The impact of the deposition process of the emitting layer on the internal structure of organic light-emitting diodes

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Abstract
Organic light-emitting diodes (OLEDs) continue to attract research interest due to their increasing applications in display and lighting markets. A current field of development is the application of solution-based deposition techniques for the organic layers. However, in general, corresponding devices do not yet reach the performance of OLEDs with vapor deposited materials. In the present work, we have used a model system with a sulfur-containing host material in the emission layer that can either be deposited by thermal evaporation or spin coating. The structure of the corresponding devices was analyzed by a combination of transmission electron microscopy and spatially resolved energy-dispersive x-ray analysis. To investigate the devices’ cross section, wedge shaped, electron transparent lamellas were prepared by focused ion beam milling. Significant differences of the spatial distribution of sulfur have been observed in the devices.

Keywords: OLED, organic semiconductors, energy-dispersive x-ray analysis

(Some figures may appear in colour only in the online journal)
contains sulfur, scanning transmission electron microscope energy-dispersive x-ray spectroscopy (STEM-EDX) [17] was applied to analyze the spatial distribution of sulfur.

2. Experimental section

2.1. Samples

All samples were provided by Merck KgaA, Darmstadt. They were fabricated on glass substrates, partly coated with a 50 nm thick indium tin oxide (ITO) layer, which forms the transparent anode. The multilayer structure of the devices consists of 100 nm HTL, 60 nm host layer, and 50 nm ETL. Finally, a 100 nm thick aluminum layer serves as the cathode. Additionally, a control sample with only a 100 nm HTL between the electrodes was investigated to rule out a possible sulfur residue originating from the solvent used.

For the solution processed HTL, a copolymer with a molecular weight of 8800 g mol$^{-1}$ has been utilized. It consists of alternating monomer units, shown in figure 1(a). The substituents on the amine units are either aryl or vinyl units. The vinyl groups are responsible for cross-linking of the polymer chains. The R groups on the indenofluorene consist of alkyle chains and improve solubility in toluene. The polymer was spin coated from a toluene solution with a concentration of 18 mg ml$^{-1}$. The rotation speed was adjusted to obtain the desired thickness which was measured with a Dektak profilometer. After deposition, the layer was annealed at 220 °C for 30 min in a nitrogen glove box, to cross link the polymer chains thermally. The electron transporting material is a triazine based molecule and suitable for a wide range of different OLED stack architectures, fluorescent as well as phosphorescent. The ETL was deposited by thermal evaporation in a Lesker tool at a base pressure of around $\times 10^{-6}$ mbar. The evaporation rate of $0.3 \text{ nm s}^{-1}$ was controlled with a quartz crystal microbalance which was calibrated for different materials using thickness measurements from a Dektak profilometer. The small molecule host used is a standard material for use with green or red triplet emitters. It consists of a triazine bonded to a dibenzothiophene unit, as shown in figure 1(b). The substituent R is a heterocyclic aromatic unit. This host material can either be solution processed or vapor deposited. Vapor deposition was carried out in the Lesker tool. The solution processed host layer was also spin coated from a toluene solution and afterwards annealed for 10 min at 110 °C.

