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вул. Підгірна, 46, м. Ужгород,
Закарпатська область, Ukraine, 88000
тел.:+38(03122)3-33-41, факс:+38(03122)3-42-02
e-mail: official@uzhnu.edu.ua
Код ЄДРПОУ 02070832

MINISTRY OF EDUCATION
AND SCIENCE OF UKRAINE

STATE UNIVERSITY "UZHHOROD NATIONAL UNIVERSITY"

46 Pidhirna St, Uzhhorod,
Transcarpathia, Ukraine, 88000
tel:+38(03122)3-33-41, fax:+38(03122)3-42-02
e-mail: official@uzhnu.edu.ua
Identification code 02070832

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Prof. *Volodymyr Mitsa*, DrSc.,
Department of information science
and physics and mathematics disciplines
Faculty of Information Technologies
Uzhhorod National University
Narodna Square 3, Transcarpathian region,
88000 Uzhhorod, Ukraine,

REVIEWER'S REPORT

On the habilitation thesis by Mgr. *Vladimír Komanicky*, PhD.,
"Electron beam induced effects in amorphous chalcogenide glass thin films"

The reviewed habilitation thesis is presented as a generalization of research results presented in twelve monothematic works and two patents, in which the author Vladimír Komanicky had a leading role, made a decisive contribution and was a corresponding author in 9 works and two patents. The research results presented in this dissertation show scientific activities of the applicant of academic title "associate professor" in such field of condensed matter physics as electron-induced effects in amorphous semiconductor films.

The habilitation thesis is written on 166 pages and consists of Introduction, 3 Chapters, References and Appendix. The work contains 39 figures, 4 tables. The bibliography contains 103 sources, 14 of which are publications and patents of the author (they are highlighted in bold in the References). Appendix (97 pages out of 166) contains works published by the author on this topic.

The relevance of this scientific work follows from the chosen object and subject of research. The research object was amorphous chalcogenide films - these are non-crystalline materials based on sulfur, selenium and tellurium. Their attractiveness for both fundamental research and practical applications is due to unique properties - photoinduced phenomena that arise when these materials interact with electromagnetic radiation in the region of their absorption edge. The research subject was electron-induced effects that arise in chalcogenide films under irradiation with an electron beam. The effects of electron irradiation have been studied most fully for dielectric materials, especially those used as electronic resists. Such effects have been studied very little for chalcogenide films and models and mechanisms of the effects are completely absent. In this regard, the topic of scientific research presented in this dissertation is very relevant, since the scientific results presented in the dissertation fill the gap in this scientific field.

The habilitation dissertation consists of an introduction, three sections, a list of references and appendices. The introduction presented a brief overview of the key physical properties of amorphous chalcogenide materials, which form the basis for practical applications of these materials in various areas. Also noted is the lack of systematic studies of the interaction of chalcogenide materials with electron irradiation. The purpose of the research presented in the dissertation is formulated, which fills this gap and makes it possible to practically use the discovered phenomena.

The first chapter presents a model of electron-induced phenomena in amorphous chalcogenide materials. This model was developed and tested on films of chalcogenide systems As-Se, Ge-As-Se, Ge-Se. Despite the difference in the structure of these films, the developed model is effectively used to interpret the phenomena of surface structuring of films of various chemical compositions under the influence of an electron beam. This is demonstrated in the author's publications [35, 53, 54, 62, 94]. An explanation of the mechanisms of formation of the surface electron-induced relief and changes in the volumetric charge density and internal electric field strength are clearly demonstrated in Fig. 7. The same section provides formulas for calculating the volumetric charge density and the internal electric field during irradiation of chalcogenide films with an electron beam.

The second chapter describes the results of studies of the features of electron-induced phenomena in chalcogenide films using the methods Atomic force microscopy, Kelvin force microscopy (KPFM), X-ray energy dispersive analysis (EDAX), X-ray absorption fine-structure (EXAFS) , X-ray absorption near-edge XANES. As a result of such complex studies, the effects of local accumulation and long-term charge retention in chalcogenide films during electron irradiation, electron-induced mass transport and surface structuring of films in the irradiation region were discovered. It has been established that the relaxation time of the positive charge in the region of low irradiation doses is significantly (5–20 times) less than the relaxation time of the total charge in the region of electron-induced space charge at high doses.

