

Depth profiling organic light-emitting devices by gas-cluster ion beam sputtering and X-ray photoelectron spectroscopy



Nicholas C. Erickson^a, Sankar N. Raman^b, John S. Hammond^b, Russell J. Holmes^{c,*}

^a Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, MN 55455, United States

^b Physical Electronics, 18725 Lake Drive East, Chanhassen, MN 55317, United States

^c Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

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ABSTRACT

The composition depth profile in organic light-emitting devices (OLEDs) is investigated using X-ray photoelectron spectroscopy (XPS) coupled with gas-cluster Ar-ion beam milling (Ar-GCIB). The XPS technique gives precise information about the surface chemistry of the organic thin films and is capable of differentiating the various charge transport, host and guest materials used in an OLED. The use of large Ar ion clusters (~1500–2500 atoms/cluster) in the milling process allows for small amounts of the organic thin film to be sputtered away without contaminating the surface or damaging the underlying material chemistry. By probing OLEDs as a function of depth, key parameters including emissive layer composition and interface quality can be assessed directly. It is found that the depth profile for graded-composition emissive layer OLEDs closely matches the intended deposition profiles, maintaining both the composition gradient and the intended endpoint compositions. The ability to resolve and correlate subtle changes in film composition to variations in device performance will help inform efforts in device design, while also serving as a diagnostic tool to better understand the mechanisms for device degradation and failure.

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1. Introduction

Highly efficient organic light-emitting devices (OLEDs) often contain layers which are comprised of multiple materials with different functionalities. These composite layers may be used for improved charge transport [1–3] or, are often employed in the emissive layer (EML) of a device. In the EML, a dilute emissive guest molecule is often doped into a host material, as in a double-emissive layer, or in multiple host materials, as in a uniformly mixed-emissive layer (M-EML) [4–7]. The overall composition and spatial composition profile of these layers have proven difficult to probe, [8–10] as the thin films are

typically mechanically soft and the various molecular species often contain only carbon, hydrogen, and nitrogen [11]. The performance of a composite EML has been shown to be strongly dependent on the mixing ratio and spatial distribution of the constituent materials. This is especially true for M-EML OLEDs, where the mixing ratio of hole- and electron-transport material (HTM and ETM, respectively) significantly impacts device efficiency [12–16]. More recently, devices employing a graded-emissive layer (G-EML) architecture, where the EML is comprised of a continuously varying composition of HTM, ETM, and emissive guest, have demonstrated high efficiency in single-layer devices [17,18]. Devices based on a G-EML show a strong dependence of performance on the exact composition profile, and optimized blue light-emitting structures have been demonstrated with profiles that contain relatively large amounts of ETM [19].

* Corresponding author.

E-mail address: rholmes@umn.edu (R.J. Holmes).

Typically, devices with composite layers are fabricated via vacuum thermal co-evaporation. While this fabrication technique allows for careful control over the relative deposition rates of the constituent materials, the spatial composition of these films has proven difficult to examine post-deposition. Given the demonstrated connection between film composition and device performance, there is strong interest in developing techniques to accurately probe the exact post-deposition composition profile. Characterization of the depth profile requires a means to determine both the identity and quantity of chemical species present at the surface of the film (or within a very shallow volume near the surface), so that exact ratios of the constituent materials may be determined. Additionally, a process to remove thin, uniform layers of material is required. This process must not damage the underlying layers nor chemically interact with the exposed surface.

Until recently, the sputtering of organic thin films has focused on the use of C_{60}^+ ion beams to remove layers of material [10,20]. Though this method has shown some positive results, it is not applicable to many organic systems where the deposition of amorphous carbon and chemical interactions at the surface render analysis of the underlying layers impossible. Promising results, however, have been obtained using large-clusters of Ar^+ ions as the primary beam in gas-cluster ion beam (GCIB) milling with time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis [21]. The Ar-GCIB process has shown large sputtering yields of organic materials with little signs of degradation of the exposed layers [22,23]. One of the primary drawbacks of the TOF-SIMS chemical analysis technique is its inability to easily quantify the various chemical states without elaborate standards and calibration processes. An alternative technique, which allows for a direct and quantitative measurement of the chemical makeup of the surface of an organic thin film is X-ray photoelectron spectroscopy (XPS). The XPS technique is capable of detecting very small differences in the chemical makeup of many organic semiconducting materials [8]. In this work, sequential Ar-based GCIB sputtering passes are paired with XPS measurements to allow for the composition depth profile of an organic thin film or device to be constructed.

