Photoluminescence Excitation Spectroscopy Characterization of Surface and Bulk Quality for Early-Stage Potential of Material Systems

Elizabeth K. Grubbs[1], James Moore[2], Peter A. Bermel[1]

[1] Electrical & Computer Engineering, Purdue University, West Lafayette, IN 47907, USA

[2] George Washington University, Washington, D.C. 20053, USA

Abstract — **Photoluminescence Excitation Spectroscopy (PLE) is a contactless characterization technique to quantify Shockley-Reed-Hall (SRH) lifetimes and recombination velocities in direct band gap experimental semiconductor materials and devices. It is also useful as to evaluate surface passivation and intermediate fabrication processes, since it can be implemented without the need for development of effective contact technologies. In this paper, we present a novel experimental PLE system for precision-based quantification of the aforementioned parameters as well as a system for which absolute PLE characterization may occur. Absolute PLE measurements can be used to directly calculate V_{OC} for new photovoltaic (PV) material systems and devices. Key system capabilities include a continuous excitation spectrum from 300 nm –1.1 µm, automated characterization, up to 1 nm wavelength resolution (up to 60x higher than prior work), and a reduced ellipsometry requirement for post-processing of data. We utilize a GaAs double heterostructure (DH) and an InP crystalline wafer as calibration standards in comparison with data from an LED-based PLE to demonstrate the validity of the results obtained from this new system.**

Index Terms – **photovoltaic cells, photoluminescence, charge carrier lifetime, gallium arsenide, indium phosphide.**

I. INTRODUCTION

Cathodoluminescence (CL), time-resolved photoluminescence (TRPL), and photoluminescence (PL) characterization techniques are invaluable diagnostic tools to measure surface and bulk properties of semiconductors. These techniques have been employed in the photovoltaic literature for the past several decades. They can briefly be described as follows.

Cathodoluminescence spectroscopy (CL) uses an electron beam to excite electron hole pairs to probe for existence of trap states, defects, and their associated energy states. CL can be used to evaluate different interface treatments and their effectivity on reduction of defect density [8-10]. Surface treatments for CdS/CdTe thin films have been evaluated with CL for quantification of grain boundary recombination velocities and grain interior lifetimes [11].

Time-resolved photoluminescence (TRPL) is another widely accepted approach, which uses pulsed lasers to generate minority carriers and measure their recombination time [1],[6]. It is commonly used to characterize bulk material lifetimes. In a numerical analysis in Sentaurus, Wang *et al.* explored the sensitivities of TRPL with respect to variable surface and bulk velocities [1]. They indicate that the technique yields reliable data across ranges of bulk recombination velocities but remains relatively invariant over a range of surface recombination velocities. This indicates that samples with high surface recombination may require a more rigorous analysis than TRPL can provide – e.g., through additional two-photon measurements [1]. For the preliminary evaluation of material systems arising from particular fabrication processes, examination of surface recombination may be more critical and require an additional but complementary characterization method to TRPL. This may also provide a simpler alternative for collecting and interpreting data from devices already containing junctions, where exponential fits of TRPL data may not directly yield physical lifetimes [5].

A third staple characterization tool in many labs, PL, requires non-trivial analysis when applied to new materials and devices [6]. PL generally utilizes a single, fixed laser excitation wavelength, coupled with a spectrometer and sensitive detector for spectral selection of output photons [12]. Often, PL (including low-temperature variants) can be utilized to identify the presence and energy of trap states. This approach can aid in the evaluation of trap annealing strategies; it is generally coupled with other characterization methods for surface and bulk parameter quantification. Nonetheless, for the purpose of prompt material and fabrication technique evaluation, a continuous spectrum is desirable to decrease lengthy equipment modifications and system recalibrations.

Furthermore, several variants of PL and TRPL have been demonstrated in literature, such as time resolved fluorescence imaging (TR-FLIM) and Quasi steady-state photoluminescence (QSSPL). These versions aim to address particular limitations of the standard techniques such as experimentally induced diffusion causing inhomogeneous PL maps and erroneous carrier lifetime estimation, respectively [13-16].

