Technological Advancement in Organic Solar Cells–A Critical Analysis

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Abstract—Energy is the basic input for the development of society. The energy demand is on continuous rise all over the world. The non renewable energy sources are not sustainable and also responsible for environmental degradation. The radiations from the Sun are nonexhaustible renewable source of energy which is free from environmental pollution. The fabrication of solar cells has passed through a large number of improvement steps from one generation to another. Silicon based solar cells were the first generation solar cells grown on Si wafers, mainly single crystals. Further development to thin films, dye-sensitized solar cells and organic solar cells enhanced the cell efficiency. Organic Photovoltaic technology is going through a cut throat competition against other 3rd generation technologies. In this article, I have analyzed the organic solar cell in reference to material, working principle, fabrication techniques, cost effectiveness and efficiency. It also includes the fabrication of Tandem Organic Solar cell where two sub cell can compliments each other spectral response thereby increasing absorption of solar radiations and hence the efficiency of solar cell.

Keywords: Renewable Energy, Solar Energy, Organic Solar Cell, Tandem Solar Cell, Efficiency.

1. INTRODUCTION

Access to affordable photovoltaic energy on a large scale is an enormous challenge given that we use hardly 1% of global energy from sun. The action of light in solidified selenium was first studied in the year 1877[1] and then first selenium solar cell was developed by Charles Fritts in the year 1883[2] which had a power conversion efficiency of less than 1%. This research successfully demonstrated the principle of photovoltaic operation. The first modern photovoltaic cell was fabricated from crystalline silicon in Bell Laboratories, with an efficiency of 6% in 1950. Later on inorganic silicon solar cells has been developed whose power conversion efficiency reached to 24.7%. The ongoing research on photovoltaic has boost the performance of conventional inorganic solar cells and power conversion efficiency tends to approach the theoretical limit of 31%. In parallel to it, another type of solar cell based on semiconductors such as GaAs, InP and their alloys has been developed which has high power conversion efficiency in comparison to silicon based solar cell. But high manufacturing cost of these devices make them suitable for some specified applications such as space applications. Cost factor has been considered in development of thin film inorganic solar cells using materials with higher absorption coefficients such as amorphous/microcrystalline silicon and polycrystalline semiconductors. With the demonstration that conductivity is possible in conjugated polymers with controlled doping on it [3], organic solar cells using conjugated polymers has been fabricated. The subsequent development in organic photovoltaic technology by researchers [4, 5, 6, 7, 8] put forwarded promising result in increasing the power conversion efficiency and so far, the highest certified record efficiency in organic photovoltaic is kept by Mitsubishi Chemicals Inc., with a value of 9.2% with very low manufacturing cost in comparison to other photovoltaic technologies. The concept of tandem organic solar cell, in which two sub cell can compliments each other spectral response thereby increasing absorption of solar radiations and hence the efficiency of solar cell is promising and the power conversion efficiency of organic solar cell is expected to be above the commercial levels in near future.

In this article, I have analyzed the organic solar cell in reference to material, working principle, fabrication techniques, cost effectiveness and efficiency. It also includes the fabrication of Tandem Organic Solar cell where two sub cell can compliments each other spectral response thereby increasing absorption of solar radiations and hence the efficiency of solar cell.

2. MOLECULAR SPECTROSCOPY OF CONJUGATE POLYMERS

Conjugated Polymers are characterized by low dielectric constant and alternate single and double bonds between the carbon atoms. In the backbone of the conjugated polymers where each carbon atom binds to three adjacent atoms, leaving an electron free per carbon atom in the p_z orbital results the formation of pi bond along the conjugate polymer backbone. This delocalizes the pi electrons along the length of the polymer. These pi electrons fill up the band and the polymer behave like intrinsic semiconductors. The filled pi band is

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called the highest occupied molecular orbital (HOMO) and the empty pi band is called the lowest unoccupied molecular orbital (LUMO). The pi electrons can be excited from HOMO to LUMO by absorption of light without changing the chemical structure of polymer. This create tightly bound electron- hole pair held together by columbic force, called excitons. The binding energy of these excitons is in the range of 0.3 to 1.0 eV which is in the range of intrinsic semiconductors(Fig. 1).

