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A Study on Conjugated Polymer Photovoltaic Devices and Components

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Abstract – In solar cells based on amorphous silicon traps play a dominant role in the description of the solar cell characteristics. In contrast, the current in OC_1C_{10}-PPV based hole-only diodes has been shown to depend quadratic on voltage and exhibit a third power dependence on sample thickness. This behavior is characteristic for a space-charge limited current (SCLC). The occurrence of SCLC enables us to directly determine the hole mobility from the current voltage characteristics. It should be noted that a material with shallow traps would also exhibit an identical voltage and thickness dependence, and the observed mobility would be an effective mobility in that case, including trapping effects. However, transient measurements demonstrated that the measured mobility does not show any evidence of trapping effects. The same holds true for the electron transport in bulk PCBM. Additionally, the electron and hole mobility in the blend of both materials have been addressed, both showing trap-free SCL current-voltage characteristics. Therefore, it can be safely concluded that trapping effects do not play a role in our devices, and hence can be neglected in our model.

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INTRODUCTION

The field of organic electronic devices, such as light emitting diodes, field-effect transistors, sensors, lasers and photovoltaic devices is rapidly expanding due to the promise of inexpensive material and device fabrication accompanied by the wide variety of functionality of organic materials. The most important functionality is the large polarizability of the extended π-conjugated electron systems of organic compounds, among which π -conjugated semiconducting polymers are one of the prominent materials. The semiconducting properties of conjugated polymers are attributed to the dimerization (i.e. Peierls distortion) of double bonds formed by the derealization of the P_z-orbitals of the carbon atoms of the polymer backbone.

Another interesting class of functional materials is fullerenes. After two decades from the initial discovery of buckminsterfullerene by Kroto et al. in 1985, these materials are being developed to various applications as antioxidants, biopharmaceuticals and active and passive additives for the polymer industry. The science and technology of plastic solar cells which will be reviewed here lies on the frontier of the above mentioned two important classes of functional materials, and shows an example how interdisciplinary research fields can merge together towards the developments of future technologies.

As the evidence for global warming continues to build, it is becoming clear that we will have to find non-CO2-releasing ways to create, transport, and store electricity. For photovoltaic (PV) cells to gain widespread acceptance as a source of clean and renewable energy, the cost per watt of solar energy must be decreased. Currently, the main barrier that prevents photovoltaic technology from providing a large fraction of our electricity is the high cost of manufacturing crystalline silicon. Although the cost per peak watt of crystalline silicon PV cells has dropped significantly over the past decade, these PV cells are still too expensive to compete with conventional grid electricity without the benefit of government subsidies. One potential alternative to crystalline silicon PV cells is cells made from thin films of conjugated (semiconducting) polymers, which can easily be cast onto flexible substrates over a large area

using wet-processing techniques. These organic PV cells could provide electricity at a lower cost than crystalline silicon solar cells if a reasonable power efficiency (~10%) and lifetime (~10 years) could be achieved on a large scale.

To reach these performance levels, however, several technological hurdles must be overcome. We begin this review with a discussion of the photovoltaic properties of organic semiconductors, including a general overview of the properties of these materials that make them attractive as candidates for use in PV cells, as well as their limitations.

REVIEW LITERATURE:

While films of copper phthalocyanine (CuPc) must generally be deposited by evaporation onto a substrate, the conjugated polymers poly(3-hexylth- iophene) (P3HT), poly[2-methoxy-5-(2'-ethylhexoxy)-1,4- phenylenevinylene] (MEH-PPV), and poly[2-methoxy- 5-(3',7'-dimethyloctyloxy)- p-phenylenevinylene] (OC1C10io- PPV) contain side chains that make them soluble in common organic solvents. This allows these polymers to be cast from solution using wet processing techniques such as spin casting, dip coating, ink jet printing, screen printing, and micro-molding. These techniques represent an enormously attractive route for producing large-area PV cells cheaply because they can be performed at ambient temperature and pressure, and because many of these techniques are scalable to large area with little material loss. Also, many of these techniques can be applied to systems that require flexible substrates, such as roll-to-roll coaters.

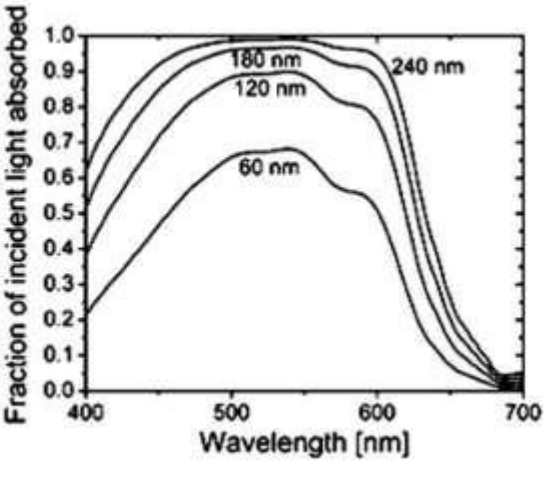

Figure: Fraction of incident light absorbed by P3HT as a function of wavelength for several different film thicknesses.