Photoluminescent excitation spectroscopy (PLE) historically is a less commonly implemented technique than TRPL, PL, and CL for the characterization of thin films or devices. Both TRPL and PL are both readily available from an assortment of vendors. No vendor sells a PLE platform; however, recent research indicates that PLE data, when coupled with simulations in Sentaurus, may offer greater insight into surface and bulk carrier action than either technique alone [1]. For example, PLE can provide information on devices with junctions such as CdS and CdTe [7]. Research into new PV materials takes considerable time and effort and a plethora of characterization tools only assists those efforts. A multi-probe approach involving PLE as one of the prongs allows for more informed decisions regarding future processing avenues, devices, and structures to investigate [18],[19].

In addition to determining lifetimes and recombination velocities, PLE is useful for examining surface passivation

quality and intermediate fabrication processes [2]. Prior work has demonstrated that for particularly high-quality samples such as GaAs, PLE measurements closely match external quantum efficiency (EQE) measurements even though they are in open circuit and short circuit conditions, respectively [3]. Recent findings by Miller *et al.* strongly support the notion that significant emission of photons in the open circuit regime, specifically from the front surface, is correlated with high radiative efficiencies, and thus is critical for achieving maximal V_{OC} [17]. More informally, a good photovoltaic cell is also a good LED. Given PLE's sensitivity to surface variability, more established characterization techniques may benefit from its use.
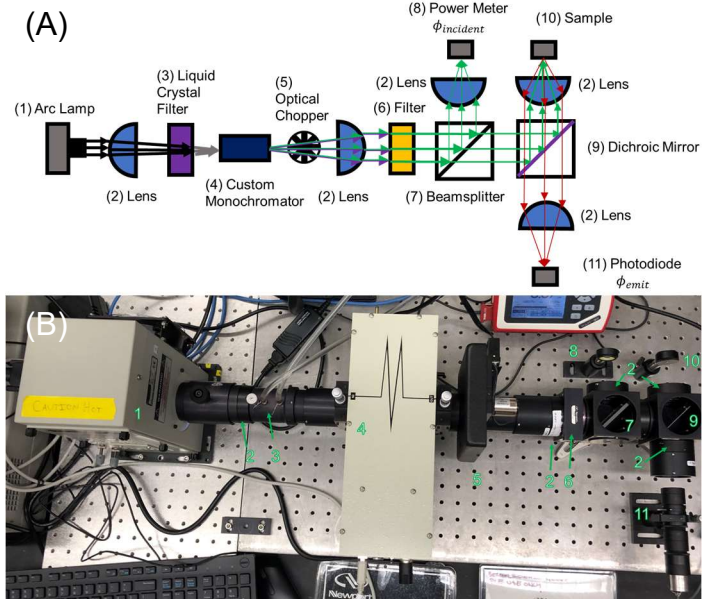

Fig. 1.   A) PLE schematic with numbered components. Arrow color indicates wavelength where black, grey, and maroon, represent broadband, broadband with IR removed, and IR light. For clarity, arrows are not dashed to represent optical chopping and light shields are not shown. B) Image of PLE experiment with annotated components and light shields shown. A post-mounted target indicates where the sample mount is located.

In this work, we present a custom PLE system with a continuous range of excitation wavelengths and improved wavelength resolution in a modular, light-tight, and automated data-taking configuration. In addition, this PLE setup has interchangeable components to accommodate for most direct band gap photovoltaic material system and devices. These specifications improve upon a previous LED-based system. The prior PLE system [4] utilized an LED array to improve excitation power in the UV and to establish a more economically viable PLE than in past literature [1],[4]. Due to the varying quality of the different LED manufacturers' parabolic lenses, inconsistent beam collimation, and varying LED positioning became nontrivial. These challenges had implications for use with the diffraction gratings and spectral filters, in that system alignment for one LED was imperfect for another. Combined with the use of geometric beamsplitting, the

experiment produced a distorted beam spot. This culminated in the use of interpolation to correlate grating angle to wavelength instead of the diffraction grating equation. This was mediated by using the LED's spectral output for determination of peak wavelengths; nevertheless, these limitations combined with the lack of a continuous range of excitation lengths as well as the use of geometric beam splitting, warranted a system redesign. In addition, the layout of the LED-based system was not conducive to integration of specialized experiments or as a platform to measure absolute PLE.