2.1 Photo-induced absorption (PIA)

Photo induced and transient absorption spectroscopy is a powerful method to monitor the generation and recombination of charges in organic hetero structures. This type of pumpprobe spectroscopy uses a pump beam to excite the semiconductor, while the probe beam monitors the excited state. The probe beam containing the information of the excited state is detected by a photodiode or a photomultiplier after passing a monochromator providing the spectral resolution. In case of the mechanically chopped continuous wave excitation, a Lock In technique is used. From the phaseshift of the Lock In signal one typically obtains the decay time of the recombination. In case of the transient absorption the recombination dynamic is observed more directly by averaging thousands of pulses with an oscilloscope.



Fig. 1 Bulk heterojunctions of donor and acceptor organic semiconductors sandwiched between high work function (ITO) & low work function (Al) electrodes

Fig. 2 demonstrates a typical spectrum observed with this technique. A 50nm thin layer of an oligothiophene derivative (DCV5T) is excited at 514nm. The resulting spectra of the excited state reveals a feature about 1020nm corresponding to the long-living triplet state excitons. In admixture of another organic semiconductor with appropriate energy levels (e.g. NTCDA) electron transfer occurs subsequently after the excitation of the oligothiophene . Therefore, also the triplet state is quenched and new features appear corresponding to radical action of the oligothiophene.



Fig. 3: PIA spectrum of DCV5T and DCV5T:NTCDA (170Hz, 10K)

The decay time of the signal is typically analyzed from the phase shift between the In-Phase (IP) and Out-of-Phase (OP) component of the Lock In signal in dependence of the modulation frequency. In Fig. 2 this is exemplarily given for the triplet state of the oligothiophene discussed above and compared to the charge carriers observed in DCV5T:NTCDA compounds. In assuming a monomolecular (linear) recombination dynamic, the intersection frequency (ω =2 π f) corresponds to the lifetime τ since $\omega \tau = 1$ if IP = OP. The examples in Fig. 3 demonstrate a shift of this intersection frequencies and therefore a cation lifetime of approx. 0.35ms in DCV5T:NCTDA compared to 30 μ s of the triplet reombination.



Fig. 4: Modulation Frequency dependence of the observed excited state transition (OSOL organic solar cells)

3. PRINCIPLE OF OPERATION

When organic semiconductor is irradiated with the sunlight, excitons are formed inside the material. Materials are referred to donor where the excitons are generated and the acceptor to which the electron is transferred in the later stage after dissociation of excitons. The electrons are transferred from the donor material and are delocalized in the acceptor medium which is highly electronegative. The force for separation for electron and hole in the excitons is determined by the energy difference between the LUMO of the donor material and LUMO of the acceptor material. The isolated holes and electrons are then freely delocalized and collected at the anode and cathode respectively. The invention of C₆₀ fullerene and its derivatives as an acceptor play an important role in organic Photo Voltaic because of their high electron-negativity and high electron mobility in the carbon shell [9].



Fig. 5: Operation of Organic Solar Cell

The layers of Organic Solar Cells are presented in Fig. 6. The top layer in the diagram, that is the back electrode, is about 100 nm for the evaporated metals or in the 100s of μ m for the Ag paste. The PEDOT:PSS layer also has a thickness on the order of 100s of μ m. The P3CT/ZnO and ZnO layers are roughly on the order of nm, while the ITO (the front electrode) is on the order of μ m. The glass is 1.1 mm thick.



Fig. 6: Organic Solar Cell (Different Layers)

In organic photo cells, light enter the device through transparent anode which is often glass or mesh conductor such as Indium Tin Oxide (ITO). Above this layer is an interfacial layer of 3,4-ethylenedioxythiophene:poly styrene sulfonate (PEDOT:PSS) whose primary function is to prevent unwanted charge carriers from reaching anode. Due to poor performance and lesser life time of PEDOT: PSS, we use metal oxides for this purpose. Moving further up into the device next is the active layer comprised of an interpenetrating network of donor and acceptor materials. The primary function of active layer is to absorb the light and to form the excitons. These excitons are later dissociated and form free charges which are carried to respective electrode. The top cathode electrode is made up of high work function metals like gold (Au), silver (Ag) or Aluminum (Al).