2. Experimental

All organic thin film structures were fabricated on either Si wafers or glass substrates pre-coated with a 150-nm-thick layer of indium-tin oxide (ITO). Substrates were cleaned and treated in UV-ozone ambient prior to film deposition. All organic layers were grown sequentially using vacuum thermal sublimation ($<10^{-7}$ Torr) at room temperature without breaking vacuum. All structures were fabricated using 4,4',4''-tris(carbazol-9-yl)triphenylamine (TCTA) as an HTM, 4,7-diphenyl-1,10-phenanthroline (BPhen) as an ETM, and *fac*-tris(2-phenylpyridine) iridium (III) ($Ir(ppy)_3$) as the emissive guest. Both M-EML and G-EML structures were fabricated via co-deposition as described previously in Refs. [17] and [19]. This work is focused on probing M-EML and G-EML structures where changes in composition can drastically impact device performance. A schematic of the layer structures of interest for depth profiling are shown in Fig. 1. Samples were packed in a nitrogen environment and transported to the composition depth profiling system where the package was opened and the samples were loaded from ambient into a load-locked antechamber within 6 h of fabrication.

The samples of interest were characterized in a PHI VersaProbe II Scanning XPS system equipped with an Ar^+ Gas Cluster Ion Beam source for depth profiling. Potential non-uniformity in sputtering was mitigated by using computerized Zalar[®] rotation of the sample during the sputter cycle. Since the layer structures were uniform across the surface substrate, XPS measurements were carried out using monochromatic Al $K\alpha$ (1486.6 eV) X-rays focused to a 200 μm spot at the area of interest. The photoelectron takeoff angle was 45° and the pass energy in the spherical capacitance analyzer was fixed at 23 eV to obtain high energy resolution for both the C 1s and N 1s spectra from species in TCTA and BPhen. The GCIB source can be operated with beam energies from 2.5 kV to 20 kV and Ar^+ cluster size from <1000 to 5000 atoms. For this study, Ar_{1500} clusters at 10 kV and 2 nA, corresponding to 6.7 eV per Ar ion, were used and raster-scanned over a 2 mm \times 2 mm area. Samples were mounted on a sample carrier with double sided adhesive tape. A dual beam charge neutralization technique with 7 eV Ar ions and 1 eV electrons was used to maintain a constant sample surface potential independent of the sample conductivity.

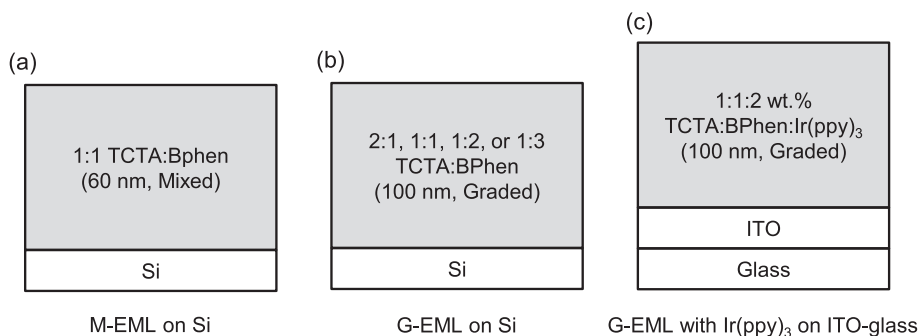


Fig. 1. Layer structures of interest for composition depth profiling. M-EML (a) and G-EML (b) structures deposited on Si substrates. (c) G-EML structure deposited on an indium-tin-oxide (ITO)-glass substrate.

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