In PLE, wavelength-specific photons are absorbed by a material sample or device. These photons, having energy greater than the band gap of the sample, excite electron hole pairs. Instead of extraction of carriers via probes in the form of current, electron-hole pairs recombine radiatively and photons are re-emitted. The incident excitation photon flux ϕ_{excite} and the emitted photon flux ϕ_{emit} are measured and used to calculate a PLE signal:

$$PLE = \frac{\phi_{emit}}{\phi_{excite}(\lambda_{excite})} \qquad (1)$$

In this work, the PLE signal is then normalized to the maximum measured PLE signal.

II. Experimental Method

The proposed PLE system utilizes a 300W Xe arc lamp as the excitation source, followed by collimation optics and a liquid crystal filter for removal of infrared radiation. This reduces the risk of any heat damage to sensitive components further along the optical path. Wavelength selection of the broadband source is achieved via a custom Ebert-Fastie monochromator with grating efficiencies of >70% for the entirety of the near UV to NIR spectrum. Entrance and exit focusing optics were selected to maximize the power throughput of the monochromator. The monochromator slits are adjustable via micrometer and allow for wavelength resolution of up to a 1 nm bandwidth. Higher order radiation blocking filters ensure that λ/2 and λ/3 radiation does not reach the sample or detectors even though they are solutions to the Bragg diffraction grating equation:

$$n\lambda = d\sin(\theta) \qquad (2)$$

Where *n* is the diffraction order, λ is the wavelength of incident light, *d* is the grating ruling spacing, and θ is the angle at which constructive interference results in a maximum.

A 30% reflection / 70% transmission beamsplitter samples the incident flux reaching the material or device under test (DUT), while maximizing the flux reaching the sample. Incident and re-emitted photons are separated via a custom dichroic mirror with a cut-on wavelength corresponding to the band edge of the DUT. For the materials and devices characterized in this work, the installed dichroic mirror has <5% and >95% transmission at 750nm and 835nm, respectively. Emitted photons are transmitted through the

dichroic mirror to the photodiode and lock-in amplifier as illustrated in fig. 1. The system employs optical chopping to reduce background noise and improve signal detection of the photodiode and power meter. The photodiode connects into a Stanford Research Lock-in Amplifier. The power meter sensor has a built-in neutral density filter and internally accounts for its spectral responsivity.

Dichroic mirrors corresponding to different cut-on wavelengths for larger or smaller bandgaps can be easily installed into the system due to the streamlined and modular cage design. The continuous excitation spectrum in this work ranges from 350nm to 750nm; however, the source emits well past 2.0μm allowing the testing of wide range of material systems and devices. Currently the system is also used to conduct photoelectric chemistry (PEC) experiments; the system can be converted to and from the PEC experiment setup in 10 minutes or less.
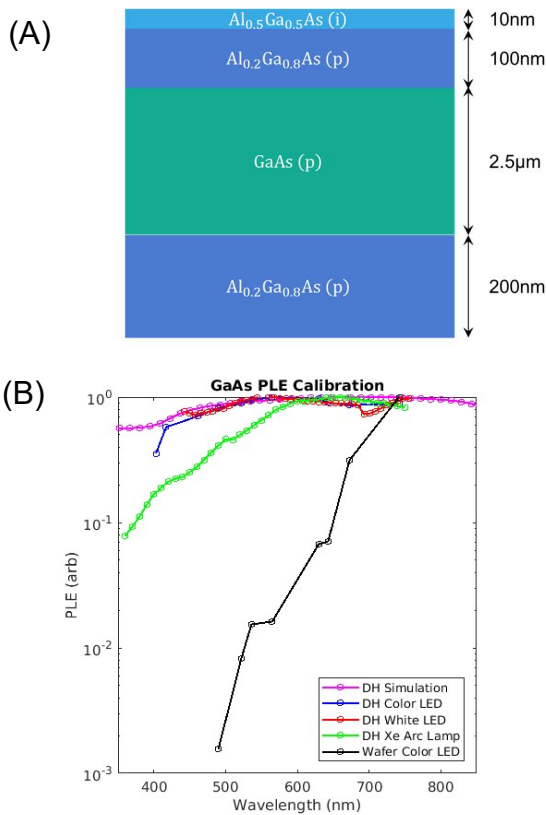
(A)