4. ORGANIC PHOTOVOLTAIC'S FOR CONVERSION OF SOLAR ENERGY IN TO ELECTRICITY

For successful conversion of solar energy in to electricity, one has to optimize the absorption of light and generation of excitons, diffusion of excitons to an active interface, charge separation, charge transport and charge collection. In order to optimize absorption of light and generation of excitons, the absorption spectrum of the organic layer should match the solar emission spectrum and the layer should be sufficiently thick to absorb most of the incident light. The optical absorption coefficient (α) of organic materials is much higher from that of crystalline or multi-crystalline silicon materials. It is found that a 100 nm thick organic layer is sufficient to reduce the intensity of the light to about 1/e times of its original value, whereas, double thickness is required in case of silicon for same absorption. Though increasing the layer thickness is often advantageous for light absorption, charge transport might be reduced because of the limited excitons length which results in a lower the fill factor. Another factor that needs optimization is the excitons transport. To get an efficient organic solar cell, all excitons formed due to incident light should leads to the formation of free charge carriers. To achieve it, all excitons have to reach the photo active interface between the donor and acceptor with in exponential life time of excitons (Texc) which is the product of reciprocal values of all radiative and non-radiative decay rates together. The distance travelled by the excitons in photoactive medium depends on the diffusion coefficient (Dexc) and exponential life time of the excitons as:

$$L_{\text{exc}} = \left[D_{\text{exc}} \cdot T_{\text{exc}} \right]^{1/2} \tag{1}$$

Since T_{exc} is limited to only several nanoseconds at most and so L_{exc} is also generally limited to about 10 nm. It means the excitons which are formed at a distance within 10 nm will contribute to charge separation. This problem was overcome by increasing the D_{exc} or to make the interfacial area much larger, so that each generated excitons is always close to an interface. This leads to completely different cell designs called

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Bulk hetero-junction Polycrystalline Solar cell.. Charge transport mechanism plays a significant role in optimizing the efficiency of organic solar cell. In organic solar cell, after the charge transfer, the electrons and holes are in close proximity due to columbic force of attraction. So there is a large chemical potential gradient that derives the charge carriers away from the excitons dissociating interface. These chemical potential is generally achieved by selecting the electrodes with maximum difference in work function. Once these charge carriers are delocalized from the interface, they can move along their respective medium and tends to reach their respective electrodes. In the path, they can encounter with opposite charge and may again bind together to form triple excitons, singlet excitons and charge transfer states. This recombination process is called bimolecular recombination and is a major loss process in PSC. This loss process can be minimized by forming a regular interpenetrating network of donor and acceptor molecules in the active medium of Polymer Solar Cells..

5. FABRICATION TECHNIQUES

The commonly used fabrication techniques for organic solar cells are as follows:

Organic materials are dissolved in a polar or non-polar solvent in all wet solution based techniques for the fabrication of active region of solar cell. Except some new methods where solutions are processed with polymerization reaction during the film fabrication with techniques like electrochemical polymerization or post fabrication techniques via heat treatment during the film forming process. If the resulting polymer film after fabrication is non-soluble then it is favorable for depositing another film over the previous one. If polymers or polymer molecule blends are directly processed from solution, techniques like spin coating, inkjet printing, screen printing, etc. are applied.

An idealized fabrication procedure is presented here. The ZnO was received in solution with chlorobenzene at a concentration of 175 mg/ml, so chlorobenzene was added to dilute it to a concentration of 50 mg/ml. Then the polymer, which was received in powdered form, was mixed with the ZnO solution and chlorobenzene to achieve concentrations of 50 mg/ml with respect to ZnO and 25 mg/ml with respect to P3MHOCT. This was subsequently stirred by a magnetic stir bar in a closed bottle for 6 hours then filtered through a Teflon syringe filter with .45 um pores. With these two solutions prepared the layers of the cell (see Fig. 6) can be spun. After first wiping the slide with chlorobenzene or spinning on a little IPA to clean it, a layer of the ZnO is spun on at 1000 RPM. Next a cotton swap wetted with chlorobenzene is used to wipe away the ZnO from everywhere except where the cell area is being defined. Then it is placed on a 310°C hotplate for 5 minutes to make the film insoluble. Following that, the polymer solution is spun on at 1000 RPM and wiped away in a similar pattern. The slide is again placed on the hotplate, this time at 210°C

for 5 minutes. Next comes a layer of PEDOT spun on at 2800 RPM, wiped, and dried at 120°C on the hotplate for 10 minutes[10].

6. TANDEM ORGANIC SOLAR CELL

The single p-i-n devices feature good device characteristics with high fill factor and high internal quantum efficiencies (IQE). However, to achieve high power efficiencies both IQE and the total absorption need to be high. The single p-i-n cells suffer from too low absorption in two respects: At first, the absorption spectra of the photoactive layers do not cover the complete range of the sun spectrum. Secondly, the photoactive layers have to be thin enough to avoid recombination losses and space charge limitation of the current flow. Therefore, they are optically thin even at the absorption maxima.

