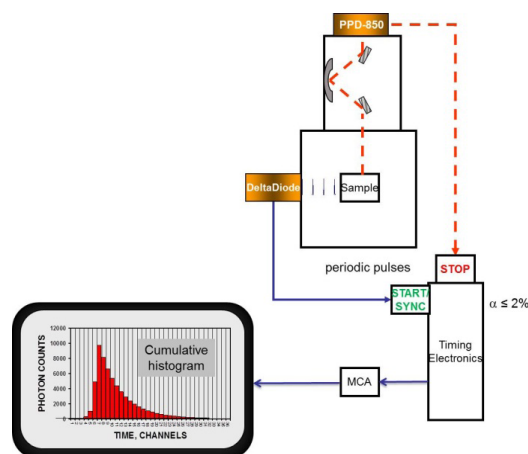


**Figure 4.** TCSPC Instrument principle.

## Examples

In the first series of measurements, KCl:Eu$^{2+}$ and KBr:Eu$^{2+}$ doped glasses were used as models for semiconductors in the TCSPC measurements – perhaps to simulate different types of defects in PV semiconductors. A 350 nm pulsed LED, DeltaDiode-350, was used for excitation. Second, a red LED was used for demonstration of the EL measurements.
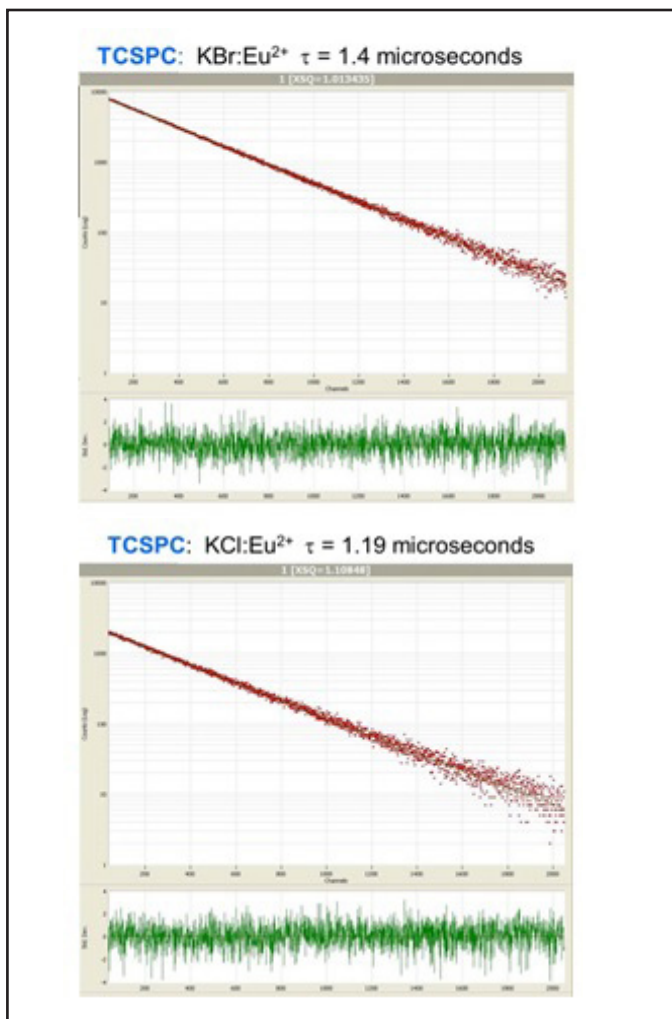
## TCSPC: KBr:Eu²⁺ τ = 1.4 microseconds



## TCSPC: KCl:Eu²⁺ τ = 1.19 microseconds



**Figure 5.** TCSPC data: (a) KBr:$Eu^{2+}$ and (b) KCl:$Eu^{2+}$

Next, electroluminescence measurements were performed. A red LED was mounted in the sample compartment (simulating an electroluminescent sample), and a pulsed current was applied as shown in Figure 6. The same detection electronics were used as with the photoluminescence measurement.

