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The use of the focused ion beam technique to prepare cross-sectional transmission electron microscopy specimen of polymer solar cells deposited on glass

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Abstract

The use of the focused ion beam (FIB) technique for cross-sectional transmission electron microscopy (TEM) specimen preparation of polymer solar cells deposited on glass substrates is described. Ultra-thin sections were prepared using the 'lift-out' technique. Electron microscopy investigations of these specimen resulted in detailed morphological information of the devices (e.g. thickness and interface roughness of the layers). In comparison with standard sample preparation routes for TEM investigations the used technique is well suited for precise sectioning of hybrid structures.

Keywords: Focused ion beam; Transmission electron microscopy; Scanning electron microscope

1. Introduction

The characteristic structure of polymer photovoltaic cells and polymer light-emitting diodes (LEDs) consists of a ~100 nm thin active layer covered with a transparent front electrode and a metal back electrode [1]. Additional layers often are introduced to enhance charge transport, promote the injection or collection of charges, or control the zone, where generation (in solar cells) or recombination (in LEDs) of charge carriers occurs. Chemical composition, processing conditions, thickness, and roughness of the layers and their interfacial integrity have been identified as important parameters for the performance of the devices. As an example, the interface roughness influences light transmission, work function of the electrodes, and homogeneity of the current density. However, establishing precise relations between these parameters and device operation is presently limited by the lack of methods for structural, compositional and morphological analysis of as-prepared devices. Hence, techniques that allow assessing the nature of devices directly after processing or after operation under working conditions are of profound interest.

Transmission electron microscopy (TEM) has proven to be the most powerful technique to visualize the morphology of materials in detail with (sub-) nanometer resolution, to gain local structural information by means of electron diffraction, and to get local chemical composition information using TEM equipped with analytical tools. However, standard preparation techniques such as ultra-microtomy and ion beam etching are not able to provide cross-sectional specimen of solar cell devices having acceptable quality, simply because such devices consist of soft polymer layers deposited on a hard glass substrate.

To overcome this bottleneck we have used a focused ion beam (FIB) microscope for the preparation of cross-sectional TEM specimen. The FIB microscope operates along the same principle as the scanning electron microscope (SEM), in that a beam of charged particles is rastered across a specimen, and the resultant signals at each raster position are plotted to form an image. However, in a FIB microscope the charged particle beam consists not of electrons, but rather of ions, which are typically positively charged (mainly gallium) and can be focused to a very fine probe size (<10 nm). Besides imaging, the FIB can be applied for selective materials deposition [2,3] and for local milling and polishing of the sample [4,5], which is often used for microfabrication [6].

Using the FIB for cross-sectional transmission electron microscopy specimen preparation of semiconductor devices was first demonstrated in the late 1980s [7] and is now a basis for the analysis of complex

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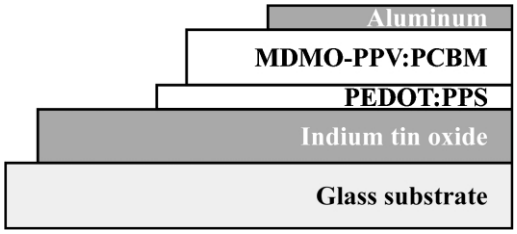

Fig. 1. Sketch of the assembly of a ready-to-operate polymer solar cell device.

materials [8]. An electron-transparent membrane is produced by FIB milling of back-to-back sections into a mechanically thinned bar mounted on a modified aperture TEM grid. Alternatively, the 'lift-out' technique was employed, whereby a similar membrane is produced in a bulk sample, then cut free using the FIB and removed for stand-alone examination in the TEM [9,10]. In the present study we have applied the latter technique to prepare ultra-thin cross-sectional specimen of polymer solar cell devices deposited on glass substrates for TEM investigations.

2. Experimental

Polymer photovoltaic devices were prepared using a glass substrate covered with a transparent anode of indium tin oxide (ITO) on which a transparent conducting polymer layer of polyethylenedioxythiophene polystyrenesulfonate (PEDOT:PSS Bayer AG, Germany) was applied by spin coating from aqueous dispersion. Subsequently, the photoactive layer was spin cast from a 1:4 wt% mixture of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) and (1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene) (PCBM) in an organic solvent (chlorobenzene). On top of this stack an Al cathode was applied by thermal deposition in vacuum [11]. Fig. 1 shows a sketch of the assembly of the ready-to-operate device.

