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Referee's opinion on the PhD dissertation

Influence of morphology on charge carrier transport in ultrathin films of Poly(3-hexylthiophene-2,5-diyl).

Wpływ morfologii na transport ładunku elektrycznego w ultracienkich warstwach poli(3-heksylotiofen-2,5-diylu)

by mgr inż. Łukasz Janasz

The research presented in the dissertation concerns a hot subject of materials science - electrical properties of organic semiconductors and of electronic devices manufactured using such materials. It is a part of a broad research program of the Molecular Physics Department of Lodz University of Technology headed since many years by prof. dr hab. Jacek Ulański, continuing pioneering studies of organic semiconductors of prof. Marian Kryszewski group in Lodz University of Technology and Polish Academy of Sciences.

The PhD thesis was prepared under supervision of prof. dr hab. Jacek Ulański and dr hab. Wojciech Pisula, prof. P.Ł. and Max Planck Institute for Polymer Research.

One of the most important advantages of organic materials in electronics is the possibility of using cheap, solution based deposition techniques (like printing) instead of costly vacuum deposition techniques. Another advantage is the possibility of manufacturing large area, flexible electronic devices. The smallest units of logic circuits being field effect transistors (FETs) such as these obtained and investigated in the presented thesis.

The main material of interest in the presented dissertation is poly(3-hexylthiophene-2,5-diyl) (P3HT). Polythiophenes are known since a long time but a rapid increase of interest dated since ca 30 years with the advent of detailed studies of so called conductive polymers rewarded with the Nobel Prize in 2000. Nevertheless the constant progress in synthesis of good quality regioregular material results in significant improvement of semiconducting properties and preparation of better and better electronic devices based on this polymer.

The presented dissertation has a form of three articles published in renowned international journals (IFs ca. 3.8, 6.1 and 8.1) and a short introduction and presentation of the most important results (30 pages, 80 references). The work is done in cooperation between 11 scientists from five institutions, so it is a problem to determine the contribution of mgr inż. Ł. Janasz. The student provided a set of statements of himself and coauthors of the papers (but not all of them) specifying the contribution of each coauthor. According to these statements Ł. Janasz was involved in the concepts of the papers, preparation of the P3HT ultrathin layers, studies of their morphology using atomic force microscopy (AFM), manufacturing FETs based on these layers and to some extend analysis of the FETs performance. He also prepared the first drafts of the papers. The contribution of mgr inż. Ł. Janasz was certainly the most important since he is the first author of all three articles.

The first paper [*Langmuir, 2017, 33* (17), 4189-4197] deals with the problem of preparation of extremely thin, even only few nanometers thick, spin-cast layers of P3HT and charge transport in them. FETs with such ultrathin (down to ca. 2 nm) P3HT active layers were fabricated via solution technique using polymers with various molecular weights (34-170 kg/mol). It was shown that hole transport can proceed even in a practically monomolecular layer, although the mobility is higher if the layers are a few nm thick. This increase was explained by a transition from 2D to 3D transport.

In the second one [*Journal of Materials Chemistry C* 2016, *4* (48), 11488] the preparation of ultrathin P3TH layers using partially aggregated solution is described. It is shown that the aggregation depends on the solvent and time (as expected by the way) and can considerably improve the transport properties of the obtained nanolayers. Although the P3HT aggregation in various solvents was studied before by other groups it was never used for preparation of so thin polymer layers.

The third paper [*ACS Applied Materials & Interfaces* 2017, *9* (24), 20696] reports preparation of films for ambipolar FETs using blends of P3HT and a fullerene derivative phenyl-C61-butyric acid methyl ester (PCBM), a well-known n-type semiconductor. The authors improve phase separation of the two components using aggregated P3HT in solutions.

Generally the papers present top level in this domain both from the point of view of the novelty of the results and the experimental methods used. A strong point of the work are

AMF studies of the film morpfology. Especially impressive for me is the quality of phase images and comparisons.

The most important achievements in my opinion are:

- Preparation of ultrathin layers of P3HT.
- Showing that only four edge-on oriented polymer layers of are sufficient for efficient hole transport in P3HT films.
- Showing that aggregation of the polymer in solution significantly improves ordering, crystallinity and consequently the hole transport in such ultrathin films.
- Showing that aggregation of the polymer in solution can improve phase separation and allows fabrication of high performance ambipolar FETs based on P3HT:PCBM blends with similar, very high mobilities (10^{-2} cm^2/Vs) for both holes and electrons (heterojunction-like systems).

The work is generally well-written and argumentation is convincing. I have only following remarks:

- I found strange a disagreement between height profiles and height images (e.g. Fig.3c and Fig 4 in [*Langmuir*, *2017*, *33* (17), 4189-4197]). In the step-high measurements the changes of the layer thickness are of the order of 1 nm or less. However on the corresponding height images the color scale is 8.2 and 3.1 nm and most of it is used. Thus the profiles from these image would show much higher variations of height.
- The phase contrast and height images in principle could be obtained from the same scan and show the same part of the sample surface. However I could not find any common characteristic features on the corresponding images.
- An information on the AFM tip radius is missing, although it may be important for analyzing so small objects because of the possible so called tip-convolution effect.
- On p. 25 the author stresses “rigidity” of both P3HT fibers and PCMB. For me this property (not being measured by the way) except qualitative conclusion from AFM) is of secondary importance. What is really important is the ordering of molecules and number of defects.
- The aggregation of P3HT in solution is similar to solution crystallization of e.g. polyethylene. The polymer is dissolved at higher temperature and aggregation or

crystallization takes place after cooling to a lower temperature (room temperature in this case. I would expect some discussion of phase separation process in polymer solution including segregation of molecules of low and high molecular weight.

- It would be interesting to check the effect of lowering the aggregation temperature, especially in the solutions in which aggregation process took weeks.
- It is surprising that crystallinity of the films prepared using aggregated toluene solution is lower than that obtained using fresh solution.
- Under each figure the author writes that it was "reprinted with permission" Did he really demanded permissions from the publishers? To my knowledge it is not necessary for PhD thesis.

Final conclusions

In summary of mgr inż. Łukasz Janasz presented an interesting research which certainly makes an important contribution to understanding of relationship between morphology and transport of charge carriers in ultrathin organic layers. Besides of three articles being a part of the presented thesis he is a coauthor of another three papers and participated in realization of four research projects.

In my opinion the presented thesis fulfills the requirements of Act on Scientific Degrees and Title and Degrees and Title in the Art of 2003 (Dz. U. Nr 65, poz. 595) and I strongly recommend passing to subsequent steps of the PhD procedure.

I also recommend the Faculty Council to acknowledge the thesis of mgr inż. Ł. Janasz as a distinguishing one.

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