(B)

Fig. 2.   A) Cross section of the tested GaAs DH structure B) Semilogarithmic comparison of GaAs DH and wafer data taken on LED based system and the Xe arc lamp system. Data was taken with entrance and exit slits at 1 mm widths, corresponding to ~10 nm wavelength resolution.

III. EXPERIMENTAL RESULTS

To validate the performance of this system, two samples were measured and compared to prior work on PLE. First, a GaAs DH structure was grown via MBE, and passivated [4]. It was then characterized on an LED-based system [1]. Finally, it was

measured using the Xe arc lamp-based system described in section II. A comparison of the PLE data in these two systems is shown in Fig. 2. A Sentaurus simulation of the GaAs DH PLE behavior is also shown. There is close agreement between the simulated PLE, Xe-based system, and the LED-based system. The same GaAs DH was characterized by both systems, 3 years apart, explaining the decreased PLE signal for <500nm. It is possible that the 10 nm layer of $Al_{0.5}Ga_{0.5}As$ (i) and the 100nm layer of $Al_{0.8}Ga_{0.2}As$ (p-type) surface layers degraded over time, resulting in an increased surface recombination velocity and therefore decreased PLE signal at higher energy wavelengths. If surface degradation is present in the GaAs DH sample, it is plausible that some of the p-type GaAs layers have been exposed to oxygen, therefore causing microcracking, resulting in an increase in defect density.
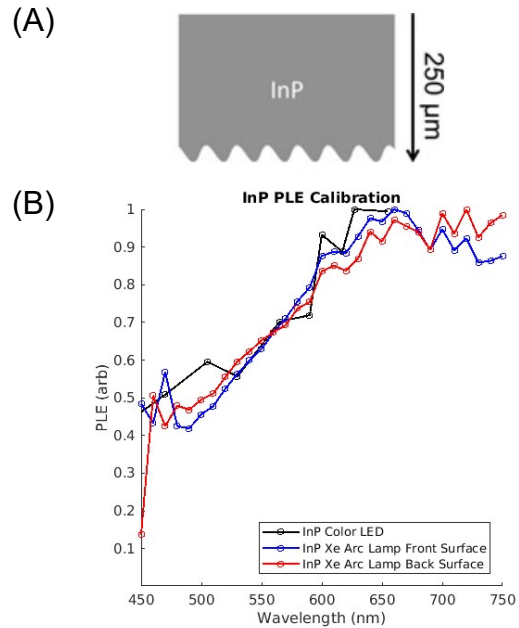
(A)

(B)

Fig. 3.   A) Cross section of tested InP wafer with $N_D = 5 \times 10^{17}$ cm^{-3} [1] 3) Comparison of InP wafer data taken on the LED based system and the Xe arc lamp system. Data was taken with entrance and exit slits at 1mm corresponding to approximately 10nm resolution.

The InP crystalline wafer tested was compared to previous data taken on the LED-based system in [1]. Both the front surface and the back surface were characterized and are shown in fig.3. with the previous work. Not only does the data from the Xe arc lamp system agree with the data from LED-based system, the increased resolution increases visibility of differences between the front and back surface of the InP wafer. This demonstrates PLE capabilities for evaluation of fabrication techniques for materials in addition to GaAs [2]. There may be further benefits from spatially resolved PLE and even PLE-based in-line characterization.

