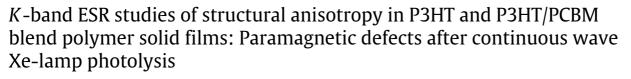
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A. Konkin<sup>a,\*</sup>, H.-K. Roth<sup>b</sup>, P. Scharff<sup>a</sup>, A. Aganov<sup>c</sup>, O. Ambacher<sup>d</sup>, S. Sensfuss<sup>b</sup>

<sup>a</sup> Ilmenau Technical University, Institute for Micro and Nanotechnologies, Gustav- Kirchhoff-Str. 7, D-98693 Ilmenau, Germany

<sup>b</sup> Thuringian Institute for Textile and Plastics Research, Breitscheidstr. 97, D-07407 Rudolstadt, Germany

<sup>c</sup> Physical Department, Kazan State University, Kremljevskaja-street 18, Kazan, Russia

<sup>d</sup> Fraunhofer-Institute for Angewandte Festkorperphysik, Tullastrasse 72, 79108 Freiburg i.Br., Germany

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#### 1. Introduction

The well-established strong relationship between chain packing in semiconductor polymer thin films and the charge transport within, [1,2a] initiates further studies of device morphology for large area electronic applications such as polymer LED, FET and photovoltaic (solar) cells. These recently published works and others (see below) were devoted to devices made from polythiophene. This perspective type of polymer semiconductors has already been successfully studied experimentally by X-ray diffraction (XRD) [1, 2a], light absorption/emission spectroscopy [2b], optical ellipsometry (OE) [7], scanning tunnelling (STM) [2c] and atomic force microscopy (AFM) [2d], optical microscopy (OM) [2e,f], photoluminescence spectroscopy (PS) [1], Raman spectroscopy (RS) [2f], selected area electron diffraction (SAED) [2g], transmission electron microscopy (TEM) [2h,g] and TEM diffraction [2i]. Of course the references cited above are only a small part of a considerable body of work existing in the literature on the P3HT morphology study by

## ABSTRACT

*K*-band electron spin resonance (ESR) technique was employed to study films of regioregular poly(3-hexylthiophene) (P3HT) and P3HT/PCBM ([6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester) blends to estimate their structural macroscopic anisotropy. As for nematic liquids (or liquid crystals) our consideration was based on the approach that the free energy of self-organised polymer molecules of P3HT is a function of molecular orientation and therefore chains in polymer films exhibit some degree of orientational order. The lamellar molecular orientation of the films was confirmed by angular-dependent ESR spectroscopy of polarons, which were considered as a localised paramagnetic centre with an unpaired carbon  $\pi$ -electron of the thiophene ring. The additional ESR signal initiated by the UV/visible CW Xe-lamp illumination of the films at air atmosphere was attributed to the negative polaron (trapped photo-electron) on the polymer chain, as well as to the radical due to chain degradation.

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different methods and are given here as examples. A brief introduction to the dependence of polymer ordering enhancement on different molecular parameters is given in [3]. An additional fruitful research in this field was already started by means of ESR [4, 5] (X-band), [6a] (K-band) and recently [6b] (W-band) results of which are in qualitative agreement with the results from XRD [2] and OE [7]. In ESR studies of ring containing conjugated polymer films (e.g. consisting of thiophene or pyrrole), one can determine the dominant orientation of the monomer ring planes of polymer chains relative to the film geometry. In this work the morphology aspects of the P3HT and P3HT/PCBM composite films study are continued by means of *K*-band ESR technique. This preliminary study demonstrates the interesting perspective of ESR measurements for the investigations of the morphology of thin semiconductors polymer films.

## 2. Experimental details

### 2.1. Materials

P3HT and PCBM (structures are presented in Fig. 1) were purchased from Aldrich. The composite films with the P3HT,

<sup>\*</sup> Corresponding author. Tel.: +49 3677 693437; fax: +49 3677 693499. *E-mail address*: alexander.konkin@tu-ilmenau.de (A. Konkin).

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