IMAGING STRUCTURE FORMATION IN POLYMER SOLAR CELLS BY HIGH RESOLUTION TOMOGRAPHY AND IN SITU *X-RAY SCATTERING*

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Summary: We have used ultra-high resolution ptychographic tomography to verify the integrity of fast, roll-to-roll coated recombination layers in tandem polymer solar cells, and to investigate the occurrence of defects that leads to fatal breakdown of performance in the completed device. The local, high-resolution information from imaging studies, are combined with fast, *in situ* X-ray scattering to relate the observations to the processing step.

1. INTRODUCTION

Structures from the atomic scale to microns have crucial impact on the performance of devices for energy applications. In recent years, 3D X-ray imaging has experienced an incredible development towards greater detail in resolution, both in terms of dimensions and resolvable contrasts [1][2].
We are also breaking ground and moving borders with X-ray scattering methods, which we now routinely apply to high-speed processsing of polymer solar cells [1][3].
Together these methods provide an encompassing view of the materials systems throughout the entire manufacturing process, from layer deposition to the final device. And what is more, we are now seeing opportunities for merging and integrating scattering and imaging methods, for truly multiscale analysis.

2. EXPERIMENTAL METHOD

Ptychographic imaging was conducted at the P06 beam line at PETRA III in Hamburg with an intensity of $8*10^6$ photons s^{-1} in a 250 nm beam, focused by silicon nano-focusing lenses with a 2.0 m sample-detector distance. Ptychographic X-ray tomography at the cSAXS beamline used the setup described in reference [4]. A coherent beam with 6.2 keV photon energy was focused by a Fresnel zone plate (FZP) with an outer-most zone width of 60 nm. The total flux provided by the FZP illumination is estimated to be about $3.6 \cdot 10^8$ photons/s. Coherent diffraction patterns were recorded with a Pilatus 2M detector placed 7.389 m downstream the sample. The resolution of the 3D dataset was estimated to be about 20 nm by Fourier shell correlation, in both experiments. *In situ* small angle X-ray scattering (SAXS) experiments during coating of the device layers were carried out on a custom SAXS setup, using a rotating anode as source. The sample was illuminated at a position close to the drying front in a series of exposures while the substrate was moved from one roll to the other at a speed of 0.5 m min^{-1}.

3. RESULTS

With 3D ptychography of the highest spatial resolution achieved so far at P06, we were able to image the complete roll-coated tandem solar cell, verifying the integrity of the 40 nanometre thin zinc oxide layer in the intermediate layer that successfully preserved the underlying layers from solution damage. We also found that the combination of the good conductivity of a porous silver electrode with the good film forming ability of a conducting polymer that infiltrates the silver electrode constitutes a substrate electrode with a smooth surface for the coating of the subsequent layers. This is what allows the coating of very thin layers, at very high speeds, still forming contiguous layers, without pinholes. The resulting polymer tandem solar cell converts 2.67 per cent of the incoming sunlight into electric energy, which is a factor of 7-8 below the efficiency of conventional solar cells. Of particular significance, however, this is the first example of a roll-to-roll coated tandem solar cell where the efficiency of the tandem device exceeds that of the individual sub-cells by themselves.
At the cSAXS beam line we investigated a novel type of organic tandem solar cell with fundamentally different types of active layers: one consisting of a bulk heterojunction and one of nanoparticles. We found that the primary