To investigate details of the layer morphology ultra-thin cross-sections of these polymer solar cell devices were prepared using a focused ion beam microscope (Strata FIB200, FEI Company, The Netherlands). Applying the lift-out technique no pre-treatment of the sample was required. In some cases a thin Pt layer was locally deposited on the sample to enhance charge and heat transfer. In the lift-out technique, the electron transparent membrane is removed from the bulk specimen and analyzed directly by TEM [12]. A large stair-step FIB trench was cut on one side of the area of interest and a rectangular FIB trench was cut on the other side of the area of interest (milling). Prior to final thinning, the sample was tilted to $>45°$ and then the bottom was cut free. Then the sample was tilted back to its starting position and the specimen was thinned to electron transparency (polishing). Last step of the sectioning procedure was the cutting of both the right and the left side of the ultra-thin specimen to disconnect it from the bulk sample. It is stated that for the applied preparation parameters the original morphology of the specimen will not be changed. For TEM investigations the cross-sections were transferred on Cu grids coated with a carbon film consisting of wove-mesh-like holes of different sizes and shapes. For this procedure a micromanipulator was used. The entire specimen preparation was done in approximately 3 h. TEM-work was performed using a Jeol 2000FX operated at 80 kV in order to enhance the contrast between the polymer layers.

3. Results and discussion

The preparation of an ultra-thin cross-sectional TEM specimen by using a FIB microscope follows the procedure as described in the Experimental part in detail. Coarse milling is the first step of this procedure to form a large stair-step trench and a rectangular trench on both sides of the area of interest, subsequently followed by the polishing and edge cutting steps. The capability in situ FIB imaging during the preparation procedure makes it possible to visualize, e.g. the final stage of the specimen preparation before transfer to the TEM grid. Fig. 2 shows a FIB image (secondary electron detector) of the ultra-thin cross-section specimen still connected on one side with the bulk sample (arrow, top view).

A FIB image of the sectioned area of the bulk sample is visualized in Fig. 3. The side-view image clearly shows the separate glass, oxide, polymer and metal layers in a stack. Also the large roughness of the top aluminum layer is visible. However, contrast between the two polymer layers and the overall resolution is rather low.

The low resolution TEM image (Fig. 4) shows a cross-sectional specimen of a photovoltaic device. The specimen has approximately a lateral size of 12 μm × 3.5 μm, a thickness of 200 nm and is deposited on a Cu grid coated with a carbon film consisting of wove-mesh-like holes of different sizes and shapes. At this magnification the glass substrate, a thick platinum top layer and a blurry layer consisting of the polymers, aluminum and ITO can be distinguished. Suitable for high-resolution imaging the central part of the specimen is highly electron transparent (thickness <100 nm).

The high resolution TEM image (Fig. 5) obtained from a cross-section of this photovoltaic device shows no visible damage to the layers and reveals various features. The thickness of the individual layers can be determined to 155 nm for the indium tin oxide, 70 nm for the PEDOT/PSS, 160 nm for the MDMO-PPV/PCBM mixture, and 70 nm for the aluminum layer, respectively. These values are consistent with layer thickness data measured by a surface profiler. At the interface of the photoactive MDMO-PPV/PCBM layer and the Al electrode a thin layer can be recognized, which has been identified using dual-beam dynamic time-of-flight secondary ion mass spectrometry (TOF-SIMS) to

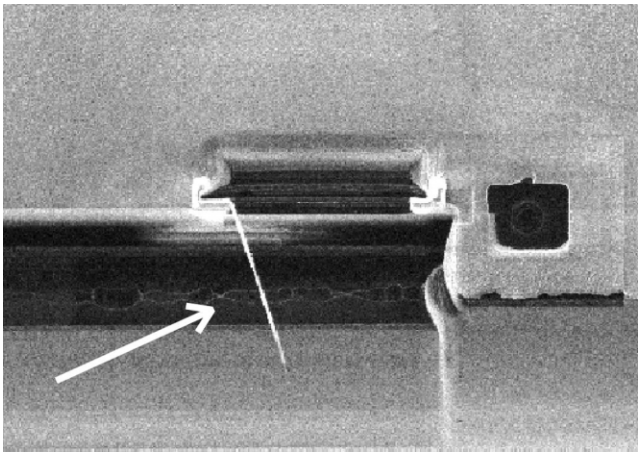

Fig. 2. In situ FIB secondary electron mode image during specimen preparation, top view. Besides other details of the sample preparation, e.g. the stair-step FIB trench in the center of the image, the white ultra-thin sample membrane is visible, indicated by the arrow.

be Al_2O_3, formed during thermal evaporation by reaction of aluminum with residual water at the polymer surface and in the atmosphere [13]. Likewise, an approximately 20 nm thin SiO_2 layer located on the glass surface can be seen in this image. TEM also gives an impression of the roughness of the different interfaces. Both the top surfaces of the PEDOT/PSS and the MDMO-PPV/PCBM layers are rather smooth while the ITO and the thermally evaporated Al have a larger roughness. This result is corroborated by atomic force microscopy (AFM) measurements of the several surfaces measured at different stages during device preparation in four separate experiments [11]. The correspondence of the appearance of interfaces inferred from TEM and AFM shows that subsequent processing steps do not significantly deteriorate layers or interfaces that were applied in previous steps, at least for the investigated devices.