VI. CONCLUSIONS

A novel Xe arc lamp based PLE has been used to characterize GaAs DH and InP wafer samples that had previously been characterized on an LED-based PLE. Similar data trends are observed while the Xe arc lamp system has nearly 6 times as many data points recorded for the same wavelength range. The GaAs DH exhibits evidence of surface degradation and the corresponding SRH lifetimes and recombination velocities can be quantified once coupled to Sentaurus simulations. The InP crystalline wafer further proves that the Xe arc lamp based PLE can be used to take more detailed measurements. Both samples show that PLE can also be used for examining surface passivation and intermediate fabrication techniques. The system proposed in this work uses a continuous source from 300nm to larger than 2.0μm, has a maximum wavelength resolution of approximately 1nm, and can currently characterize materials with band gap energies corresponding to emissions of >850nm.

The modular, light tight, and interchangeable features of this system were meticulously designed to serve as a platform for more specialized experiments in the future. For example, the improved sensitivity and wavelength resolution should allow solution-processed nanoink based PV materials and devices such as CIGS to be characterized on the current system. Materials with emission peaks <850nm could easily be tested with a second dichroic mirror with a different cut-on wavelength. Also, with the introduction of a second monochromator, this PLE system could also take PL data to serve as a dual PLE and PL setup. Spatially-resolved PLE could be explored with a micrometer driven sample holder. The most exciting prospect for this system is absolute PLE measurement capabilities, which would require either a NIST traceable standard or an integrating sphere. Incorporation of absolute PLE capabilities in the current system may enable quantum yield experiments as well. To the authors' knowledge, no PLE-based V_{OC} spatial map of lateral inhomogeneities has been published previously. Absolute PLE measurements would enable direct calculation of V_{OC} for novel materials and devices, as well as determination of the degree of uniformity of materials as fabricated, thus aiding the evaluation of their viability for PV applications.

REFERENCES

[1] X. Wang, J. Bhosale, J.E. Moore, R. Kapadia, P. Bermel, A. Javey, and M.S. Lundstrom "Photovoltaic Material Characterization With Steady State and Transient Photoluminescence" *IEEE J. Photovolt.* vol. 5, no. 1 (2015): 282-287.

[2] G.D. Pettit, J. M. Woodall, and H. J. Hovel. "Photoluminescent characterization of GaAs solar cells." *Appl. Phys. Lett.*, vol. 35, no. 4 (1979): 335-337.

[3] D. Berdebes, J. Bhosale, K.H. Montgomery, X. Wang, A.K. Ramdas, J.M. Woodall, and M.S. Lundstrom, "Photoluminescence excitation spectroscopy for in-line optical characterization of crystalline solar cells". *IEEE J. Photovolt.*, vol. 3, no. 4 (2013): 1342-1347.

[4] J. Bhosale, J.E. Moore, X. Wang, P. Bermel, M.S. Lundstrom. "Steady-state Photoluminescent Excitation Characterization of Semiconductor Carrier Recombination," *Rev. Sci. Instr.*, vol. 87, no. 1 (2016): 017601.

[5] R.K. Ahrenkiel, "Influence of junctions on photoluminescence decay in thin-film devices," *J. Appl. Phys.*, vol. 62 (1987): 2937-2937.

[6] D. Kuciauskas, A. Kanevce, J.N. Duenow, P. Dippo, M. Young, J. V. Li et al. "Spectrally and time resolved photoluminescence analysis of the CdS/CdTe interface in thin-film photovoltaic solar cells," *Appl. Phys. Lett*, vol. 102 (2013): 173902.

[7] J.E. Moore, X. Wang, E. K. Grubbs, J. Drayton, S. Johnston, D. Levi, M. S. Lundstrom, and P. Bermel, "Photoluminescence excitation spectroscopy characterization of cadmium telluride solar cells," *2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC), 2016.*

[8] B.D. White, L.J Brillson, M. Bataiev, L. J. Brillson, D. M. Fleetwood, R.D Schrimpf, B. K. Choi, D. M. Fleetwood, and S. T Pantelides, "Detection of trap activation by ionizing radiation in SiO2 by spatially located cathodoluminescence spectroscopy," *Journal of Applied Physics*, vol. 92, no. 10, pp. 5729-5734, 2002.

