**The identification and characterization of electronic defect bands in organic photovoltaic devices**

by

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**Abstract**

In any microelectronic device, fundamental physical parameters must be well understood if electronic properties are to be successfully optimized. One such prominent parameter is energetic trap states, which are well-known to plague amorphous or otherwise impure semiconducting materials. Organic semiconductors are no strangers to such states and their electronic properties are evidently tied to these defects. This dissertation aims to elucidate these states in organic photovoltaic (OPV) devices. The literature to date is first reviewed and the author’s contributions are subsequently detailed.

Within the community, several techniques have been leveraged to study these mid-gap states. Atop the list are optical, capacitance and current based measurements and each has provided important pieces to the overall defect profile. Piecing together the works to date, organic photovoltaic materials are depicted as disordered semiconductors with a seemingly continuous distribution of both energetically shallow and deep trap bands. Upon blending the pure materials to create the modern day bulk heterojunction – the currently preferred photovoltaic architecture – energetic disorder increases and new trap bands appear. These states have been shown to stem from both intrinsic (e.g. structural disorder) and extrinsic (e.g. oxygen and synthesis contaminates) sources and it is quite clear that such states can have profound effects on, if not completely control, the electronic properties and long term stability of OPV devices. Most prominently, these states are known to enhance trap-assisted recombination, induce Fermi-level pinning and generate space-charge effects. Though these mid-gap traps have a large negative impact, they also can give an advantageous inherent doping, improving conductivity and interfacial electric fields. Evidently, continued progress in understanding the nature, sources, affects and possible mitigation of these defects in both current and future materials will be crucial to the optimization of this promising technology.

The primary work of this study is to build upon these reports and to further the current body of knowledge on the identification and characterization of defect states in OPV devices. Capacitance techniques are heavily employed herein. As such, the accurate capacitance characterization in OPV devices was first visited. It was found that, owing to thinner films and larger series resistance, the series based parasitics could not be neglected in the typical frequency range of interest or significant errors and misinterpretations were introduced. Armed with this more accurate model, deeper, previously unknown trap states were then identified using low frequency capacitance measurements coupled with a point by point differential of high frequency capacitance-voltage measurements. The discovered defects remain important as it is those states closer to the midgap which more efficiently contribute recombination and can be detrimental to device performance. More generally, the presented technique gives a generic overview of the capacitance response of OPV devices – resolving anomalies and enabling others to better study the defect profile in their devices. Lastly, the pre-exponential factor of trap emission, also known as the attempt to escape frequency, was studied. This parameter is essential if trap occupancy kinetics are to be accurately described – important for any measurement or model dependent on the detrapping dynamics. It was found that the polymer based devices studied herein have a prefactor within a similar range, yielding similar trap capture cross sections. Not only does this give guidance as to the proper value to be used in the detrapping measurements/models, but also indicates that the trapping mechanisms in these devices are likely similar.