4. Conclusion

The focused ion beam technique was successfully used to prepare cross-sectional specimens of polymer solar cell devices deposited on a glass substrate for transmission electron microscopy investigations. Ultra-microtomy as the standard preparation technique for bulk or layered soft polymer materials as well as ordinary ion beam etching applied for thinning of hard condensed matter samples, e.g. metal, ceramic or inorganic glass, are not able to provide thin sections of layered hybrid materials consisting of soft and hard components having exactable quality for detailed TEM investigations. On the other hand, TEM analysis of specimens prepared by using the focused ion beam technique gives comprehensive information on layer thickness, layer roughness and the overall morphology of the solar cell device.

In the world of polymer science and technology morphological studies of soft/hard matter interfaces—authentic coatings on metal substrates, polymer light emitting diodes (LED) on glass substrates, etc.—by means of electron microscopy techniques are very limited, because of the described preparation problems. However, beside others, interface features dominate the performance of hybrid structures. Thus, the characteristics of the interfaces have to be studied to understand structure/property relations

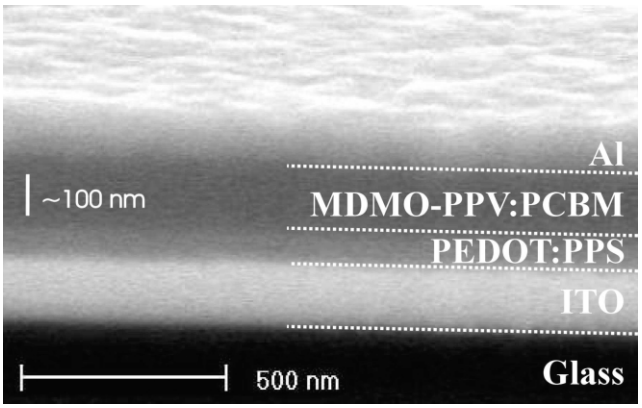

Fig. 3. FIB image of the sectioned area of the bulk photovoltaic device; the dotted lines indicate the layer interfaces.

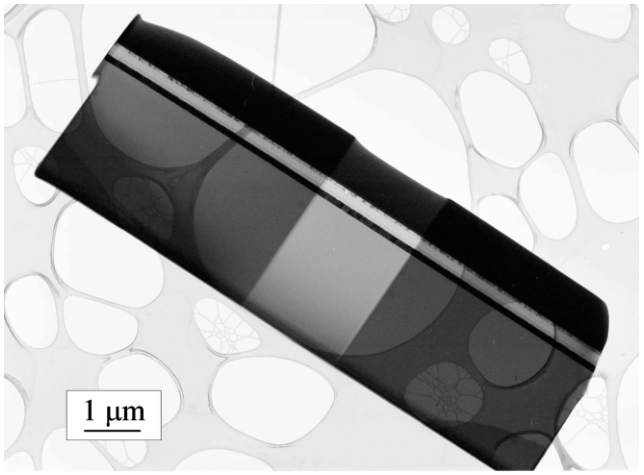

Fig. 4. Low resolution TEM image of a cross-sectional specimen of a photovoltaic device deposited on a Cu grid coated with a voided carbon film.

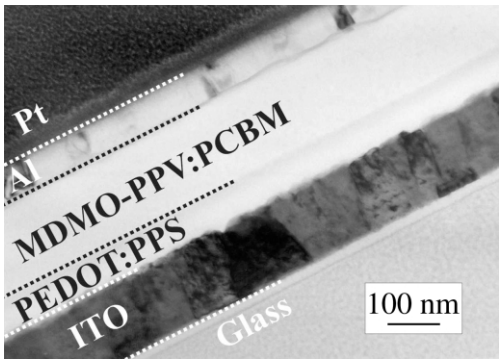

Fig. 5. High resolution TEM image of a cross-sectional specimen of a photovoltaic device; the dotted lines indicate the layer interfaces.

of the samples and to control the performance of devices. With the help of the introduced focused ion beam technique for preparation of ultra-thin cross-sectional TEM specimens of layered hybrid materials the obvious lack of useful preparation tools related to the characterization of soft/hard interface may be reduced.

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