[9] D. M. Zhernokletov, M. A. Negara, R. D. Long, S. Aloni, D. Nordlund, and P. C. Mcintyre, "Interface Trap Density Reduction for Al2O3/GaN (0001) Interfaces by Oxidizing Surface Preparation prior to Atomic Layer Deposition," *ACS Applied Materials & Interfaces*, vol. 7, no. 23, pp. 12774–12780, 2015.

[10] M. J. Romero, K. Ramanathan, M. A. Contreras, M. M. Al-Jassim, R. Noufi, and P. Sheldon, "Cathodoluminescence of Cu(In,Ga)Se2 thin films used in high-efficiency solar cells," *Applied Physics Letters*, vol. 83, no. 23, pp. 4770–4772, 2003.

[11] J. Moseley, P. Rale, S. Collin, E. Colegrove, H. Guthrey, D. Kuciauskas, H. Moutinho, M. Al-Jassim, and W. K. Metzger, "Luminescence methodology to determine grain-boundary, grain-interior, and surface recombination in thin-film solar cells," *Journal of Applied Physics*, vol. 124, no. 11, p. 113104, 2018.

[12] H.-P. Wang, C. M. Sutter-Fella, P. Lobaccaro, M. Hettick, M. Zheng, D.-H. Lien, D. W. Miller, C. W. Warren, E. T. Roe, M. C. Lonergan, H. L. Guthrey, N. M. Haegel, J. W. Ager, C. Carraro, R. Maboudian, J.-H. He, and A. Javey, "Increased Optoelectronic Quality and Uniformity of Hydrogenated p-InP Thin Films," *Chemistry of Materials*, vol. 28, no. 13, pp. 4602–4607, 2016.

[13] J. A. Giesecke and W. Warta, "Microsecond carrier lifetime measurements in silicon via quasi-steady-state photoluminescence," *Progress in Photovoltaics: Research and Applications*, vol. 20, no. 2, pp. 238–245, 2011.

[14] J. A. Giesecke, M. C. Schubert, D. Walter, and W. Warta, "Minority carrier lifetime in silicon wafers from quasi-steady-state photoluminescence," *Applied Physics Letters*, vol. 97, no. 9, p. 092109, 2010.

[15] A. Bercegol, G. El-Hajje, D. Ory, and L. Lombez, "Determination of transport properties in optoelectronic devices by time-resolved fluorescence imaging," *Journal of Applied Physics*, vol. 122, no. 20, p. 203102, 2017.

[16] G. El-Hajje, D. Ory, J.-F. Guillemoles, and L. Lombez, "On the origin of the spatial inhomogeneity of photoluminescence in thin-film CIGS solar devices," *Applied Physics Letters*, vol. 109, no. 2, p. 022104, 2016.

[17] O. D. Miller, E. Yablonovitch, and S. R. Kurtz, "Strong Internal and External Luminescence as Solar Cells Approach the Shockley–Queisser Limit," *IEEE Journal of Photovoltaics*, vol. 2, no. 3, pp. 303–311, 2012.

[18] R. V. K. Chavali, S. Khatavkar, C. V. Kannan, V. Kumar, P. R. Nair, J. L. Gray, and M. A. Alam, "Multiprobe Characterization of Inversion Charge for Self-Consistent Parameterization of HIT Cells," *IEEE Journal of Photovoltaics*, vol. 5, no. 3 (2015): pp. 725–735.

[19] R. V. K. Chavali, S. D. Wolf, and M. A. Alam, "Device physics underlying silicon heterojunction and passivating-contact solar cells: A topical review," *Progress in Photovoltaics: Research and Applications*, vol. 26, no. 4 (2018): pp. 241–260.