Analytical TEM in Organic Electronics

New Possibilities in Polymer Preparation and Analysis

This work is situated in the research field of organic electronics. The aim is the ability to investigate organic electronic devices in the Transmission Electron Microscope (TEM) supporting the development and improvement of the manufacturing process. The challenges are the sample preparation and the characterization via TEM due to the lack of distinguishing features of the used materials. In this work advanced analytical methods for the investigation of organic devices in the TEM are presented.

Organic electronics is a field of research with growing interest in the last years. Many applications are already entering industrial commercialization, but the search for new materials and the improvement of the used processes are still in progress. Organic electronics is a promising technology especially for applications where large-area coverage, diversity in substrates (including flexible ones) and low temperature processing is important. As the device demands emerge to more advanced products such as smart objects and intelligent sensor networks, the performance parameters of the involved circuits become more and more challenging. The miniaturization of the structures is a substantial requirement, achieving faster devices with a lower driving voltage and higher integration density. With regard to the optimization of organic electronic devices, transmission electron microscopy provides an excellent method to systematically study the various device manufacturing steps. Moreover it contributes to the interpretation of the electrical characterization output by giving cross section insight into the device. This TEM characterization is continuously challenged by the on-going transition to all organic materials, due to the lack of distinguishable features between the materials.

The organic thin film transistor (oTFT) is a prominent device to optimize the production processes as well as the used materials. All polymers analyzed in this work are part of such a device or are used during the manufacturing process.

Experimental

The oTFTs presented in this work are produced following the self-aligned technique
The main advantage of this technique is the automatic alignment of the source and drain electrodes with respect to the gate structure. This not only makes an automated alignment routine obsolete with regard to fast roll-to-roll processing, but also defines very accurately the overlap of the electrodes which is important for the device performance. The manufacturing process is started by structuring the gate electrode. The structuring can be done either by a shadow mask process or for smaller structures by nanoimprint lithography [2, 3]. The gate structure is transferred into a positive photoresist by UV exposure through the substrate from the backside of the device using the gate electrode as a mask. Thereby a precise alignment of the source and drain electrodes with respect to the gate electrode, as well as a minimized overlap is achieved (fig. 2a). The different materials are grown or applied by physical vapor deposition (metal layers, pentacene), by inkjet printing (metal inks, PEDOT:PSS, polymer) and by spin-coating (polymers, pentacene).

All TEM specimens shown in this work are prepared with a focused ion beam instrument (FIB) (FEI NOVA 200 dual beam system). We use the FIB instrument to prepare our TEM samples, because a site specific preparation is easy to perform, which is a huge advantage for investigating a certain TFT out of a whole circuitry. Considering the radiation and temperature sensitivity of the materials we perform a FIB lift-out with an improved patterning strategy. This so called interlacing strategy reduces chemical and morphological damage due to a reduced thermal impact [4, 5, 6]. A window milling technique is applied to improve the mechanical stability of the final lamella.

The TEM investigations are done on a Tecnai F20 and a Titan3 60-300 (FEI) both equipped with a Gatan Imaging Filter (Tridiem and Quantum, respectively). Spectrum acquisition and analysis are performed using DigitalMicrograph (Gatan).

**Results**

The channel region is a critical area during manufacturing, as well as the overlap between the electrodes [7]. In addition the thicknesses of the layers and also possible residuals have a crucial influence on the device performance and are targets of the investigations. The task of TEM investigation gets more challenging as the material layers get thinner and more similar in elemental composition.

As a first example we show an all polymer layer stack. Preparing similar samples with conventional FIB preparation problems occurred with the intermixing of the
polymer layers (e.g. the sulfur of PEDOT:PSS (Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate) is found in the adjacent layers). The sample presented here consists of four different polymer layers on a Kapton (Polyimid) substrate (fig. 1). Two of the polymers are used as dielectric material (PVCi (poly(vinyl cinnamate) derivative) and BCB (divinyl-tetramethylsiloxane-bis(benzocyclobutene) derivative)) whereas PEDOT:PSS is used as the conductive polymer. In STEM mode a spectrum image (SI) is acquired across all layers using the electron energy loss (EEL) signal. After background subtraction the elemental signals are extracted and plotted individually and superimposed (C: red, O: white, N: yellow, S: blue and Si: green, fig. 1). It can be seen that the individual layers are well separated. With the improved FIB preparation no intermixing of the layers is present which can be seen very nicely by our results.

In figure 2b an energy filtered TEM (EFTEM) image of the overlap region of the electrodes of an oTFT can be seen. The oTFT has the following set up:

- substrate: modified Polycarbonate
- gate: Al
- dielectric layer: xPMMA
- source/ drain electrode: Au
- semiconductive layer: pentacene

For EFTEM a 2 eV wide energy selective slit is set to 6 eV and thereby a distinction of the semiconductive layer and the dielectric layer is possible. With this method the thickness of the dielectric layer is determined to around 60 nm, which is a very quick and easy way of differentiating polymer materials.

The last application example shows a cross section of a layer stack built up of two polymer layers (imprint resist, PEDOT:PSS) and Cr-Au layers on a PET (poly(ethylene terephthalate)) substrate (fig. 3). As the fine structure of the C-K edge is sensitive to the type of chemical bonding (fig. 3c), slight differences between the C-K edges of the polymers are expected. The energy range around the edge is subdivided into different regions (π*, gap and σ*) of which the intensities are determined (integral regions are shown in fig. 3c). By trial combinations of these integrated intensities the differences in the near edge fine structure of the C-K edge can be used for a chemical differentiation as shown in figure 3b. The π*/ gap and σ*/π* ratio maps are shown as well as a map of the onset of the π* peak and thereby all three polymers can be distinguished.

**Conclusion**
Organic electronics is a fast evolving field. Transmission electron microscopy with its variety of analytical techniques provides an excellent method to give explanations for problems during the fabrication process, to help to interpret the electrical characterization output by giving cross section insight into the devices, as well as to confirm the successful output of the manufacturing processes. We could show in this work that we can prepare TEM specimens suitable for analytic investigations without the introduction of artefacts by a new patterning strategy and also that we are able to give answers to upcoming questions in the field of organic electronics. This can be successfully achieved by extracting the required information from EELS data (low-loss and core-loss regime) as well as with energy filtering.

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References

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