A second major requirement for the active layer in a PV cell is that it should absorb a significant fraction of the sun's light. The high $(\sim 10^5\ \text{cm}^{-1})$ peak optical absorption coefficient of many conjugated polymers makes them excellent candidates in this regard. While crystalline silicon PV cells must be made $\sim 100\ \mu m$ thick to effectively absorb incident light, organic semiconductors have a direct band gap and generally must only be 100-500 nm thick to absorb most of the light at their peak absorption wavelength. Above Figure shows the fraction of incident light absorbed by P3HT as a function of wavelength for several different film thicknesses. At a P3HT film thickness of 240 nm, greater than 95% of the incident light is absorbed over the wavelength range 450-600 nm, neglecting reflective losses. However, Figure also highlights one of the biggest existing hurdles to reaching high efficiency PV cells with conjugated polymers: the band gap of these semiconductors is too large and the absorption bandwidth of these materials is too narrow to absorb a large fraction of the solar spectrum. While the photon flux of the AM1.5G solar spectrum peaks around 700 nm (1.8 eV), P3HT, MEH-PPV, and OC1C10-PPV absorb strongly only over the wavelength range 350-650 nm (3.5-1.9 eV). As a result of this mismatch between the absorption spectrum of the organic semiconductor and the solar spectrum, the 240 nm thick film of P3HT shown in Figure absorbs only about 21% of the sun's photons. Although a semiconductor with a 1.9 eV band gap could still be used to make an efficient PV cell if an open-circuit voltage could be attained that is close to 1.9 V, thereby giving a high power efficiency (defined as the maximum power produced by a PV cell divided by the power of incident light) despite only converting a small fraction of the sun's photons to current, in practice this has proven difficult to achieve in a PV cell made from conjugated polymers. In these cells V_{oc} values typically range between 0.5 and 1.2 V for devices that have reasonable photocurrents $(>1\ \text{mA/cm}^2)$ under AM1.5G illumination.

RESEARCH METHODOLOGY:

Although it is possible to generate a built-in field in an inorganic semiconductor through the controlled placement of n- and p-type dopant atoms, it is difficult to controllably dope most conjugated polymers. As a result of this, conjugated polymers are usually made as pure as is practically possible and can effectively be considered to be intrinsic semiconductors. Generating built-in electric fields within a film in the dark requires sandwiching the polymer between electrodes with varying work functions or incorporating interfaces with a second semiconductor into the device structure. In one of the first reported conjugated polymer PV cells, a photovoltaic effect was observed in a device made by spin casting and thermally converting an undoped thin layer of PPV on top of a transparent indiumtin oxide (ITO) electrode and then evaporating on a low work-function top contact. When light with $\sim 10\ \text{mW/cm}^2$ intensity was shone on the PV cell, an open-circuit voltage between 1.2 and 1.7 V was produced, depending on the metal used. In most cases the open-circuit voltage was roughly equal to the difference in work function between the top and bottom electrodes divided by the charge of an electron. This showed that in single-layer conjugated polymer PV cells, the sign and magnitude of V_{oc} could at least be partially attributed to an electrode work-function difference. However, it must be added that further research has shown that there are several other important factors that contribute to V_{oc} such as non negligible dark current, Fermi level pinning, and chemical potential gradients.

Although single-layer PV cells tend to produce a reasonable $V_{oc},$ their photocurrent is typically very low. For example, at an excitation wavelength of 458 nm, the above ITO-PPV metal device had only 0.1-1% external quantum efficiency (EQE, defined as the number of electrons produced by a PV cell for each incident photon). The discrepancy between the large fraction of photons absorbed at the wavelength of maximum absorption by a ~ 100nm thick conjugated polymer film $(> 50\%)$ and the low EQE (1%) of single-layer PV cells reveals the strong tendency of photo generated electrons and holes to recombine in conjugated polymers.

There are two major causes for this phenomenon. First, while the exact nature of the interaction between the electron and hole in a conjugated polymer is still a subject of debate, it is clear that the predominant tendency of these materials is to form bound excitons that decay rather than dissociate at room temperature. Second, even when free carriers are created in conjugated polymers via charge injection or exciton dissociation at an interface, these carriers typically have very low mobilities. The disordered nature of these semiconductors causes the transport of carriers to occur through a hopping mechanism rather than through bandlike transport. Hole mobilities that have been reported for conjugated polymers range from 10^{-1} to 10^{-7} cm^2/(V s), while electron mobilities are typically lower (104^{-1}(T9 cm^2/(V s)). By contrast, the hole and electron mobilities in crystalline silicon are 475 and 1500 cm^2/(V s). With carrier mobilities in polymer semiconductors that are many orders of magnitude lower than their crystalline counterparts, re combinative carrier loss can occur in polymer PV cells even under short-circuit conditions. The wide range of reported carrier mobilities in conjugated polymers results primarily from extreme sensitivity of the mobility to the morphology of the polymer film. There is also evidence that the carrier mobility in conjugated polymers increases with carrier concentration.