2.2. FIB milling

TEM lamellas were prepared from the OLED samples by FIB milling using a FEI Helios NanoLab 600i. The instrument is equipped with an electron as well as an ion column [18]. After applying a platinum protection layer, the surrounding material was removed on two sides, the resulting lamella was cut free and attached to a copper lift out grid. From each sample type, at least two lamellas were prepared. An electron transparent lamella should have a thickness of less than 100 nm in order to obtain high quality images [19]. In general, TEM lamellas are manufactured with a uniform thickness. The probability of interaction between electron beam and sample depends, among others, on the atomic number of the sample, as well as the sample thickness. For STEM-EDX measurements, the low thickness combined with the organic material may lead to insufficient characteristic x-ray emission for the elements of interest, and, therefore, to an unsatisfactory statistical quality of the x-ray data acquired. A higher count rate would improve the data from EDX analysis. Increasing the spectrum acquisition time leads to higher intensity. However, due to damage of the sample material by the 200 keV [20], the measurement time cannot be increased indefinitely. Another way to increase the EDX signal is to measure thicker samples, as the total interaction between electron beam and sample material depends on the thickness. In order to reach electron transparency, on one hand, and reliable EDX data, on the other, the lamellas were deliberately thinned into a wedge shape [21]. Figure 2 shows scanning electron microscope (SEM) images of a wedge shaped lamella. The tip of the lamella is less than 100 nm thick. In this region, TEM images can be recorded. In the middle of the thinned part of the lamella, where it has a thickness of about 300 nm, EDX measurements can be performed. The major drawback of the increased thickness is a decreased spatial resolution limit. However, the latter only has a little effect on the measurements in our study, as the particular organic layers are relatively thick. Thus, preparing wedge-shape lamellas was an ideal sample preparation method to obtain high quality TEM images.
images as well as good EDX spectra from the same sample. Additionally, the wedge shaped form provided a higher long term stability of the lamellas, which facilitated repeated measurements. The lamellas were investigated with a Jeol JEM2100F TEM equipped with two Gatan CCD cameras and a bright field (BF), a dark field (DF), and an Oxford X-Max 80 silicon drift detector (SDD).

3. Results

3.1. TEM images

From the TEM images, ITO and aluminum electrodes are clearly identifiable (see figure 3). The glass substrate and the platinum protection layer, which was added during FIB milling, are also clearly distinguishable. Within the organic layer stack, no contrast difference is observable between the layers at the tip of the lamella. This is due to the similar average atomic number of the materials in the layer stack [22]. In thicker areas, a slight contrast difference within the organic layers is observable. But in those areas, it is not possible to achieve good TEM images at higher magnification, as the pictures stay blurred. The thickness of all organic layers taken from TEM images is in good agreement with the values specified in the fabrication process.

3.2. EDX measurements

To study the spatial distribution of elements across the device layers, EDX area scans were performed in STEM mode. BF images were used to plan and position the EDX scans. As these images were taken in the thicker part of the wedge shaped lamella, the host layer shows a contrast difference to the surrounding organic layers.

Figure 4(a) displays the positions of the area scan on the sample with the vapor deposited host layer. The corresponding data for the sample with solution processed host layer is presented in figure 5(a). An x-ray spectrum was collected for each point, which are represented by the white crosses in figures 4(a) and 5(a). The distance between neighboring measurement points was 10 nm. Spectra were fitted using AXIL (analysis of x-ray spectra by iterative least squares), part of the QXAS package [23–25]. The model for the deconvolution was determined using a sum spectrum. For certain elements, the net counts are displayed in elemental maps (figures 4(b) and 5(b)). The net counts are color coded using a heat scale. The minimum count is coded black, while the maximum is white. Next to each element map, the corresponding maximum and minimum net counts are shown. For sulfur, the distribution along the cross section has been additionally displayed as a line plot. The values are the mean ones for each cross section line, while the error bars show the standard deviation. The
resulting curve for sulfur is shown in figures 4(c) and 5(c), respectively.

The plots for sulfur, aluminum, copper, and indium in figures 6 and 7 present the distribution of these elements along the cross section of the device for differently prepared samples. For optimal presentation of the strongly different counts, each curve has been normalized to its maximum. The normalized plots clearly demonstrate the layered structure of the samples and help identifying possible fitting artifacts, e.g., as a result of increased spectral background. Due to the device architecture, aluminum and indium are only present in the respective contacts.

The copper signal is caused by scattered electrons and bremsstrahlung x-rays exciting the copper grid the lamella is attached to. In the materials used for organic layers, no copper is present. The scattering of electrons in the sample depends on the average atomic number of the area of impact of the electron beam. The copper signal is, therefore, related to the average atomic number at the measurement position. This is clearly visible in the element maps and in good agreement with the TEM images taken at the lamellas’ tip. Along the cross section, there is a significant copper signal for spectra in the aluminum electrode, relatively few counts are observed for measurements in the organic layers and high counts for the ITO electrode. High electron scattering in the sample also leads to a larger overall spectral background, due to the scattered electrons reaching the SDD. A lower peak to background ratio increases uncertainty of the net counts. Contamination
with platinum originating from the protection layer and gallium implants from the ion beam are negligible, when the lamella was thinned properly.

