

SUMMARY

The desired deliverable of the project was to produce a solar cell device based on small molecules for which the impact of the interfacial ordering can be understood and the efficiency can be modified by changes to that ordering. Over the course of the fellowship project, we have managed to produce a workhorse device structure, modify the interfacial structure and control the device performance, giving us insights into how engineering of those interfaces can be used in the next generation photovoltaic devices. Thus, we consider this project a success.

Heterojunctions are inherent in and crucial to the efficiency of organic microelectronic devices. Specifically, the structure of the interface between the inorganic electrodes and the organic active layer plays a significant role in the performance of organic photovoltaics. In this project, we produced photovoltaic cells from low molecular weight organic molecules, where the efficiency could be tuned by modification of the structure of the interfacial layer. Using atomic force microscopy, Kelvin probe force microscopy, X-ray diffraction and transmission electron microscopy, we examined the growth and dispersion of LiF, a commonly used dielectric material, on the highly ordered organic thin films we used for device manufacture. For LiF thin films grown on inorganic substrates, the structural, morphological, and optical properties are strongly dependent on the main deposition parameters including the type of substrate, temperature during growth, total film thickness, deposition rate and evaporation geometry. The problem of examining the structure of a thin LiF overlayer is not trivial, as the complex morphology of the underlying organic molecules makes it very difficult to determine the structure of the overlayer. On such rough substrates, it is difficult to definitively assign observed topographic features to a specific component. To help understand these complex systems, we developed a technique, based on the separation of features in reciprocal space (Fourier subtraction), to deconvolute a heterojunction surface into two real space images. This technique allows us to separate the impact of the underlying roughness to quantify, for the first time, the real texture parameters of the overlayer of interest (e.g. LiF).

Though thickness, as measured by a quartz crystal microbalance (QCM), is often given as a measure of the amount of LiF at the interface, we have confirmed that on both electron acceptors and donors, LiF forms nano-sized (~5-10nm) single crystalline islands. As the QCM measured deposition thickness increases, the average island height stays the same ($\Delta=1\text{\AA}$) but the number of LiF islands increases. At around 1nm, full coverage of the surface is observed. For solar cell devices, the power conversion efficiency as a function of the deposited "thickness" is observed to have a window of performance enhancement when coverage is less than 70% (6\AA). Once a complete layer has been formed on the surface ($\sim 9\text{\AA}$), device performance deteriorates below even that of bare Al. Performance enhancement can be attributed to the formation of an electrical passivation layer at low coverage, ensuring an Ohmic contact; once the layer is full, charge carriers can no longer tunnel through the barrier, and the interface becomes insulating. For the useable range of LiF in devices, therefore, it is more appropriate to discuss the LiF as a function of the coverage, rather than the thickness.

The lattice constants for the crystalline organic films are much larger than those of LiF, making epitaxial growth unlikely on these organic surfaces. However, we have observed that the LiF islands are highly textured on the large flat terraces of organic films. This $\langle 100 \rangle$ texture is completely different from the reported texture for LiF films on amorphous surfaces. We have confirmed that on both inorganic and organic films, the texture of the LiF crystallites can be tuned using the surface roughness, from the $\langle 100 \rangle$ texture on ultra-flat (RMS $\sim 1\text{\AA}$) to the $\langle 16\ 9\ 7 \rangle$ ($\langle 111 \rangle$ type) texture expected on amorphous films (RMS $\sim 20\text{nm}$). In organic devices, this texture modification is likely to affect the interface dipole leading to a tunable device performance.

As LiF forms nanoscale islands on the surface, the dispersion can also be used to tune the device performance. We have developed two methods of dispersing nanoscale LiF islands on surfaces. In the first method, we can force the LiF islands to segregate to grain boundaries in the organic film, by

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decreasing the deposition rate. This has been observed to have two major effects on the organic films and devices. Firstly, the segregation of LiF to grain boundaries helps to prevent the dewetting of the molecules from the surface of ITO, a common transparent electrode used as a substrate for most organic devices. Though this stabilization effect had been previously observed for other organic molecules, we were able to confirm that the dewetting mechanism for diindenoperylene can be related to this pinning of the grain boundaries. Secondly, we observed that the device efficiency decreases as the LiF segregates to the grain boundaries. This effect is a result of a decrease in the short circuit current, indicating that the grain boundaries are playing a major role in the transport of carriers in the device.

A second approach to controlling the dispersion of LiF on the surface is to produce a 2D nanoparticle array using polymeric micelle reactors, rather than by thermal evaporation. Scanning Kelvin probe analysis of crystalline LiF nanoislands (20nm) produced in this way revealed a coverage dependent increase in the surface work function of a substrate. These findings indicate that sol-LiF may be a tunable electrode alternative for organic solar cells.

In order to examine the impact of LiF on the structure of organic photovoltaic devices, we first had to produce both single carrier and heterojunction devices from ordered organic molecules. For diode device structures, the vertical transport of charge carriers across the device is expected to dominate the performance. In the planar organic molecule of interest in this study, the π -stacking direction is normal to the main body of the molecule, such that charge transport is highly anisotropic and related to the orientation of the molecules relative to the substrate. By using ultraflat (RMS <1nm) ITO, we have confirmed with AFM and X-ray scattering (reflectivity and grazing incidence X-ray diffraction) that diindenoperylene (DIP), an electron donating photoactive molecule, and PTCDI-C8, an electron acceptor, form large crystalline domains consisting of tilted, upright standing molecules. Similarly to that observed on SiO₂ substrates, the domain size can be tuned by adjusting the substrate temperature during growth. However, we discovered that the low roughness substrates, though ideal for growing thin films, are not optimal for devices. We have attributed this to poor injection/extraction at the bare surface, due to the anisotropic nature of the molecules. This has limited slightly the maximum device efficiency that was achievable during the course of the project. To counteract these effects, we have employed an interlayer between the active layers and the substrate. In addition to PEDOT:PSS, which is widely used, we have discovered some promising candidates for self-assembled monolayers that induce different structures of the molecules at the interface, which have allowed us to produce diodes with higher operational efficiency.

In the course of the project, we examined 4 different combinations of molecules, both as sequential planar heterojunctions and as co-evaporated bulk heterojunctions. At the start of this project, the attempted combinations were not being widely used for photovoltaics, though there were indications that they might be effective. Our first working devices showed efficiencies of around 10⁻⁵%, too low to adequately investigate the impact of the LiF interlayer. After some processing optimization, we have been able to produce devices with efficiencies as high as 1.4%, which is very close to our goal of 2% efficiency devices, given the limitations due to the substrate (see above paragraph). Though more optimization to improve the efficiency may be possible, it is beyond the scope of this project; therefore, we determined that the combination of DIP and fullerenes with sequential evaporation produces diodes that can act as the workhorse for examination of the impact of the LiF. The controllable island size of DIP with substrate temperature allowed us to engineer the donor-acceptor interface, to produce a natural "bulk heterojunction." Such a configuration allowed us to have both highly crystalline thin films, and a long exciton dissociating interface, overcoming both the exciton diffusion bottleneck and the charge transport bottleneck that can limit device performance.