

MASTER'S THESIS

Defect characterization of organic/inorganic semiconductors using photothermal deflection spectroscopy and thermal admittance spectroscopy

Cheung, Sin Hang

Date of Award:
2019

[Link to publication](#)

General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

Abstract

Traps are ubiquitously present in semiconductors. Their presence results in ineffective charge transport and thus limited the device performance. For organic semiconductors, traps can present intrinsically via structural disorder or extrinsically during synthesis or device fabrication. A thorough understanding of traps is important to optimize the device performance and material design. This thesis employs two trap measurement techniques, photothermal deflection spectroscopy (PDS) and thermal admittance spectroscopy (TAS), to investigate the trap density in the materials.

The subgap optical absorptions of several high performance bulk-heterojunction (BHJ) systems for organic solar cells have been studied by PDS. The charge transfer (CT) states are, in particular, looked into detail. CT states are intermediate bound electron-hole pairs at the donor/acceptor (D/A) interface of an organic solar cell. The dynamics and energetics of CT states are crucial to free charge generation and recombination processes. With the help of PDS and external quantum efficiency (EQE) measurements, the CT states the delocalized CT states (hot) from the localized CT states (cold) are observed and differentiated directly. It is discovered that the localized CT states are more pronounced when the acceptor concentration reaches its percolation limit. As the acceptor concentration reaches its optimized composition, the intensity of these CT states is significantly reduced due to the reduced recombination. Using the CT

energies measured from PDS, the open-circuit voltage losses from the BHJs are determined.

Besides PDS, thermal admittance spectroscopy (TAS) is employed as an alternative method to measure the trap densities. TAS measures the frequency dependent capacitance response of a semiconductor under a small ac signal excitation. This technique is useful to measure the trap depth and trap density of a semiconductor. The defect profiles in two classes of materials are investigated, they are perovskite compounds and an organic hole transporter with an intentional dopant. The trap density are determined by TAS is compared with that obtained by PDS.

Table of Contents

DECLARATION	i
Abstract	ii
Acknowledgements.....	iv
Table of Contents.....	vi
List of Tables.....	ix
List of Figures	x
Chapter 1 Introduction	1
Chapter 2 Basic Principles and Theory	14
2.1 Introduction to organic semiconductors.....	14
2.1.1 Traps in organic semiconductors and their effects on device performance	15
2.2 Photothermal Deflection Spectroscopy (PDS).....	19
2.2.1 Basic principle of PDS	22
2.2.2 Thermal properties	24
2.2.3 Probe beam propagation.....	28
2.3 Optical bandgap (E_g).....	30
2.4 Urbach Energy (E_U)	32
2.5 Optical sum rule	34
2.6 Thermal admittance spectroscopy (TAS).....	36
2.6.1 Admittance Response of trap states	37
Chapter 3. Experimental details	48
3.1 Photothermal deflection spectroscopy	48
3.1.1 PDS sample preparation	48
3.1.2 PDS measurement	48
3.1.3 Pump beam power measurement	57
3.1.4 Normalization of PDS spectrum.....	59

3.1.5 Transmission measurement	61
3.1.6 Absorption coefficient calculation	63
3.2 Thermal Admittance Spectroscopy (TAS)	64
3.2.1 Sample preparation	64
3.2.2 Device characterization	68
Chapter 4 Observing subgap optical absorption features in bulk-heterojunction blends with photothermal deflection spectroscopy	72
4.1 Introduction	72
4.2 Experimental Details.....	77
4.3 Results and discussions.....	79
4.3.1 Reliability of PDS setup.....	79
4.3.2 Subgap absorption features of polymer, fullerene, and their BHJs	81
4.3.3 Assigning non-localized (hot) CT states	84
4.3.4 Assigning localized (cold) CT states	86
4.3.5 Cold CT states intensity and BHJ compositions.....	89
4.3.6 Cold CT states in other BHJ systems.....	93
4.3.7 Relationship between cold CT states and V_{OC} loss	96
4.4 Conclusion.....	98
Appendix I: PDS spectra of PTB7:PC71BM at different D:A compositions.	99
Appendix II: Full scale subgap EQE spectrum of PTB7:PC ₇₁ BM.....	100
Chapter 5 Defect characterization using thermal admittance spectroscopy	105
5.1 Introduction	105
5.2 Experimental Details.....	108
5.3 Results and discussions.....	111
5.3.1 Effect of PCBM passivation on CH ₃ NH ₃ PbI ₃ Perovskite material	111
5.3.2 Thermal Admittance Spectroscopy measurement for NPB:DCM1	119

5.4 Summary	124
Chapter 6 Conclusion	128
Selected Publications and Patents.....	130
Conference Presentations	133
CURRICULUM VITAE.....	134