3.3. Comparison of vapor deposited and solution processed host layers

Spatially resolved EDX analysis results reveal the highest sulfur net counts in the host layer for both sample types. The latter was expected as only the host material contains sulfur. In the vapor deposited ETL material, no significant sulfur net counts were detected. For samples with a vapor deposited host layer, this is also true for the HTL. In addition, measurements of the lamella from the control sample, with solely a HTL between the electrodes, show no considerable sulfur content. If there is a low sulfur residue from the solvent used, it remains below the detection limits of EDX.

For samples with a solution processed host layer, a significant sulfur content was detected in the HTL. The sulfur counts are evidently lower compared to those in the host layer and can be found across the whole HTL (see figure 5(c)).

A comparison of results of the samples with vapor deposited host to those with solution processed host layer is given in figures 8 and 9. A direct comparison of the sulfur counts is not reasonable, as the same thickness of all measurement areas cannot be guaranteed. For correlation, the sulfur counts for each lamella were normalized to the highest counts which were always found in the host layer. This semi-quantitative approach allows for the comparison of the sulfur counts in ETL and HTL.

Using the BF images of the measurement areas (figures 4(a) and 5(a)), the individual spectra were assigned to ETL, host layer or HTL. For each layer, a mean sulfur net count was calculated from this segmented data. Data from transition points was excluded. Results from this analysis are shown in figure 9.

Additional to the area scans, line scans along the center of a layer in all three organic layers have been performed and compared. As for the area scans, the average net sulfur counts were calculated and normalized to the averaged counts in the host layer. Results from the line scans are shown in figure 8.
Both figures 8 and 9 show significantly increased sulfur content only in the HTL of samples prepared with solution processed host layer. Since the manufacturing process represents the only difference between the two sample sets, it is reasonable to expect that the penetration of sulfur into the HTL is due to the solution-based deposition of the host layer. This might be the reason for the previously mentioned performance differences between the sample types.

Beside the significant sulfur counts in the HTL, the sulfur signal appears to drop sooner for the samples with a solution processed host layer (see figures 4(c) and 5(c)). To investigate this phenomenon further, several line plots, resulting from area scans, have been correlated. Again, it is not expedient to compare the line plots directly, due to different values of the thickness of the lamellas at the measurement positions, leading to large variations in sulfur net counts. Therefore, all plots were normalized to their maximum value. Another obstacle is the positioning. The measurement position has been determined using a BF image of the sample. To enable the comparison of different area scans, it is necessary to align the measurement positions. The latter was achieved by identifying the transition from the ETL to the host material as a reference point. An error in the range of the EDX scan resolution, thus, 10 nm, may still remain.

In figure 10, the superimposed line plots are displayed. Each area scan was acquired on a different lamella. For equally prepared samples, the scans show a good agreement. However, when comparing both sample sets, the host layer for the samples with solution processed host is significantly thinner than the corresponding layer for the samples with vapor deposited host. As mentioned before, a significant sulfur signal was detected in the HTL of samples with solution processed host layer. From the data plotted, it appears as if sulfur from the host layer moved partially to the HTL. It remains unclear which mechanism causes such behavior. One possible explanation might be that the solvent used for deposition of the host layer partly dissolves the underlying HTL and thereby enables diffusion processes.

4. Conclusions

In the present study, the cross sections of differently prepared OLEDs were investigated to gain information on the influence of the preparation method on the layer structure. Wedge shaped lamellas facilitated high quality TEM images as well as reliable STEM-EDX data. In addition, they were also mechanically more stable than regularly thinned lamellas.

Spatially resolved EDX measurements show distinctly different sulfur content values for differently prepared OLEDs. Samples with a thermally evaporated host and the control sample with HTL only show no significant sulfur content in the HTL. However, in samples with solution processed host layer, sulfur could be found in the HTL. Here, a significant amount of sulfur was detected throughout the HTL. These differences in the sulfur distribution may be the cause of the measurable difference in OLED performance.

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