Photoreflectance (PR) Photothermal Deflection Spectrometry (PDS) for new Material Research

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Abstract
Recent advances in photovoltaic research, particularly in novel material synthesis, require the use of optoelectronic characterization techniques to complement standard photoluminescence measurements. Photothermal Deflection- and Photoreflectance- Spectroscopy (PDS and PR) have shown to be particular useful in the study the optoelectronic properties.
In this paper, we introduce the basic measurement principles and data analysis of each technique. We demonstrate the data extraction on are three applications: the determination of critical points at the absorption onsets, Urbach energy and sub-bandgap absorption, interface electrics fields from field effect passivation layers, and built-in junction electric field in full devices. The paper concludes with a comparison of each techniques strength and a status update of the development of these techniques at UNSW.

Introduction

With the development of novel photovoltaic materials, driven by the push to find the ideal tandem-on-silicon material [1], accurate characterisation of various energy levels is needed to optimize material synthesis [2, 3]. These includes the basic bandgap energy, the critical points within the band structure, as well as sub-bandgap defect- and Urach- energies. In addition, a measurement of electric fields at interfaces would be useful to compare surface field-effect passivation layers of new materials without requiring full device fabrication [4]. Moreover, it provides a method to measure the built-in electric field (or voltage) of a finished device [5-7].
At UNSW, we identified two complementary measurement techniques to be particular useful on thin film materials. These are the Photothermal Deflection spectroscopy (PDS) and the Photoreflectance Spectroscopy (PR).
Even though the more established Photoluminescence (PL) spectroscopy techniques also provide some optical band energy data, compared to PDS and PR it does lacks significantly in sensitivity.

The Photoluminescence (PL) Technique

PL spectroscopy uses a laser with an energy above the bandgap energy of the sample to generate excess charge carriers, see Figure 1, which both radiatively and non-radiatively recombine. The radiative recombination results in photoluminescence that is measured with a spectrometer. The energies of the photons are those of the electrons that occupied the states near the bandgap before they optically recombined. The rate of photons are directly proportional to the excess charge carrier concentration. Thus, it is possible to measure the carrier lifetime if the measurement is done with a time dependent laser / light source.
The full paper will include a short section of theory and an example of measured data.

The Photothermal Deflection Spectroscopy (PDS) Technique

PDS measures extremely small changes in temperature. This is particular useful for the measurement of the ‘dark’ recombination of charge carriers, a recombination that otherwise cannot be measured.

A small area of the sample is sequentially illuminated through the wavelengths of the optical spectrum to be measured. The illuminated area generates excess charge carriers that recombine either radiative (photoluminescence), or non-radiative (thermalisation). Thermalisation is the primary recombination channel for low lifetime samples.

A thermalisation generates a small amount of heat that also warms up the immediate surrounding volume, which creates a temperature gradient in the liquid in which the sample is suspended. The liquid is chosen to have a refractive index that strongly changes with temperature. We choose perfluoromethylcyclopentane C_6F_{12}. In this way, the local temperature gradient is also represented as a gradient in refractive index. In other words a local GRIN lens was created due to local heating. A laser is used to measure the strength of this GRIN lens. For that its beam grazes across the surface of the sample and passes through this lens. As further the beam is deflected from it's straight path, as stronger the lens. As the strength of this GRIN lens is directly proportional to the amount of heating, and therefore to the amount of optical absorption, the amount of laser deflection is linear with the amount of optical absorption.

At a distance, the deflection can be measured with a position sensitive detector. Not only is the deflection direct proportional to the amount of heat, but also is the technique extremely sensitive with up to 5 orders of magnitude of dynamic range.
The full paper will include a short section of theory and an example of measured data.

