Role of LiF nanoparticle interlayer dispersion in degradation stability of OLEDs and OPVs

F. Maye,[1] L. Kojovic[2], L. S. Hui[2], K. Liang[2], G. Hanta, J. Heidkamp,[1] M. Bumstead[2], A. Turak,[1,2]
[1]: Department of Low Dimensional and Metastable Materials, Max-Planck-Institute for Intelligent Systems (formerly MPI for Metals Research), Stuttgart, 70569, Germany,
[2]: Department of Engineering Physics, McMaster University, Hamilton, Ontario L8S 4L7, Canada
*Corresponding author: turaka@mcmaster.ca

Abstract — **Using AFM, XRD, XPS, and TEM, we have examined the growth of LiF on highly ordered organic thin films. We were able to confirm that LiF universally forms nano-sized (~3-5nm) single crystalline islands. The island density increases until full coverage is reached at around 1.5nm. Applying a variety of spatial statistics analyses, we examine the relationship between the evolution of the distribution of particles and organic device performance and stability. Below a critical thickness, the nanoparticle films boost efficiency; improve device shelf life and prevent dewetting. The trade-off between device stability and performance limits the use of LiF interlayers to sub-monolayer films.**

Keywords—LiF nanoparticles; spatial dispersions; disLocate; dewetting; shelf-life; organic electronics

Though many different materials have been used as electrode interlayers in both OLEDs and OPVs, it has proven difficult to completely replace the most commonly used interlayer, LiF, due to its extremely high performance in both OLEDs and OPVs. The role of LiF in organic devices has been widely studied. For Al electrodes, LiF improves both performance and stability for OLEDs and OPVs. However, this improvement is not universal; some metal cathodes, such as Mg, show significant degradation of device properties with the introduction of a LiF interlayer.[1]

To further understand the role of LiF, we have examined in detail the growth of LiF on a variety of organic molecules, as well as with a number of metal electrode materials. All of the examined planar molecules form large crystalline islands with lateral size ranging from 0.1-1µm. Deposition of LiF on top of these flat surfaces (see fig. 1) leads to the formation of disconnected islands, for calibrated nominal LiF thickness of 0.3-0.5nm. We were able to confirm that this behaviour at low deposition thicknesses is universal, showing similar nanoparticle structures on inorganic surfaces, and on rough amorphous organic films. As the QCM measured deposition thickness increases, the average island height stays the same (Δ=0.1nm) but the number of LiF islands increases (Δ=116%), as seen in figure 1 for LiF growth on DIP. We see complete coverage, with the formation of a closed LiF layer, at nominal thicknesses of around 2nm.

These disconnected islands have three major effects in organic devices. Firstly, below a critical coverage, they improve device performance. In small molecule planar heterojunction solar cells, introduction of LiF initially improves high open circuit voltages and prevents the formation of s-shape JV characteristics. Small amounts of LiF are sufficient to establish an ohmic contact and to prevent diffusion of Al. However, as the thickness increases, the s-shape kink sets in again, accompanied by a decrease in the Voc and power conversion efficiency. As the number density of LiF islands increases, the LiF is no longer concentrated at defect sites, where it can prevent Al diffusion and exciton quenching, it also covers areas of high mobility, leading to a decreased device performance. With greater deposition, the LiF layer eventually closes, and the device efficiency and Voc are even worse than the pristine device.

The second major impact is that they improve the shelf life of the device. To isolate the effect of the interlayer, we focused on symmetric Al/LiF/C_{60}/LiF/Al diodes. As C_{60} is highly susceptible to oxidation, such devices decay quickly,[2] with t_{10}<10mins for Al electrodes. As seen in the inset to figure 2a, 0.5nm LiF is sufficient to increase t_{80} to 60mins. However, a 0.5nm LiF provides only limited protection for the Al cathode,[3] and the device does not last more than one day. A slightly thicker layer improves the shelf time by nearly a factor of three, reflective of the noticeable passivation of the Al surface with 1nm of LiF.[3] Above 2nm, the shelf time becomes independent of the LiF thickness, in keeping with the finding that complete coverage of the interface with LiF has occurred at around 2nm.

The continued exponential decay of the devices after the initial loss due to interfacial oxidation occurs with a thickness independent rate, suggesting reversible degradation of the C_{60} layer with oxygen doping; this is supported by the complete recovery of tunnel diode characteristics by vacuum annealing for 24h.[2]

Extremely thick films (20nm) of LiF[1,4] completely block oxygen penetration to the organic layer; thinner layers show evidence of chemisorbed O and Al throughout the interlayer thickness.[1] The nanoporous nature of the ultrathin LiF layers, as an agglomeration of evaporated LiF nanoparticles, aids in trapping oxidized Al ions away within the interlayer. Therefore, the LiF interlayer encourages conduction by both scavenging oxygen within the LiF layer and preventing oxidation at the critical injection region.

