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Prof. Grzegorz Mlostoń

University of Łódź,
Department of Organic & Applied Chemistry
Tamka 12, 91-403 Łódź, POLAND
Tel. (48) (42) 635 57 61
Fax: (48)(42) 665 51 62
e-mail: grzegorz.mloston@chemia.uni.lodz.pl

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Review

of the PhD Thesis entitled 'Organic selenium compounds and their modern application' by Ing. Jaroslav Charvot (University of Pardubice)

The reviewed work has been prepared at University of Pardubice under supervision of Professor Filip Bures; part of experimental work was also performed at University of Erlangen-Nürnberg in the research group of professor Julien Bachmann. Professor Filip Bures is a well-known expert in the field of heterocyclic chemistry but in recent years he also has successfully been working on problems related to materials chemistry. This stream of the research interest of the supervisor is clearly demonstrated by the PhD Thesis submitted by Ing. Jaroslav Charvot. The main problem elaborated in the course of this project was elaboration of efficient protocols which could be applied for deposition of inorganic, selenium compounds in the form of atomic monolayer on the surface of diverse materials with potential, further application in materials chemistry and related fields of applied physics. As the basic methodology for preparation of target materials covered with atomic monolayer of respective metal selenide, a known technique, namely 'atomic layer deposition' (ALD) was selected and explored in experiments performed by the candidate.

The ALD-technique is based on sequential gas-phase thermolysis and chemical vapours (thermolysate) deposition on the desired material. The majority of ALD reactions involve two substances (substrates) also called as 'reactants'. ALD is widely applied as a key process in fabricating semiconductor devices, and also as a tool for preparation of other nanomaterials with special physico-chemical

properties. For this reason, in recent decades, there is a great demand on elaboration of efficient methods for preparation of desired precursors and on optimization of thermal processes leading to the formation of the mono-layer with required properties. Similar to most of high-tech techniques, ALD possesses clear advantages but also some disadvantages can be pointed out. Among important advantages, a very controlled production of a film to an atomically specified thickness has to be stressed. From disadvantages, high purity of the applied substrates is rigorously required, what results in substantial enhancement of total costs of the applied synthetic procedures. Keeping in mind all these facts, one can underline that the topic of the reviewed PhD work was correctly formulated and it corresponds to modern trends in development of methods for fabrication of novel nanomaterials, based on metal selenides, which are known as unique compounds with special importance for diverse branches of nanotechnology and related areas, e.g. materials engineering.

Submitted PhD Thesis consists of five main chapters (70 pages), conclusions (3 pages), and the list of cited literature with 143 references prepared in accordance with international standards on abbreviation of journal titles and bibliographic data. There is also the list of 5 publications from the period 2020-2021 prepared on the basis of the results collected mainly by Ing. Jaroslav Charvot and for this reason, in four of them he appears as the first Author. In addition, he also is a co-author of 3 more publications which appeared in 2020 and relate to some problems of materials chemistry related to questions discussed in his dissertation.

Brief 'Introduction' and 'Aims of the dissertation' are followed by quite extend 'Literature review part' (31 pages) which introduces the reader into most important problems related to ALD technique and application of metal selenides thin films in selected fields of nanotechnology.

Experimental part consists of detailed procedures which were applied for preparation of a series of pure selenoorganic compounds which subsequently served as precursors of reactive selenium intermediates in the course of fabrication of metal selenides mono layers via ALD. This part deserves a brief comment; all preparative procedures were

carried out carefully and demonstrate excellent laboratory skilfulness of the candidate. Due to instability of numerous selenoorganic compounds and in most cases, very unpleasant odorous effects which accompany laboratory operations, their preparation and purification is a challenging task. On spite of all these problems, Ing J. Charvot obtained selenylated silanes as designed precursors for pyrolytic decomposition, generally, in good to excellent yields (up to 98%).

An analogous, tellurium containing precursor, i.e. compound **29** was also obtained in good yield of 68% and it was involved in the study. Structures of all compounds were elucidated on the base of spectroscopic data and along with typical techniques (^{1}H, ^{13}C-NMR) rarely applied heteronuclear spectroscopy, such as ^{77}Se-, ^{29}Si- as well as ^{125}Te was also applied. In all cases, molecular formula was determined by registration of the EI-MS spectrum. I can guess that instability of synthetized seleno-silicium heterocycles was the main reason for the missing elemental analysis. In addition to cyclic selenides, also some acyclic representatives, containing labile Si-Se (compounds **23** and **24**) or Sn-Se (compounds **5** and **7**) bonds were also prepared and involved in the study.

In a series of preliminary experiments, thermal analysis of seleno-organic precursors was carried out and the results are discussed in Subchapter 13.3. Based on results of this analysis four candidates, i.e compounds **9**, **10**, **19** and **20** were selected as promising candidates for efficient fabrication of metal selenide thin films in reactions with $MoCl_5$ and $SbCl_5$. Deposition of $MoTe_2$ using tellurium containing precursor **25** was also carried out and the results obtained in this series are discussed in a brief Subchapter 13.7..

Final ALD experiments and analysis of quality of the obtained thin monolayers revealed that two compounds, namely six-membered **19** and four-membered **20** are the best candidates for deposition of $MoSe_2$ thin layer. In addition, two linear selenides **5** and **7** (and rather not **6** as suggested in 'Conclusion' on page 71) were also successfully applied for the formation of Sb_2Se_3 in reaction with $SbCl_3$.

In general, text of the reviewed PhD Thesis is well written and experimentally obtained data convincingly proof the formulated conclusions. Presentation of reactions by structures and equations is well organized and helpful for correct understanding of

the discussed results. List of cited literature, being an important part of any scientific paper, is well prepared and correctly reflects the most significant contributions of other groups to the studied subject of metal selenides thin layers, produced by ALD technique.

Two critical comments are following:

1) the term '.. asymmetric compounds ...' (e.g. page 71) should be replaced by 'non-symmetric compounds'. The term 'Asymmetric compounds' is reserved for the group of compounds possessing chirality center/centers. In this part of organic chemistry which deals with the problem of asymmetry, the term 'asymmetric synthesis', leading to optically active products (organic and inorganic compounds), is also used.

2) Apparently, stannyl selenides '.. **5** and **6** ...' should be given the numbers '... 5 and 7 ...', respectively. In fact, I could not find 'stannyl selenide **6**' prepared in 'Experimental' and it was cited in 'Literature review part' only (Scheme 6, page 19).

However, both comments do not diminish excellent achievements presented by Ing. Jaroslav Chavrot and in summery of my opinion I would like to emphasize that his PhD Thesis should be considered as a valuable contribution to a better understanding on the important problems related to metal selenides thin layer deposition via ALD technique. Described results are important not only from the point of view of fundamental characteristics of the studied class of Se-heterocycles but also enable the chemical community better cognition of their physico-chemical properties and practical utility for fabrication of thin layers wanted by nanotechnology.

I am fully convinced that the reviewed PhD Thesis fulfils all requirements expected for a scientific work, which can be considered as a proper base for graduation with the PhD title in chemistry at University of Pardubice and it opens the way to the planned public defence. I recommend Ing. Jaroslav Charvot to enter the next stage of the dissertation procedure scheduled by the proper body of the Faculty of Chemical Technology.

Taking into account international standard of the reviewed dissertation and high quality of the research, confirmed by publishing of practically all results in internationally recognized peer-reviewing journals, I suggest nomination of eng.

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Jaroslav Charvot either to the Prize of the Rector of the University of Pardubice or alternatively, to the Prize of the Dean of the Faculty of Chemical Technology.

Łódź, June 5th, 2022

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