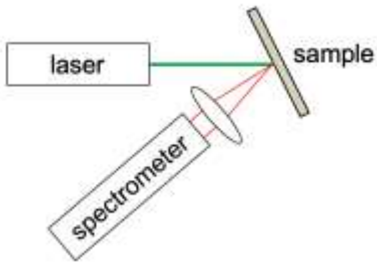

Figure. 1 The basic PL setup

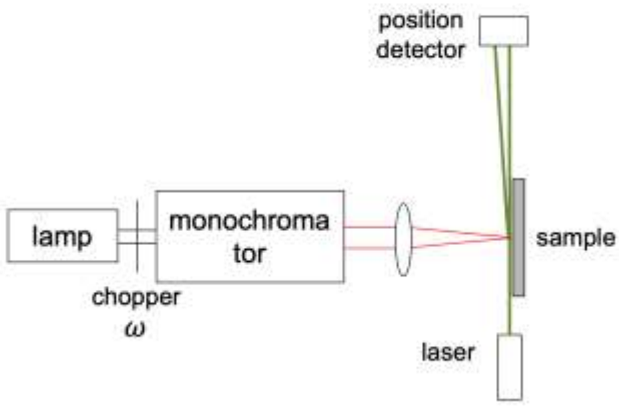

Figure. 2 The basic PDS setup

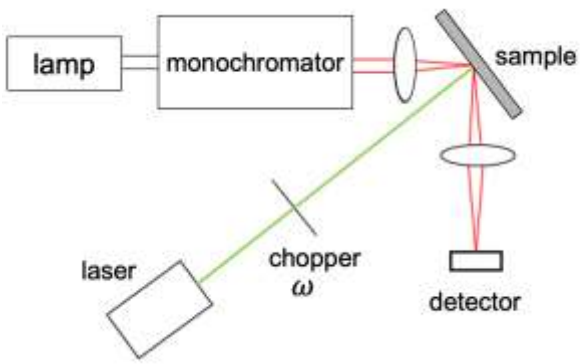

Figure. 3 The basic PR setup

The Photoreflectance (PR) Technique
PR changes, or modulates, the characteristics of the semiconductor itself (and measures these changes) and thus belongs to the category of modulation spectroscopy [8,9]. It is important to distinguish this from the modulation that is used in the PL and PDS techniques. Their modulation is not changing the characteristics of the sample but fulfils only the purpose of noise reduction.

PR analyses the change in spectral reflectance of a sample caused by additional generated excess charge carriers that are generated by a laser, or other strong optical bias. The reflected spectrum is

measured via monochromatic light and a photodetector, see Figure 3. The presence of excess charge carriers creates internal electric fields that slightly shift (or bend) the energy bands near surfaces and interfaces. As a consequence, also the dielectric function around critical points (such as band edges) are changing, which alter the optical reflection properties of the sample. The result are distinct sharp features in the energy spectrum around optical transitions, or critical points [3].
The full paper will include a short section of theory and an example of measured data.

Further development
Recently the PR setup at UNSW was extended to a double modulation configuration [7] as seen in Figure 4. The simultaneous modulation of pump beam (laser) ω_2 and probe beam ω_1 generates a signal at the side-band frequency $(\omega_1 + \omega_2)$. The advantage of using a sideband signal is, that it does not contain unwanted photoluminescence signals at ω_2 from samples with strong radiative characteristics. While normally such a double demodulation technique requires sequentially connected lock-in amplifiers, we are working on an arrangement that allows the use of a single lock-in amplifier. In addition, we are working on a detector electronic that has narrow frequency gain to increase the dynamic range of the setup.

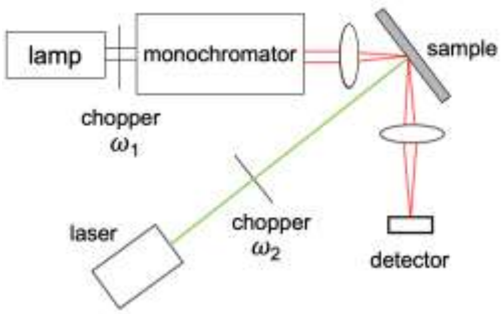

Figure. 4. The double demodulation [7] PR setup.

The PDS technique is further developed towards commercialisation through Open Instruments. The challenges that are typical for this measurement technique have already been overcome. These include e.g. difficulties to align the laser beam to the sample reliably, sufficiently supress vibration sensitivity and to eliminate power noise from the laser beam. Expression of interest can already be placed.

Conclusion
PDS and PR remains valuable techniques for research into semiconductor materials and optoelectronic devices. With the breadth of new materials under study in the photovoltaic community, photoreflectance directly complements more common optoelectronic characterization techniques such as PL. PDS has sufficient sensitivity to measure directly the absorption spectrum and defect levels of newly synthesized thin-film materials, where PL excels especially in measuring the electric field of surfaces and interfaces of device stacks.
Table 1 summarises differentiating key characteristics of these three techniques. PL, as being the most commonly and easily understood technique, is also the least sensitive on thin films.

Table.1 Strength of the PDS and PR techniques

	Photo**l**uminescence Spectroscopy (PL)	**P**hotothermal **D**eflection **S**pectroscopy (PDS)	**P**hoto**r**eflectance Spectroscopy (PR)
Depth	approx. absorption depth of laser	first several um	interface(s) where laser is absorbed
Insensitive to substrate		✓	✓
Radiative recombination	✓		
Bandgap energy	✓	✓	✓ (direct only)
Urbach & defect energy		✓	
All dark recombination		✓	
Band structure			✓
Electric fields at interfaces			✓
Build in potentials			✓

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