Time-Resolved Photoluminescence Mapping of CIGS Devices Using a Combination of a Superconducting Nanowire Detector and a Confocal Microscope

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Over the years, luminescence spectroscopy has become one of the fundamental methods for analyzing the photophysical properties of a variety of samples, ranging from organic molecules to semiconductor materials and photovoltaic (PV) devices. It is worth emphasizing that detection sensitivity is a key parameter to meet today's demands for handling weak luminescent samples and forshort measurement times in the optical evaluation of PV devices. The introduction of single-photon counting based data acquisition has proven to yield a major sensitivity increase and very high dynamic range – it is the ideal method for measuring weak photoluminescence (PL).
The commonly used steady-state luminescence spectroscopy methods provide valuable insights into the photophysics of a sample. However, such results give only a partial view of the sample's behavior after photoexcitation. A further piece of the puzzle is often revealed by performing time-resolved luminescence spectroscopy, as it provides deeper insights into the photophysical processes occurring in the sample under investigation. An even more comprehensive picture is gained by including spatial information. Acquiring time-resolved spectroscopic data at regions of interest in the sample can help in inferring structural-to-photophysical relationships in PV materials.

Gathering such information is an important step toward the optimization of structure as well as preparation process of such materials in order to increase the performance of PV devices.
In terms of detector performance, superconducting nanowire single-photon detectors (SNSPDs) stand out due to achievable close-to-unity detection efficiency in NIR spectral range, picosecond time resolution (down to < 20 ps (FWHM)), and low dark noise (< 100 counts/s)[1,2]. SNSPDs are a rather new technology that is being used in multiple applications in the field of quantum optics, luminescence lifetime measurements, and singlet oxygen detection.

The high quantum efficiency is especially important for material science applications in the NIR-range beyond 1000 nm, where other available single photon detectors have low sensitivity, high dark noise and slow time response.
In this report we demonstrate the combination of the MicroTime 100 upright confocal fluorescence lifetime microscope with the Single Quantum Eos SNSPDs as a powerful tool for photophysical research on CIGS (Cu(In, Ga)Se_2) devices, yielding spatial and temporal information on semiconductor samples studied through PL emission. While one of the used SNSPDs had a classical single-mode fiber coupling to guide the light onto the sensor, the other detector used an internal multi-mode fiber instead2. We detected a significant increase in photoluminescence sensitivity of both designs compared to a standard NIR-PMT (H10330-45, Hamamatsu) as well as a several times higher sensitivity of the multi-mode fiber coupled nanowire compared to the singe-mode fiber one, in spite of comparable photon quantum efficiencies in this wavelength range for the sensor only. The increased sensitivity combined with the lower dark count rate resulted in an increase of the signal-to-noise ratio by more than three orders of magnitude compared to the NIR-PMT. Moreover, the very high sensitivity of the SNSPD as well as high temporal resolution (instrument response function of the overall system was below 100 ps) reveals clearly the differences in the PL decay profiles of the defect and unquenched areas of the weakly luminescent thin-film CIGS sample[3] even at low illumination levels, which is extemely difficult to resolve when using the NIR-PMT detector.

[1] https://doi.org/10.1063/5.0045990
[2] https://doi.org/10.1364/AO.58.009803
[3] https://doi.org/10.1021/acsaem.9b01370