The final critical effect of the nanoparticle islands is to prevent dewetting of the organic films. Morphological instability has been linked to device failures in a number of small molecule systems.[5,6] To examine this effect, we used highly metastable films of diindenoperylene.[7] Thin films of this molecule initially grow layer by layer in seemingly continuous films, but the mismatch in surface energy with oxide surfaces, such as ITO, tend to strong columnar growth with mild thermal treatments or long term storage.[5,8] This can be counteracted with LiF nanoparticle decoration at the defect sites, which stabilize the films against ripening (see figure 3).

Thermal evaporation of LiF initially forms disconnected 5nm nanoparticle, that eventually coalesce into a full coverage film around 2nm as measured by QCM. Though a complete film does improve shelf life, the device performance decays rapidly above a nominal coverage of nanoparticles. An optimal thickness of ~1nm corresponds to the best trade-off between improved performance and enhanced stability.

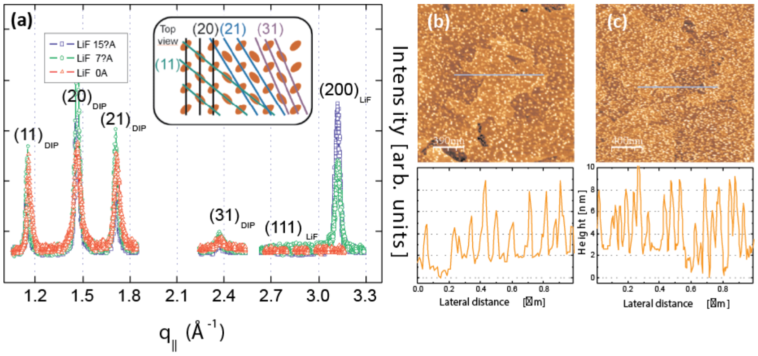

Figure 1 Thickness dependent LiF deposition on top of planar ML by ML grown DIP for (b) low coverage (~0. 7nm) and (c) high coverage (~1.5nm). GIXRD data (a) supports the formation of crystalline nanoparticles on organic molecules.

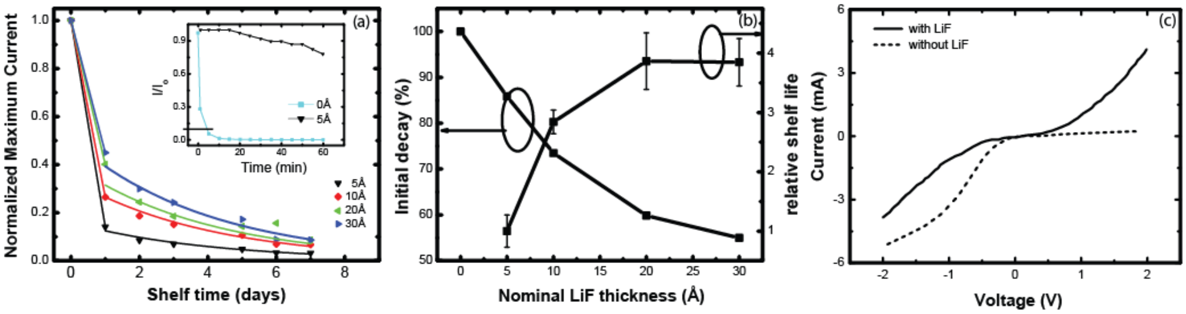

Figure 2 (a) (a) Shelf lifedecay curves for C_{60} based OLED devices with Al/LiF cathodes of varying LiF thickness. After one day of exposure to ambient, the device performance decays exponentially, with the same decay constant, as shown by the solid lines. Inset shows the decay curve during operation for electrode/C_{60}/eletrode diodes with Al and Al/0.5nm LiF electrodes. (b) The loss of performance after one day, and the shelf life (t_{10}) relative to the 0.5nm LiF interlayer, as a function of LiF thickness for C60 based OLED devices with Al/xLiF cathodes. The lines are a guide to the eye. (c) I–V characteristics of electrode/C_{60}/electrode sandwich diodes after exposure to air for 1 h followed by baking in vacuum for 24 h.

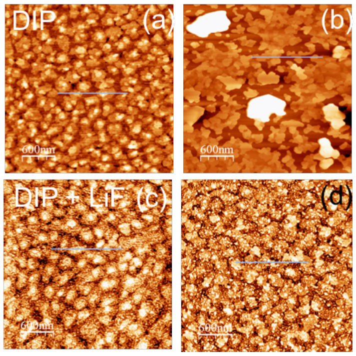

Figure 3 Stability of diindenoperylene film (a) decorated with 0.5nm deposition of LiF nanoparticles (c) as deposited and after exposure to 90°C dry air for 18 hr (b,d).

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