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Report on the Ph.D. thesis of MSc Izabela Tszydel on:

" Thin Film Organic Field Effect Transistors with n-type channel "

presented to the Technical University of Lodz

The Ph.D. thesis prepared by MSc. Izabela Tszydel is focused on the preparation and characterization of n-type organic field effect transistors (OFETs). Particularly, it attempts to exploit a zone casting method for the deposition of organic semiconductors into an active channel of the transistor. The technique of zone casting of organic materials had been previously developed in the laboratory of the supervisor at the Lodz University of Technology. As a major advantage it offers a possibility to prepare well defined structures of organic materials, particularly those having an extended planar molecular structure. Since the charge transport properties of organic semiconductors, and n-type organic semiconductors in particular, depend in a large extent on the effective overlap of π-electron orbitals of adjacent molecules, the possibility of controlling the material structure on a molecular level is of great importance and one of the main prerequisites required to observe the field effect in the transistor device. The work represents a valuable contribution to the development of the material base for the flexible large area printed electronics. This booming area of science, which is already merging an industrial level, bringing new concepts in several applications like smart packaging, functional textiles, flexible displays etc., should bring the reduction of the manufacturing costs but, additionally, it should allow the production of cheap disposable electronics with mechanical flexibility that is needed when the electronic device has to be combined with other flexible materials. At the same time, the best solution for the mass production are multifunctional materials, which could combine several functionalities like photogeneration of charge carriers and good charge carrier transport properties, i.e. they might be used in several devices with only a small modification.

Although the concept of this Thesis is not completely new MSc. Tszydel showed some original and interesting results. Most interesting seems to be the finding of the influence of the potential stress on the decrease of the threshold voltage and the asymmetry of the current between the source and drain electrodes with regards to the casting direction during the thin film preparation:

The work was purely experimental and consists of three major parts: (i) technology part aimed at the optimization of the zone casting method for obtaining the required structure yielding the best performance of the OFET, (ii) in the characterization part various methods were applied to obtain the electrical and morphological characterization of the prepared structures, and (iii) in the short application part the attempt was made to apply the prepared structures in the flexible devices on polymer substrates and combine the n-type semiconductors with p-type materials in ambipolar devices. The synthesis of the materials used for the study was not the aim of the doctoral thesis, materials from a cooperating laboratory in Warsaw were used instead, together with some commercially available organic semiconductor.

The text of the submitted thesis is rather short, consisting of 89 pages included 62 figures, divided into 6 chapters, Abstract and List of abbreviations and acronyms. The text flow is classically structured. On 35 pages it offers an introduction to the area of organic electronics, organic semiconductors and organic field effect transistors. All the experimental methods used in the study are described briefly on 10 pages and remaining 36 pages are dedicated to the results and discussion. A long list of 147 references at the end of the thesis shows that the actual state-of-the-art of the studied topic is well covered.

The text is written by simple and understandable English. It is written properly from the logical point of view. From the formal point of view I would object many spelling and typing errors. Writing the thesis would evidently require rather more attention and care.

Concerning the submitted text I have several objections and questions:

1. There are some inaccuracies within the text:

a) First reports on organic semiconductors occurred in the literature much earlier than in late sixties as written in the introduction. First papers where the studied materials were described as organic semiconductors appeared in 50s already: see e.g. H. Akamatu et al. „Organic semiconductors with high conductivity. Complexes between polycyclic aromatic hydrocarbons and halogens. Bulletin of the Chemical Soc. of Japan 29(2), 213-218, 1956 or M.M. Labes: Organic semiconductors. Some characteristics of the p-phenylenediamine-chloranil complexes. J.Chem.Phys. 32(5) 1570-1572, 1960.

b) Page 8: p-type organic semiconductors are characterized with low ionization potential and not with the high one as written in the Thesis. This is probably only an unfortunate expression of the fact that the HOMO level is located higher in the energy scale.

c) Equation 2.1 is probably wrong with regards to V_D.

d) In the form 2.4 on the page 17 "V" should mean "V_G"

e) Page 25 – organic materials are sublimed and not evaporated – it makes a difference from the physical point of view.

f) Figure 4.7 yields the same information as Fig. 3.6 and, hence, it is redundant.

g) The dose during the zone casting should be probably in μl/s , not μm/s

2. Some additional comments and questions:

a) Page 9: For the increase of the stability it is advised to lower HOMO level in the energy scale. What would be the simultaneous effect in this case on the hole mobility?

b) There are not many n-type materials available as it is in the case of p-type organic semiconductors. What is the reason for it?

c) On p. 18 the higher threshold voltage is ascribed to the presence of traps. However, the dielectric constant seems to have primary importance.

d) If it was necessary to adjust the casting conditions for different seasons during the year due to the varying humidity and ambient temperature, why a closed box with a defined tempered environment was not used?

e) According to the Fig. 5.2 the polarized absorption of NBI-4-t and NBI-4-n-BuPh gives opposite relation between the polarization vector of light and the zone casting direction. This is quite interesting since these two materials differ only in the isomerization of the butyl group. Is there any reason known that could explain this behavior?

f) The discussion of the bias stress effect and of the effect of the assymetry of the I_{SD} with regards to the zone-casting direction is rather scarce. It would be advised also to use the capacitance measurements to confirm the sketched explanations. There are very interesting phenomena confirming the strong influence of the molecular ordering in the vicinity of the electrodes on the performance of the OFETs.

g) There is a difference around 14° in the diffractograms of TIPS pentacene shown in Fig. 5.28 a) and b). This is an experimental error or it shows a presence of a different polymorph?

Despite some objections and critical comments that can be probably answered by MSc. Tszydel during the defense of her thesis, the presented work contains many interesting new experimental results and provides their interpretation, although sometimes in a rather brief way. The author MSc. Tszydel has proved his ability to design and perform experiments and to critically interpret results. This can be also documented by the fact that she is a coauthor of 5 publications in impacted international journals, in one of them she is a first author. In my opinion her work represents an important and original contribution to the field of organic electronics.

I recommend to permit MSc. Izabela Tszydel to defend the presented Thesis.

Dr. Jiří Pfleger