Properties of the Detectors and Setup

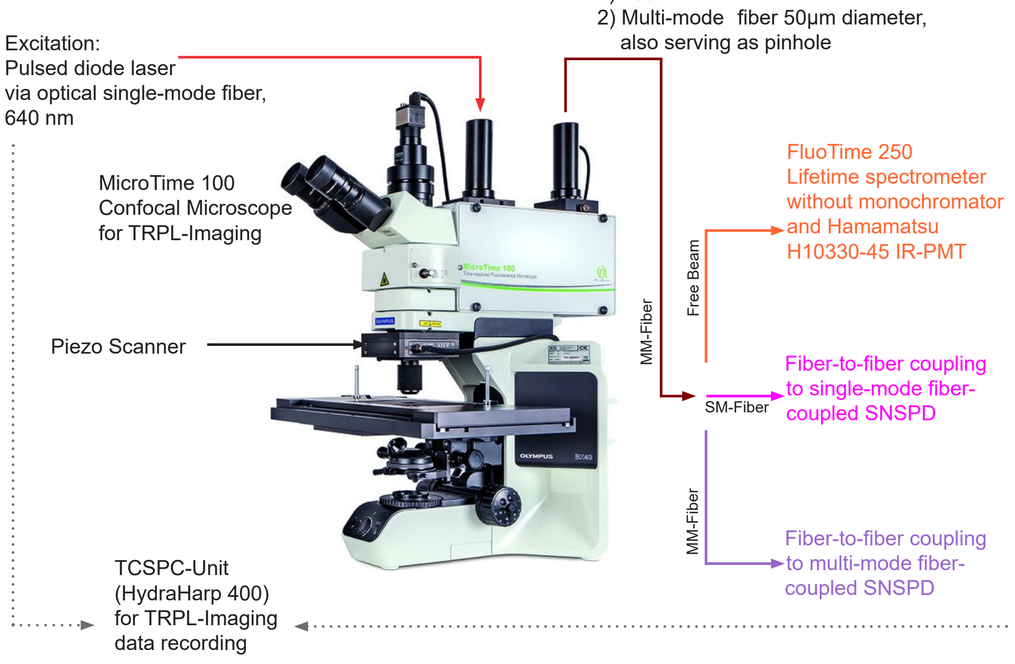
Single Quantum Eos CS
single photon detection system

Detector specifications

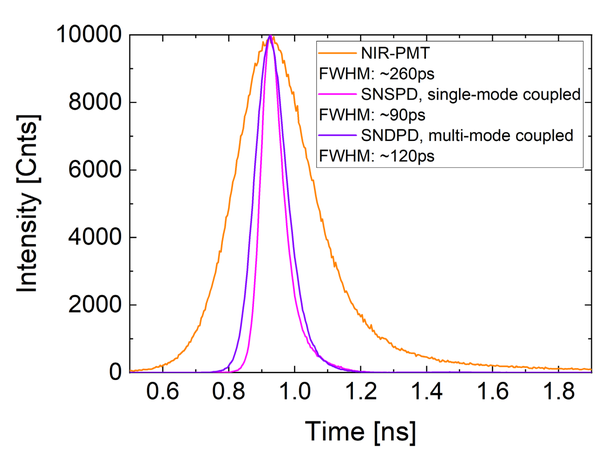
	IR-PMT H10330-45 (Hamamtsu)	SNSPD, single-mode coupled (Single Quantum)	SNSPD, multi-mode coupled (Single Quantum)
Quantum Efficiency:	(1-)2% 950 - 1400 nm	45% (1064 nm) 21% (1278 nm)	57% (1064 nm) 3% (1278 nm)
Detector time jitter:	<400 ps	21 ps	52 ps
Dark counts:	<20000 cps	<10 cps	<300 cps

