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Combined Ultramicrotomy and Atomic Force Microscopy Study of the Structure of a Bulk Heterojunction in Polymer Solar Cells

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Abstract—A method for visualization via atomic-force microscopy of the internal structure of photoactive layers of polymer solar cells using an ultramicrotome for photoactive layer cutting is proposed and applied. The method creates an opportunity to take advantage of atomic-force microscopy in structural investigations of the bulk of soft samples. Such advantages of atomic-force microscopy include a high contrast and the ability to measure various surface properties at nanometer resolution. Using the proposed method, samples of the photoactive layer of polymer solar cells based on a mixture of PTB7 polythiophene and $PC_{71}BM$ fullerene derivatives are studied. The disclosed details of the bulk structure of this mixture allow us to draw additional conclusions about the effect of morphology on the efficiency of organic solar cells.

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1. INTRODUCTION

Solar cells based on organic materials have recently been developed and intensively investigated in laboratories and companies. One of the most promising directions in this field is the development of polymer solar cells (PSCs) with an energy-conversion efficiency of over 10% [1–3]. The attained efficiency of such cells in combination with their simplicity and low cost make them economically attractive. To further increase the efficiency of moderns PSCs, it is necessary to have detailed knowledge of the morphology of the photoactive layer, which is a mixture of the organic donor and acceptor forming a bulk heterojunction [4].

The structure of the bulk heterojunction determines a number of very important processes occurring in PSCs, including exciton diffusion and dissociation and charge transport to electrodes.

Among the most widespread methods for studying the nanostructure of photoactive layers are atomic force microscopy (AFM) and transmission electron microscopy (TEM) [5–9]. These two techniques yield complementary information about the sample's nanostructure, since AFM is intended for surface investigations and TEM reveals information about the bulk structure projection. In AFM investigations of the photoactive-layer structure, a film is usually deposited by centrifuging onto glass coated with indium tin oxide (ITO). An upper electrode and transport layers are not deposited, so the AFM probe has access to the photoactive-film surface. In the TEM measurements, the photoactive layer is transferred from such a sample to a standard TEM measuring lattice. It is extremely important to obtain information on the film structure in the plane perpendicular to the surface, i.e., between electrodes. This is a complex problem to be solved; it requires the use of different surface modification techniques with nanometer spatial resolution. Samples with a photoactive-layer cross section are usually prepared by microtomy or cutting lamellae using a focused ion beam (FIB) [10]. Prepared PSC cross-section samples have predominantly been investigated by high-resolution (as a rule, better than 1 nm) TEM methods, which allow chemical analysis (e.g., energy-filtered transmission electron microscopy (EFTEM)) [11]. In addition, the sample cross sections obtained by cleaving in liquid nitrogen are often studied by scanning electron microscopy, which, as a rule, does not ensure the required resolution. The TEM data obtained on organic samples have poor contrast because of the low atomic number of elements contained in the materials; in addition, the samples are