The discovery in some chalcogenide films under certain experimental conditions of a state of hydro-electrodynamic instability was a unique researches result. An asymptotically sharp nanostructure (the Taylor cone) was formed on the film surface as a result of this instability. The generation of a Taylor cone in liquid (molten) metals in specially designed capillaries under the influence of a strong electric field is used to manufacture ion beam sources. A beam of molten metal ions is emitted from the top of the Taylor cone. However, in the observed phenomenon here, a Taylor cone is formed on the surface of chalcogenide films only under the action of an electron beam. The indicated electron-induced phenomena for chalcogenide films, as well as the formation of Taylor cones under the influence of electron beam irradiation, were discovered and interpreted for the first time. All these processes have been studied in detail in chalcogenide films As_xSe_{100-x}, $Ge_xAs_ySe_{100-x-y}$, Ge_xSe_{100-x} at different concentration ratios of the initial chemical elements.

The third chapter presents of applications based on electron-induced effects in amorphous chalcogenide materials. The implementation of surface nanostructuring processes during electron irradiation makes it possible to use amorphous chalcogenide films as electronic resists. In this work, in contrast to known dielectric polymer resists, we demonstrate the possibility of implementing a process of direct one-stage recording of images on chalcogenide films without chemical etching. The possibility of implementing a process of direct one-stage recording of images on chalcogenide films without chemical etching have been demonstrate in this work, in contrast to known of two-stage lithography on dielectric polymer resists. The ability to implement both positive and negative lithography on the same chalcogenide film is a separate feature of such electron lithography. The examples that are demonstrated in the work indicate the effectiveness of the developed recording method and the prospects for expanding its practical use.

The increase in the catalytic activity of thin platinum films catalyst as a result of its deformation under the influence of photoinduced mass transport in the chalcogenide film is also an important practical application of the effects induced by a laser beam in chalcogenide films. The deformation of the platinum catalyst was achieved as a result of surface structuring of the chalcogenide film under the action of a polarized laser beam. As a result, an almost 7-fold increase in catalytic activity in oxygen reduction reactions was achieved.

The unique physical phenomenon of Taylor cone formation is proposed to be used for the production of asymptotically sharp structures, for example, in the production of scanning probe microscopy tips. A patent has been written for the implementation of such a process - applications for atomic force microscopy and nanoemitters. A patent has also been written for obtaining a micro-relief structure in a layer of chalcogenide glass for the production of periodic nanostructures, arrays of nano-sized ion sources, rewritable information storage devices, focusing devices for new types of integrated optics.

It can be stated that the presented habilitation thesis represents a well-planned scientific work which was carried out on a high scientific level with used a modern experimental equipment. As a result of which: 1) new physical phenomena have been detected and studied in a wide class of non-crystalline materials - amorphous chalcogenide films; 2) the obtained results were interpreted and the mechanisms were established and a model of electron-induced processes in chalcogenide films and glasses was developed; 3) the application of the detected effects was proposed and successfully tested. The first two points emphasize the scientific value of the research results. The third point indicates their practical use. The author took advantage of the high level of his nanolaboratory during these scientific studies. He was able to carry out unique pioneering experiments on the interaction of the electron beam of a scanning electron microscope with amorphous semiconductor films and to observe are new interesting physical phenomena. Using AFM scanning of nanostructured films in various modes, as well as the use of Kelvin force microscopy, It was possible to establish the mechanisms and develop a model of electron-induced processes for such a wide class of amorphous semiconductor materials as chalcogenide films succeeded using AFM scanning of nanostructured films in various modes, as well as the use of Kelvin force microscopy.

The applicant possible to overcome during the research a significant technical problem associated with the reaction of chalcogenide films to electron irradiation and laser irradiation during AFM scanning. In particular: 1) the surface of chalcogenide films is quickly charged when forming matrices of irradiated dots at various doses, as well as logos during electron lithography and then further directed irradiation with an electron beam becomes impossible; 2) the photosensitive chalcogenide film is illuminated by a laser beam past the cantilever during scanning of the surface relief in AFM. The solution to these technical problems is briefly indicated in some of the author's publications. However, in the future, it would be useful to publish a separate work devoted to the technical implementation of studies of electron-induced processes in chalcogenide films and overcoming these difficulties. This would make it possible obtaining unique asymptotically sharp structures - Taylor cones in other scientific laboratories and others electron induced structures.

In conclusion, it can be stated that the presented habilitation thesis establishes the author as a mature scientist physicist. I evaluate the habilitation thesis as a whole positively and consider it a convincing basis for assessing the applicant's competence in terms of claims for the professional erudition of a university associate professor. I believe that the presented dissertation meets all the requirements for such habilitation dissertations. Therefore, on its basis and after a successful habilitation procedure, I recommend appoint Mgr. Vladimir Komanicky, Ph.D. for associate professor title in the field "Physics".

Uzhhorod, 30.05.2024

Prof. Volodymyr Mitsa, DrSc.

Prof. Myroslava Lendel
Vice-Rector