Cryogenic system
with fiber input

System Integration

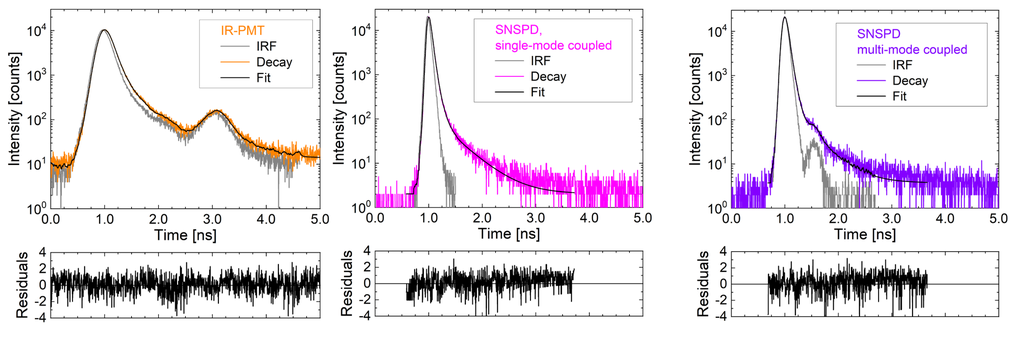


Time Resolution and Fitting Limits



- In Fluorescence Microscopy, fluorophores with extremely fast ps-decay times can be used for IRF-measurements
- Here we approximated fluorescence of the dye 3274y in ethanol as IRF
- The measured IRF is mainly determined by the detector response time for the PMT, and by pulse width of the diode laser for the SNSPDs.

Fluorescence lifetime measurements of single wall carbon nanotubes (SWCNTs)



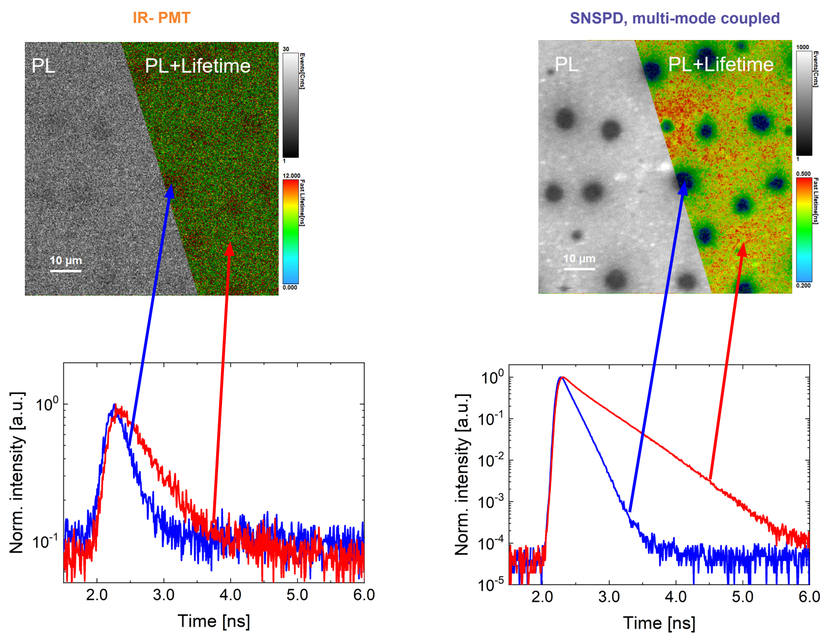
IR-PMT	SNSPD, single-mode coupled	SNSPD, multi-mode coupled
τ_1 = 30 ± 5 ps (99%)	τ_1 = 12 ± 2 ps (97%)	τ_1 = 12 ± 1 ps (97%)
τ_2 = 210 ± 25 ps (0.9%)	τ_2 = 66 ± 8 ps (3%)	τ_2 = 68 ± 8 ps (0.3%)
τ_3 = 2900 ± 800 ps (0.1%)	τ_3 = 400 ± 67 ps (<0.1%)	τ_3 = 360 ± 74 ps (<0.1%)
$\tau_{av, Int.}$ = 70 ± 5 ps, χ^2 = 1.04	$\tau_{av, Int.}$ = 28 ± 2 ps, χ^2 = 1.1	$\tau_{av, Int.}$ = 27 ± 2 ps, χ^2 = 1.25

The fluorescence decay behaviour of single wall carbon nanotubes (SWCNTs) could be accessed with the SNSPDs only, while the instrument response function (IRF) of the standard IR-PMT is too broad.

