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Self-assembly of functionalized fullerenes

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Abstract

We report on the fabrication and characterization of ultrathin self-assembled fullerene films. Using a carboxy-functionalized fullerene and poly(ethylen imine) we prepare fullerene films with the technique of layer-by-layer adsorption. Our structures exhibit a modulated electron density as evidenced by the observation of a quasi-Bragg reflection in X-ray reflectivity studies. This relatively high degree of order is attributed to the formation of hydrogen bonds.

Keywords: Fullerenes and derivatives, Self-assembly, Solar cells

1. Introduction

Buckminsterfullerene C_{60} exhibits various properties that render this material suitable for a use in optoelectronic applications. The use of fullerene molecules in composite systems with conjugated polymers is particularly promising. After photoexciting the conjugated polymer, the C_{60} can act as an efficient electron acceptor in a photoinduced electron transfer process[1,3]. Most of the experiments until now, however, have been limited to the investigation of simple blend system where the fullerene and the polymer are mixed in the same solvent and then spin cast into a thin solid film. In order to understand the fundamental photophysics in such systems and for a design of novel heterostructures it is desirable to develop techniques for the fabrication of ultrathin fullerene films.

In this contribution, we report on the fabrication and characterization of self-assembly multilayer films of poly(ethylen imine) (PEI) and a C_{60} derivative. We characterize the thin films via X-ray reflectivity studies and find a Bragg-peak that indicates a relatively high degree of vertical order.

2. Experiment

The C_{60} derivative ($C_{69}H_8O_2$ M=868) was prepared by Diels-Alder cyclo-addition and dissolved in toluene with a concentration of 10^{-4}M. As the second component for the layer-by-layer adsorption technique we use the commercially available poly(ethylen imine) (PEI) dissolved in water. The multilayer films were prepared by alternately dipping the substrate into the two different solutions.

The detailed fabrication of the multilayer films via molecular self-assembly and the details of the specular X-ray reflectivity setup can be found in previous papers[2,3].

3. Results and Discussion:

Figure 1 depicts the specular X-ray reflectivity spectrum of a 10 bilayer self-assembled film deposited on a very smooth float glass substrate (roughness of few Å). Kiessig oscillations due to interference of beams reflected from the upper and the lower interfaces are clearly seen. As an interesting feature , we observe a Bragg peak around $2\theta \approx$ 2.5~3.5, This feature can be seen more clearly in the R/Rf spectrum shown in the inset. From the Bragg equation we derive a layer thickness of 29.4Å. In agreement with this value the overall film thickness of our multilayer structure depends linearly on the number of layers with a value of 28Å per PEI/C_{60} layer. We note that a Bragg peak is typically not observed in organic self-assembly films as e.g. multilayers of poly(p-phenylene vinylene) (PPV) and a sulfonated polystyrene (SPS) [2]. From our measurements, we conclude that the $C_{69}H_8O_2$/PEI layer assemblies exhibit a high degree of vertical order leading to an electron density contrast. We attribute this order to hydrogen bonding being responsible for the layer-by-layer growth. By comparison of the FTIR spectrum of PEI alone and the self-assembled multilayers we obtain direct evidence for the formation of hydrogen bonds. For PEI the absorption at 3366cm^{-1} is shifted to a lower energy peak at 3312cm^{-1} in the multilayer. This shift in the FTIR spectrum is very similar to what has been previously observed in a conjugated polymer multilayer where hydrogen bonding interactions were proposed [4].

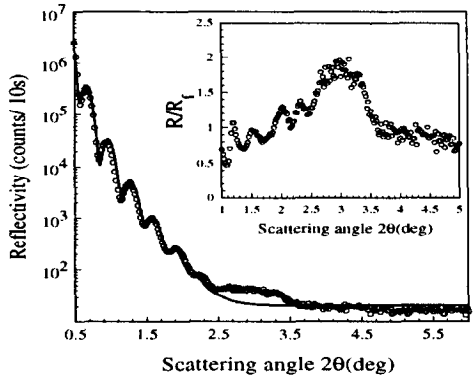

Figure 1 Typical specular X-ray reflectivity spectra of 10 bi-layer self-assembled film of PEI/C_{60} derivative

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