An approach to overcome these problems is to stack several junctions with either identical or complementary absorption spectra on top of each other. The open circuit voltage (VOC) is then given by the sum of the open circuit voltages of the individual cells. The flow of photocurrent in stacked junction cells requires easy recombination of charge carriers with low energetic losses at the interface between the individual cells.



Fig. 7: Tandem Organic solar cell with two junctions.





In stacked cells the control of thin film optics is essential: In our approach we use the basic p-i-n cell, explained in the previous sections, as an optimized building block that can be introduced into a final stacked solar cell structure. The advantage is that we do have spacer layers between each photoactive layer sequence, namely the doped wide-gap transport layers. We can thus place the photoactive layers of each single cell at the position of maximum optical field strength. Due to the doping, the thickness of the transport layers can be varied in a wide range without losses due to series resistances, allowing to realize nearly every required device configuration. [11]

An inverted tandem organic solar cell, consisting of two bulk heterojunction subcells with identical poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61 active layer, and an intermediate layer made of ultrathin multiple metal layers of Ca/Al/Ag and metal oxide MoO3, is reported. This intermediate layer is of advantage in high transparency and low series resistance. Moreover, it serves as the charge recombination center effectively, and renders an exact summation of the open-circuit voltages (1.18 V) of the two subcells and a high fill factor (61.8%). The maximum power conversion efficiency obtained is 2.78% under simulated 100 mW/cm2 [air mass (AM) 1.5G] solar irradiation, comparable to those of the two subcells.

7. POWER CONVERSION EFFICIENCY OF ORGANIC SOLAR CELL

In late 1950s, Kallmann and Pope[12] fabricated the first organic photovoltaic device using the conjugated molecule anthracene with a power conversion efficiency of very much less than 0.1%. In the 1980s, Tang [13] fabricated the first organic hetero-junction solar cell with a bi-layer hetero structure of the electron donor and acceptor materials yielding a power conversion efficiency of about 1%. Subsequently, the first polymer based solar cell was fabricated by Marks et al.[14] in the early 1990s. A major breakthrough in the history of organic solar cell was the introduction of bulk heterojunction solar cells by Halls et al.[15] who employed an MEH-PPV/CN-PPV polymer/polymer blend and by Yu et al.,[16] who employed an MEH-PPV/C60 blend and observed a significant improvement in power conversion efficiency as compared to bi-layer hetero-junction solar cells. However in the period 1995 to 2004, the power conversion efficiency of organic solar cells remains below 3%. The intensive research in this field and application of semi crystalline hole transporting polymers P3HT led to polymer/fullerene solar cells with an efficiency of about 5%. Heliatek, Germany reported a record 12% power conversion efficiency of organic solar cells. The evolution of power conversion efficiency of organic solar cells are shown in Fig. 9 and 10.[17,18]The present results are linked to the local testing procedure and so irreproducible and are in need of common testing procedures and protocols that can allow more harmonized procedures and can deliver reproducible results.



Fig. 9: Evolution of the power conversion Efficiency of Organic Solar Cell..



Fig. 10: Enhancement in Power conversion efficiency with time.

8. APPLICATIONS

Applications for organic solar cell are summarized in mainly niche application form where life time span of 3 -5 years is good enough [19]. Organic solar cells can be printed atop flexible and transparent PET substrate. This type of solar panel can be folded and carried along for charging electronics devices such as laptops, phones, cell phones and MP3 players. It can be integrated with cloths, backpack and on the tents. This makes them useful to generate electricity and supply power to military equipment such as night vision scopes and Global Positioning System receivers.



Fig. 8: Flexibility of Organic Solar Cells



Fig. 9: Organic Solar Cells in use.

9. SUMMARY/CONCLUSION

In this paper, I have analyzed the organic solar cell in reference to material, working principle, fabrication techniques, cost effectiveness and efficiency. It also includes the fabrication of Tandem Organic Solar cell where two sub cell can compliments each other spectral response thereby increasing absorption of solar radiations and hence the efficiency of solar cell. It can be seen that organic photovoltaic have the potential to be part of the world's solution to the future of energy, but still face many challenges. They have the promise of being a cheaper alternative to inorganic solar cells, but must increase in efficiency and improve operating stability before they will become widely used. The fundamental mechanism behind the photovoltaic effect in organic heterojunctions is now understood. The key to future improvements in this field lies in better understanding the materials involved and their structures.

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