Electron microscopy as a tool for morphology control in nanocomposite solar cells

Wernfried Haas^{1,3}, Armin Zankel¹, Thomas Rath^{2,3}, Eugen Maier², Alejandro Santis^{2,3}, Achim Fischereder^{2,3}, Gregor Trimmel^{2,3} and Ferdinand Hofer¹

1. Institute for Electron Microscopy and Fine Structure Research, Graz University of Technology and Graz Centre for Electron Microscopy

Institute for Chemistry and Technology of Materials, Graz University of Technology
Christian Doppler-Pilotlaboratory for Nanocomposite Solar Cells

wernfried.haas@felmi-zfe.at

Keywords: solar cell, morphology control, TEM, ESEM, HAADF

Controlling the morphology in nanocomposite solar cells consisting of a conjugated polymer and semiconducting nanoparticles is crucial to improve their efficiencies. Electron microscopy is one of the most powerful tools for this purpose as already described by Yang et al [1].

However, a review of the literature reveals that only a limited set of electron microscopy techniques has reached broad use in the field of organic solar cells so far. Transmission electron microscopy (TEM) imaging and electron diffraction (SAED) are commonly used to investigate the organization and changes in morphology of cross sections in organic solar cells and devices [2]. Furthermore scanning electron microscopy (SEM) is used to gain insights about surface organization and looking at cross sections [3].

In this work we aim to apply advanced electron microscopy to the study of a system using copper indium sulfide (CIS) as inorganic semiconductor phase and poly-paraphenylene-vinylene (PPV) as organic phase. The active layer is prepared *in situ* by spincoating a solution of the polymer, the metal salts and thioacetamide as the sulphur source. In a thermal annealing step the precursors decompose and form inorganic nanoparticles within the organic layer. This is a critical step as the polymer also changes its properties while heating up. The influence of the state of the polymer on the formation of the CIS nanoparticles is not yet fully understood.

The appearance of solar cells before and after annealing has already been investigated in the past. In a new approach, we focus on *in situ* investigations of the heating process using an environmental SEM (ESEM) equipped with a heating stage. Examples of a measurement are shown in Figure 1. While these SEM investigations can be done directly on the solar cell, TEM investigations need thin films, prepared by spin coating the polymer and precursor solution onto NaCl single crystals. After thermal annealing the NaCl crystals are dissolved in aqua dest., the remaining films are mounted on a nickel grid.

In our work, we extensively use SAED as well as X-ray diffraction for analysis of solar cells. Using the lattice constants from previous measurements and reference data enables us to identify the CIS nanoparticles both from different precursors as well as within different polymers.

While bright field images at high resolutions contain phase contrast from both CISnanoparticles and polymer, the use of scanning transmission electron microscopy (STEM) in combination with high angle annular dark field (HAADF) results in images with a strong Zcontrast. Selecting the collected scattering angles by adjusting the camera length of the microscope allows us to primarily image the CIS-nanoparticles contained within the polymer layer (fig. 2).

- 1. X. Yang et al, J. Macromolecules, **40** (2007) p1353
- 2. B. Schaffer et al, J. Ultramicroscopy, **101** (2004) p123
- 3. H. Hoppe et al, J. Adv. Funct. Mater., **14** (2004) p1005
- 4. Financial support by the Christian Doppler Research Association and the ISOVOLTA AG.



Figure 1. Investigation of surface changes in a polymer based solar cell during annealing using an ESEM.

Image a taken at starting conditions (room temperature) shows almost no visible contrast. During annealing the roughness of the surface increases as can be seen in image b (180°C).



Figure 2. Comparison of bright field and STEM images using a HAADF detector.

a: Bright field image of CIS-nanoparticles inside the PPV layer.

b: Inverted STEM image of a similar region.