Time-Resolved Photoluminescence (TRPL) Imaging of a Weakly Luminescent CIGS Semiconductor Device

The Cu(In,Ga)Se_2 (CIGS) absorber layer was grown on 1 mm Mo/SLG glass substrate using a single stage co-evaporation process and underwent a KF treatment by spincoating 0.2 M KF solution in air and annealing the sample in N_2 atmosphere for 20 minutes at 400 degrees*. The layer thickness was 500 nm. The sample was measured using the MicroTime 100 as described above, using 40 MHz laser repetition rate and a laser power of 17 µW at the sample. The measurement time per pixel was 5 ms. The decays below were obtained by point measurements of 30 s at the defect sites (blue) and away from the defect sites (red).

** de Wild et al., High V_{oc} upon KF Post-Deposition Treatment for Ultrathin Single-Stage Coevaporated Cu(In,Ga)Se_2 Solar Cells, ACS Appl. Energy Materials, 2, 8, 6102-6111 (2019)*

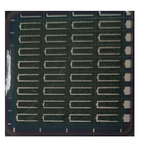


The low intensity of this device makes TRPL measurements difficult when using a standard IR-PMT.

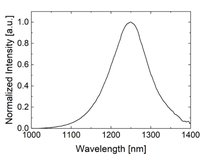
Comparison of the Sensitivity on Imaging a CIGS-device

This significantly brighter CIGS sample was imaged using 2 µW excitation power and a measurement time per pixel of 2 ms.

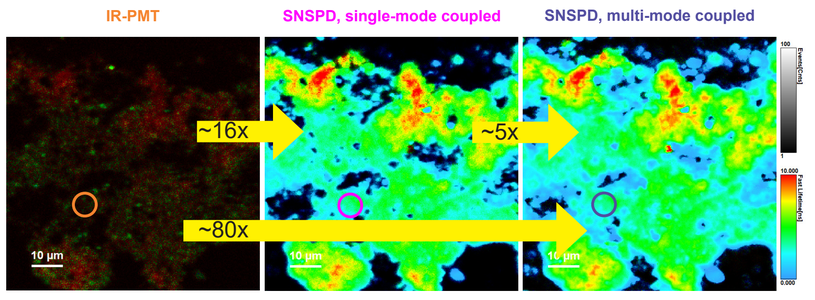
CIGS-device



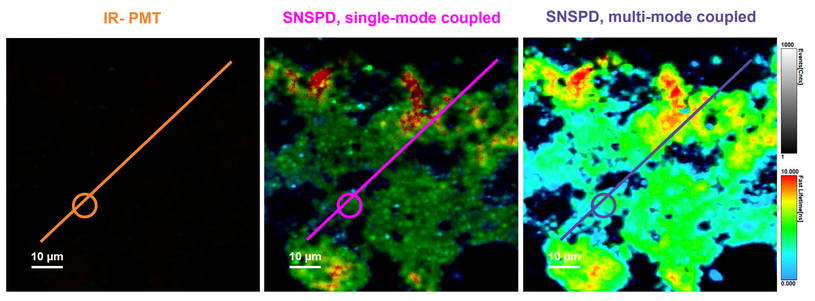
Emission spectrum



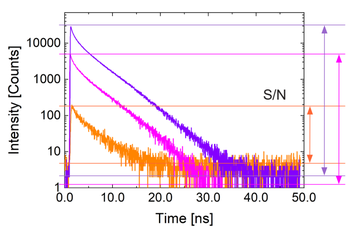
Intensity Scale: 1-100 counts



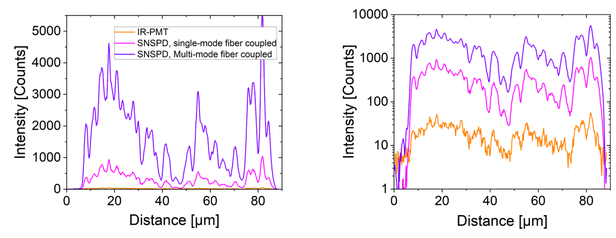
Intensity Scale: 1-1000 counts



Decays from ROI



Line Profiles



The increase of the signal is already significant for a single-mode coupled SNSPD, but even more striking for a multi-mode coupled device.