Abstract

In this dissertation organic thin films were prepared and studied. These films were used for the fabrication of Organic Photovoltaics (OPVs). The main study was focused on the photoactive layer which consists of a blend of two organic semiconductors. Much attention was given to the study of the photoactive layer morphology which defines the generation, transport and collection of charges from the electrodes, parameters which define also OPV Power Conversion Efficiency (PCE).

As a photoactive layer the blend polythiophene:fullerene was mainly used. Firstly the effect of solvent in which the blend components are dissolved on thin film morphology was studied. When high boiling point solvents were used such as chlorobenzene it was found that during the slow drying process the blend molecules have the time possibility to arrange into a more favorable thermodynamic semicrystalline state. This process was enhanced by post deposition thermal annealing during which a vertical phase separation between the blend components took place. The percentage of the lower free energy component (P3HT) increased at the film surface, while the higher free energy component (PCBM) accumulated near the bottom electrode. This vertical phase separation after thermal annealing results in a morphology which is not appropriate for charge collection in conventional BHJ solar cells.

Then micorphase separation which can take place in P3HT:PCBM thin films with PCBM crystallization was studied. The study of the structural and nanomechanical properties of thin films showed that the thermal annealing can increase the crystal size of PCBM up to several microns depending on temperature.

The development of P3HT:PCBM thin films from a low boiling point solvent (chloroform) was investigated. In this case during the deposition process by spin coating the polymeric mixture is frozen into a disordered state similar to that of solution. This amorphous and well mixed structure is unsuitable for the generation and transport of charges due to inadequate separation of the two components. However this initial state of good mixing permitted the better morphology control of films morphology during subsequent thermal annealing which resulted in controlled crystallization of the polymer and at the same time it’s separation from PCBM. Ellipsometry measurements performed on blends onto which very thin aluminum films (5nm) were deposited showed that the vertical phase separation can be reversed if annealing is applied after the metal cathode deposition. After the optimization of annealing conditions (time and temperature) the devices showed excellent electrical

characteristics with high short circuit current densities (10-11 mA/cm^2), high fill factors (~58 %) and PCE values up to 3,75 %.

The effect of the hole transport layer, (HTL) PEDOT:PSS physical properties on the P3HT:PCBM morphology and its influence on the performance of solar cells was investigated. A clear correlation between the surface free energy of the HTL substrate and the vertical composition profile within the active layer was established. The P3HT surface enrichment and PCBM segregation at the bottom interface, were promoted when the BHJ was deposited onto more hydrophilic PEDOT:PSS substrates. Decreasing the surface free energy of the HTL was found an effective way to avoid the PCBM segregation at the active/HTL interface. Moreover the increase of the HTLs conductivity resulted in significant reduction in device series resistance which improved Fill Factor and PCE.

Then new semiconducting materials such as fullerene derivatives acting as electron acceptors and polycarbazole derivatives acting electron donors were tested. The system P3HT:ICBA gave higher PCE (up 4,30 %) due to the higher LUMO energy lever of ICBA. Moreover electron donors PCDTBT:PC70BM and Si-PCPDTBT:PC70Bm were combined with electron acceptor PC70BM. The higher PCE obtained was 3.1 % without any thermal treatment which deteriorated device electrical characteristic when it was applied.

Finally the probability of the use of conducting polymer PEDOT:PSS as an electrode in replacement of the inorganic Indium tin oxide (ITO) was tested. For this purpose PEDOT:PSS PH1000 formulation was modified by the addition of DMSO solvent which increased thin film conductivity up to 862 S/cm. Devices fabricated with these films exhibited good electrical characteristics in comparison with the reference device (with ITO) with main characteristics the increased series resistance and lower short circuit current.

In conclusion, in the present dissertation the effect of experimental parameters such as the solvent and the conditions of thermal annealing on the morphology and structure of various polymer-fullerene systems was studied. At the same time functional OPVs were fabricated and studied. The correlation of thin films morphology with the device electrical response resulted to the fabrication of OPVs with high PCE.