Catching the sources of organic LED degradation in action

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Synchrotron-based techniques can reveal the mechanisms behind the dark spot formation of organic light-emitting devices.

Though great improvements have been made in recent years, organic light emitting diodes (OLEDs) still have limited lifetimes. In general, the degradation of OLEDs manifests itself as a decrease in device luminance with time. Three distinct modes of deterioration have been recognized: dark spot generation, catastrophic failure, and intrinsic degradation.\(^1\) In the first mode, non emissive regions appear on the emitting surface. Catastrophic failure occurs when electrical shorts cause large leakage currents. In the third mode, changes in the organic material properties cause long-term decreases in the emissive area brightness.

So far, methods for investigating these phenomena have involved chemical and physical techniques, like high-performance liquid chromatography and nuclear magnetic resonance.\(^2\) These methods typically destroy the device under investigation in order to extract the byproducts of the degradation. Often, using solvents to extract each chemical specie for analysis requires chemical modification.

Using synchrotron radiation-based surface techniques, we have developed a new way to investigate dark spot formation. This approach can be applied to any multilayered structures, such as OLEDs. This analysis method enables physical and chemical investigations of real devices, in some cases, even when they are operating. Moreover, synchrotrons offer surface-sensitive techniques to characterize the topmost molecules, without damaging the underlying layers.

We applied a typical surface science approach to determine the properties of a thin-film multilayer structure, similar to a small molecule-based OLED. Because it is possible to tune the impinging beam photon energy on the sample, synchrotron radiation can increase the chemical sensitivity of techniques like x-ray photoemission spectroscopy, x-ray absorption near-edge spectroscopy, x-ray transmission, and x-ray fluorescence.

Another advantage is the ability to focus the beam to obtain spatially resolved chemical maps of the surface. However, synchrotron-based methods have extremely high photon flux that could electrically charge or damage the organic layer. Therefore, the success of the study relies heavily on choosing the right investigation technique.

We used soft x-ray scanning photoemission microscopy to investigate the problem of dark spot formation. We focused the x-ray beam with a spatial resolution of approximately 100nm on a working OLED aluminum cathode. The cathode operated in an ultrahigh vacuum. In addition, we recorded the chemical map of...
the original cathode, tuning the electron analyzer to distinguish the different chemical species present on the cathode surface. We captured the degradation of the device in action, revealing the explosion of bubble-like defects on the cathode surface. The chemical map highlighted the presence of significant amounts of indium from the disruption of the indium tin oxide (ITO) anode.

Figure 1 shows a photoemission image acquired by collecting the In3d signal around an exploded bubble. The strong signal from the center of the damaged region comes from the ITO film. It reveals the complete removal of the organic layers. The intensity increase near the crater is due to the transport of indium from the substrate to the aluminum cathode. We used this technique to investigate the essential contribution of the ITO anode morphology and chemistry on dark spot formation.3–5

The current approach allowed us to investigate dark spot formation. Next, we plan to study intrinsic OLED degradation using synchrotron radiation. We will analyze the chemical changes that can occur in aged OLED devices using infrared spectromicroscopy and x-ray transmission spectromicroscopy. These techniques will enable us to get images sensitive to chemical bonds, and to determine the chemical fingerprint and distribution of organic materials in a complete multilayered device. We may also study organic layer morphology in operating devices.

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