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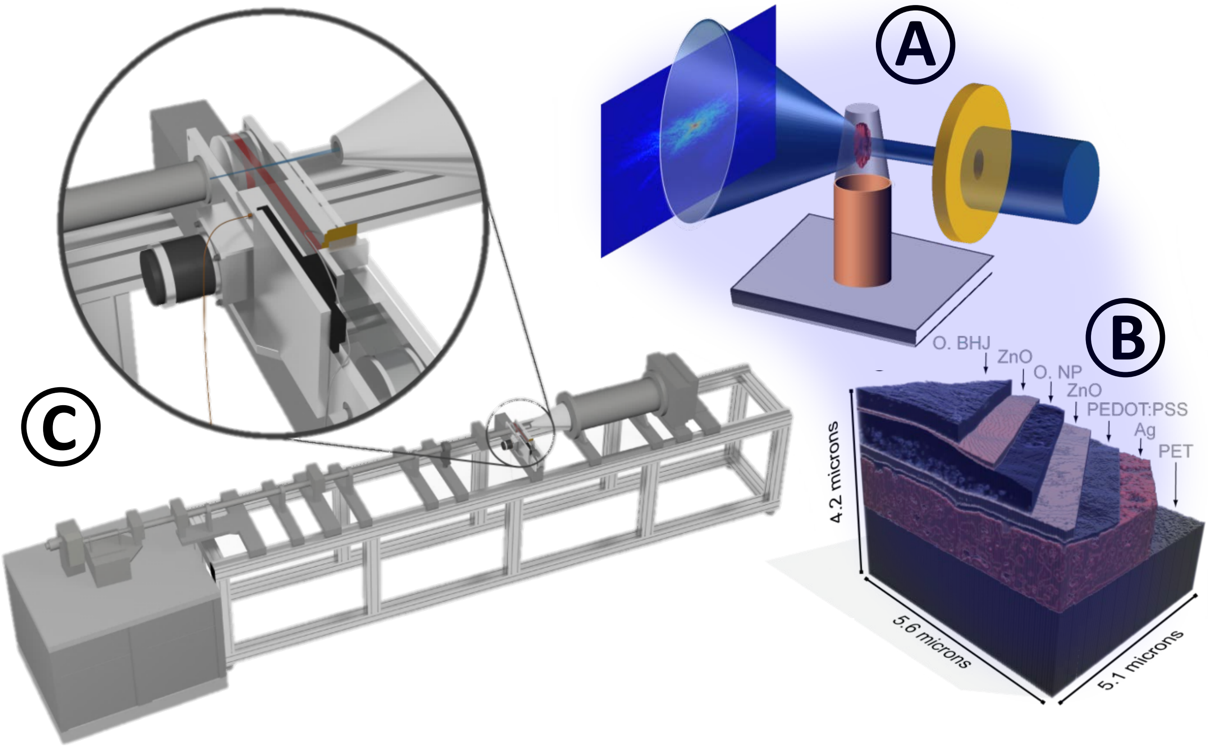

A. Coherent diffraction data are collected with a large number of overlapping illuminations from angles covering 180° to allow full 3D reconstruction of the sample volume, which is then **B.** converted into quantitative electron density distributions and segmented into the material constituents for further analysis. **C.** *in situ* setup for acquiring grazing incidence scattering data while coating solar cell device layers from solution.

failure mechanism of the device is short circuits connecting electrodes through the layer of active nanoparticles.

The electron densities extracted from the ptychographic tomography revealed that layers cast from zinc oxide nanoparticles only have 60% of the expected density for the bulk materials, indicating a porous layer or less dense material packing due to the nanoparticle structure. The silver electrode is porous with large air cavities. Similarly, the organic layer containing active nanoparticles has sub-resolution porosity i.e. below 20 nm. A thorough and state-of-the-art interface analysis showed how all layers with the exception of the active nanoparticle layer have a positive top-bottom interface correlation. The active nanoparticle layer on the other hand has negatively correlated top- and bottom interfaces, which also implies a wide distribution in layer thickness and a high interface roughness. The surface roughness is gradually reduced in subsequent layers and it never decreases to the levels observed below the nanoparticle active layer. To make nanoparticle active layers a viable alternative to bulk heterojunctions, the coatability of the active nanoparticles will need to be improved. The otherwise unobtainable tomographic information makes ptychographic tomography a critical tool to face the nano-engineering challenges one must overcome to realize organic photovoltaics as a technology.

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