Abstract

In this research thesis, the properties of thin films of inorganic and hybrid barrier materials, of electron donor and electron materials and their blends were studied and evaluated. The optical properties, the growth mechanism, the glass transition temperatures of the hybrid polymers and the morphology of the donor:acceptor blends were studied by Spectroscopic Ellipsometry (SE). The study of the surface nanotopography was performed by atomic force microscopy (AFM). The evaluation of the surface free energy was studied by a contact angle meter. Finally, the barrier properties were evaluated by the calcium test and the MOCON device for the water and oxygen permeability respectively. The main results of this thesis can be summarized as follows:

In the case of the inorganic barrier (SiOx, AlOx) in-situ and real time SE were applied for the study of their growth mechanism onto different flexible substrates. Their barrier properties were also measured and compared with the theoretical ones in order to evaluate the quality of the barrier films and to investigate the factors affecting the barrier response. The results showed that the growth mechanism as well as the barrier of the thin films were affected by the chemical structure of the substrates and the nanotopography. The selected inorganic barrier materials are thin films of $SiO_{x(x \rightarrow 1.7)}$ and AlO_x that grow onto flexible substrates with low surface roughness.

Concerning the hybrid barrier films ($ORMOCER^{®}{}_{S}$) the effect of the chemical composition, the addition of nanoparticles and the growth conditions on the optical and barrier properties were studied. Regarding the chemical composition of the hybrid barrier materials the results showed that the amount of the solid content affected their properties. As a consequence the hybrid barrier material/inorganic barrier material/flexible substrate selected the for the development of the barrier system is the SiO_x as inorganic barrier material in combination with a hybrid barrier material with lower solid content (F33, F38). Furthermore, the study of the addition of silicon dioxide nanoparticles (SiO_2-NPs) showed that the addition of low range of SiO_2-NPs (1-5%) in the hybrid barrier material F38 induced the improvement of the barrier response. The barrier properties are also affected by the printing conditions such as the printing speed (curing time) and the drying/curing temperature. In overall, the results show that the value of the refractive index of the barrier material, which is related to the material density, is the factor for the evaluation of the barrier properties. This is attributed to the fact that in all cases the higher values of the refractive index lead to the improvement of the barrier properties. Finally, the in-situ and real-time SE were used to determine the glass transition temperature of the hybrid barrier material F38 which was found to be equal with 122^{o}C.

Afterwards, thin films of organic semiconductors were developed to be used as electron donors and electron acceptor and their properties were studied in order to select the most promising materials for OPVs. The effect of thermal annealing in the properties of the P3HT thin films was evaluated. The results showed that the thermal annealing leads to the decrease of the energy gap value and to the increase of the optical

absorption. This behavior is attributed to the increased crystallinity and p-conjugation length of the thin films.

Subsequently materials exhibiting lower band gap than P3HT as C-PCPDTBT and Si-PCPDTBT were evaluated. From the comparison of properties of C-PCPDTBT and Si-PCPDTBT it was concluded that small modification in the chemical structure of the polymer could lead to materials with improved properties. In more detail the replacement of the carbon atom by silicon atom in the position 5 of the cyclo-pentadithiophene lead to a material that show stronger absorption in visible, higher crystallinity and improved mobility. Furthermore, from the synthesis of statistical copolymers of C-PCPDTBT with F8BT we can conclude that the increase in the content of F8BT leads to an increase of ω_g and to lower mobility, making the material insufficient to be used as a donor in OPVs. The results showed that the materials selected as electron donors for the development of OPVs are the P3HT $\mu_h = 5\cdot10^{-2}cm^2/Vs$) due to the high mobility and the C-PCPDTBT and Si-PCPDTBT due to low band gap value ω_g (1.37eV) and the good mobility ($\mu_h = 5\cdot10^{-3}cm^2/Vs$ και $1\cdot10^{-2}cm^2/Vs$ respectively).

In the last section of the thesis, the factors that affect the optical response and the morphology of the donor:acceptor blends were studied. In order to achieve this study the suitable ellipsometric model for the study of the optical properties and the vertical phase separation of the blend constituents was developed. The results can be correlated with the PCE of the OPV, since this depending strongly on the blend morphology and the optical response. From the application of the ellipsometric model in P3HT: PCBM and PCPDTBT: PCBM blends it was found that many factors affect the optical response and the blend morphology. Such factors are the thermal annealing duration and temperature. The increase of these parameters results in increased absorption of the blend. Moreover, the thermal annealing promotes the vertical phase separation of the blend and the enrichment of the top regions of the film with the P3HT constituent, whereas the PCBM molecules are segregated towards the bottom parts of the blend film. The morphology of the blend is also affected by the value of the surface free energy of the substrate. In more detail the use of low surface free energy substrates lead to the uniform vertical distribution of the blend constituents. Also, the blend morphology is affected by the thickness of the photoactive blend. Specifically the results showed that the decrease of the film thickness induced to a blend exhibited a donor rich top surface. This morphology affects the performance of the OPV since the PCE increased by increasing the thickness of the photoactive blend.

In conclusion, in this thesis thin films of inorganic, hybrid and organic materials were developed and evaluated in order to select the most suitable materials for OPV applications.