SYNTHESIS OF CONJUGATED POLYMERS

There are several synthetic strategies available for the formation of a single bond between two unsaturated carbons. In addition to electrochemical or chemical oxidative polymerizations, transition metal-catalyzed cross-coupling reactions provide a particularly powerful synthetic strategy for Csp2-Csp2 and Csp-Csp2 bond formation. The cross coupling reaction involves a transition-metal-catalyzed oxidative addition reaction across the C-X bond of an electrophile followed by trans-metalation with a main group organo-metallic nucleophile, which again is followed by a reductive elimination step leading to the carbon-carbon bond formation. The most commonly employed transition metal catalysts are nickel or palladium based complexes. The organometallic nucleophiles can be Grignard reagents (Kumada-Corriu), stannyl (Stille), boron reagents (Suzuki-Miyaura) or copper (Sonogashira). Thus, conjugation lengths can be extended through consecutive transformations in the catalytic cycle.

Kumada-Corriu reaction : Ni or Pd catalyzed cross-coupling reaction of Grignard reagents with alkyl, vinyl or aryl halides is named Kumada cross-coupling reaction. McCullough used this reaction to synthesize head–tail region-regular poly(3-hexyl thiophene) as shown in Scheme. The regioregular polymerization of 3-alkylthiophene can be achieved by selective lithiation of 2-bromo-3-alkylthiophene with lithium di-isopropylamide followed by transmetallation using magnesium bromide to yield the organomagnesium intermediate. The use of a NiCl$_2$ catalyst for the polymerization of this intermediate gives the corresponding poly(3-alkylthiophene) with over 90% head-tail regioselectivity.

McCullough reported another method for the synthesis of region-regular poly(3-alkylthiophene) by Grignard metathesis (GRIM). Treatment of 2,5-dibromo-3-hexylthiophene with a variety of alkyl Grignard reagents resulted in two metalated regioisomers. Introduction of a catalytic amount of NiCl$_2$ to this isomeric mixture afforded poly(3-hexylthiophene), which contained greater than 95% region-regularity.

Stille cross-coupling reaction : Stille coupling is more suitable for thiophene-containing polymers using monomers with stannyl groups on the thiophene ring. For example, Li et al synthesized phenothaizine/thiophene copolymer by utilizing the Stille cross-coupling reaction. They used 3,7-dibromo-10- octylphenothiazine and distannyl derivative of thiophene as monomers and Pd(PPh3)4 as the catalyst.

CONCLUSION:

The conjugated polymer-PCBM bulk hetero-junction is currently the best conjugated polymer-based PV cell. One significant improvement to this device structure was made recently by Shaheen et al., who found that the morphology of the blend could be optimized by casting the polymer and PCBM from a solvent that prevents long-range phase separation and enhances the polymer chain packing. A second improvement came when it was found that switching the conjugated polymer from PPV derivatives to P3HT could give a further increase in hole mobility, giving photovoltaic cells with EQE above 70% at the absorption maximum and 3.5% power efficiency under white light illumination.

If a high degree (>95%) of exciton dissociation can be guaranteed in the PV cell by intermixing the two phases well enough, as is generally the case in the polymer-PCBM PV cell because of the high co-solubility of the two constituents, then achieving high external quantum efficiency will result from extracting the separated carriers from the film before the competing process of interfacial recombination can occur. This recombination process, called back electron transfer, occurs when a hole on the conjugated polymer recombines with an electron on the electron-accepting material. For the OC1C10-PPV- PCBM system, this process typically occurs in the first 1-10 μs following exciton dissociation, although a small fraction of the excitations are long-lived and require milli-seconds to recombine. In conjugated polymer-PCBM films thicker than 100 nm, this recombination rate becomes competitive with the transport time for carriers to reach the electrodes, resulting in recombinative loss rather than increased external current. Because PCBM does not absorb strongly and an 80% weight fraction of PCBM is required to optimize transport properties, a PV cell with an optimal film thickness of 100 nm is ultimately limited by the ability of the film to absorb light. For example, in the case of a 100 nm film of 20 wt % OC_1C_{10}-PPV and 80 wt % PCBM, only slightly more than half of the incident photons are absorbed at the wavelength of maximum absorption. To achieve improved light absorption using films with an optimal film thickness of several hundred nanometers, it will be necessary to reduce the transport time for carriers to reach the electrodes.

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