First, a current was applied to the LED to generate a constant emission spectrum, shown in Figure 7. Then a pulsed current source was connected from the TTL output of the pulse generator to the Start port of the DeltaHub and the PMT was connected to the Stop port of the DeltaHub in order to measure the luminescence lifetime using the same Horiba TCSPC system. The TREL data are shown in Figure 8.
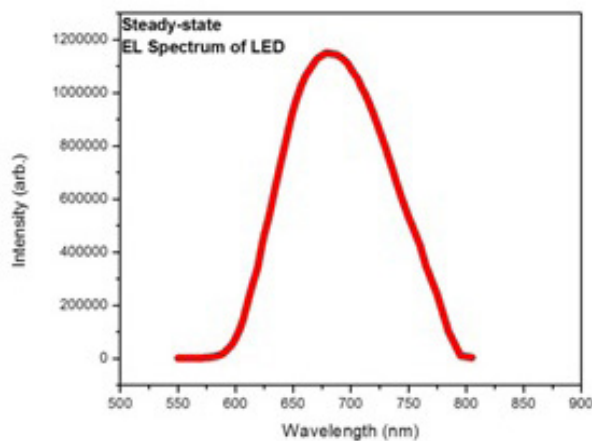


**Figure 7.** Electroluminescence emission spectrum of the red LED

The steady state spectra for these two samples are very similar, since the fluorescence signal comes from the $Eu^{2+}$ ion. However, the TRPL signals are quite different for the KBr and KCl compounds, reflecting the differences in the crystalline matrix environment for the two compounds. The steady state PL results would not be sufficient to distinguish between KBr:$Eu^{2+}$ and KCl:$Eu^{2+}$, but the TRPL results provide positive identification.
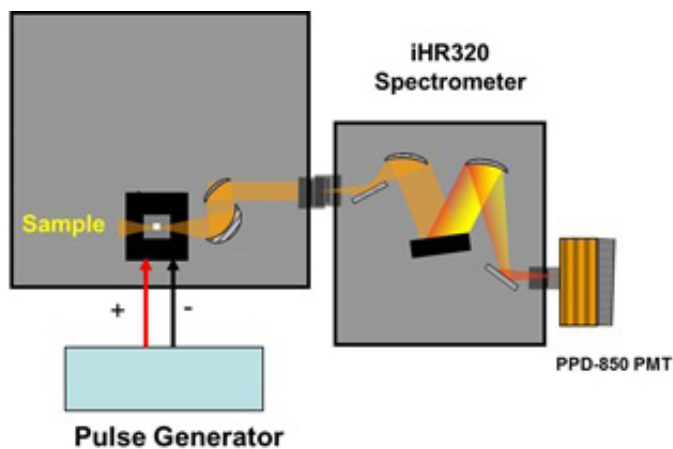
### EL Sample 1: 2 exponential fit τ 1= 257ns (92%), τ 2= 109ns (8%)



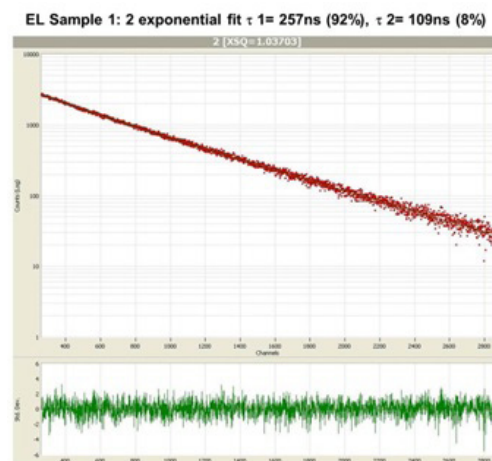**Figure 8.** Electroluminescence lifetime measurements



**Figure 6.** Electroluminescence measurement schematic.

The time resolved EL results have been fit to a double exponential rather than a single exponential. This result indicates that there are two radiative recombination processes responsible for the electroluminescence emission rather than a single process.

## Conclusions:

The modular, compact Horiba Time-Correlated Single Photon Counting system described here provides a convenient and accurate way to measure electroluminescence and photoluminescence lifetimes of electro-optical materials, for PV and other applications.

## Additional Reading:

D.V. O'Connor and D. Phillips, Time-Correlated Single Photon Counting, 1984, Academic Press, New York.

## References

1. M.A. Lourenco, M.S.A. Siddiqui, R.M. Guilliam, G. Shao, K.P. Homewook, Physica E 16 (2003), 3760381.
2. T. Kuroda, N. Horio, K. Taniguchi, H. Sato, C. Funaoka, and A. Tackeuchi, Phys. Stat. Sol., 0(1), 25-28, 2002.
3. Lakowicz, J.R., Principles of Fluorescence Spectroscopy, 2001, Third edition, Springer, New York.
4. Time-Resolved Fluorescence Technical Note TRFT-1, http://www.horiba.com/fileadmin/uploads/Scientific/Documents/Fluorescence/TechNote-1b-Time-resolved_fluorescence_lifetime_measurements.pdf

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