REVIEW

on the PhD thesis for the educational and scientific degree "Doctor"
Professional field 4.2. Chemical Sciences, Scientific specialty "Electrochemistry"

Scientific organization: Institute of Physical Chemistry, Bulgarian Academy of Sciences (BAS), Sofia

Author of the PhD thesis: Vesselina Stefanova Milusheva, PhD student

Title of the PhD thesis: "Obtaining and characterization of nanostructured layers of copper and anodic aluminum oxide"

Prepared by: Nikolai Stoianov Boshkov, Professor, PhD, Eng. (Institute of Physical Chemistry, Bulgarian Academy of Sciences)

1. General information and brief biographical data about the candidate

Veselina Stefanova Milusheva was born on September 25, 1972. For the period 1990 - 1995 she studied at the University of Chemical Technology and Metallurgy, Sofia, where she obtained a Master's degree in Chemical Engineering in the specialty "Inorganic and Electrochemical Production". Subsequently, in 1995 - 1996, she attended the Institute for Postgraduate Qualification at the University of National and World Economy, Sofia, where she obtained a qualification as a manager "specialist in management and accounting activities". She is currently a part-time lecturer at the Department of Chemistry at the Technical University, Sofia, and also holds the position of "chemist" in the Department "Electrochemistry and Corrosion" at the Institute of Physical Chemistry - BAS. Since January 2018, she has been a part-time doctoral student at the Institute of Physical Chemistry - BAS with scientific supervisors Associate Professor Dr. B. Tsaneva and Professor Dr. M. Petrova. Her professional interests are in the field of applied electrochemistry - electrochemical deposition of metal coatings, preparation of nanowires, metallization of dielectric surfaces. Her scientific activity is related to the electrochemical preparation of nanostructured oxide layers based on anodic aluminum oxide and their application as a matrix. In her experimental and scientific activity, V. Milusheva uses English and Russian languages at a very good level, as well as partially German.

2. Description of the submitted materials and relevance of the topic of the PhD thesis

The submitted materials include PhD Thesis, Abstract, Reference for contributions to the thesis, List of conference participations, List of the scientific publications included in the dissertation, List of all scientific publications, List of citations and CV of the PhD student. The PhD thesis itself is mainly based on a group of eight publications in total, all with co-authors. Of these, one article was published in a journal with a quartile Q2, two are with a quartile Q4, and the remaining five publications are in scientific forums and in a journal without a quartile, having a DOI, ISSN or ISBN. In four of these articles, V. Milusheva is the first, in two - the second and in two others - the third author. There is also one article in a journal with a quartile Q1, which, however, is not on the topic of the dissertation.

In addition, information has been submitted about a total of six of her participations in scientific forums, at one of which V. Milusheva gave an oral report, and the remaining reports with her participation were poster presentations. In five of the author teams of the publications in these forums, the doctoral student is the first author, and in one - the third.

So far, I have no information that any of the above-mentioned publications or reports have been used in another PhD thesis for the educational and scientific degree of "doctor". From the materials given to me for review, I can conclude that the current PhD thesis fully complies with the requirements of the Regulations on the Conditions and Procedure for acquiring Scientific degrees and for occupying Academic positions at the Institute of Physical Chemistry - BAS.

The PhD thesis is written on 140 pages, including the cited literature from 163 sources, as well as the List of the scientific publications, scientometric data, conclusions and contributions. The text part presents a total of 69 figures and photographs, 19 tables, 35 equations, as well as an additional List of symbols and abbreviations used.

The PhD thesis is very well structured and contains the following parts: Symbols and abbreviations used; Introduction; Literature review; Goals and objectives of the dissertation work; Methods, materials and experimental conditions; Experimental results; Contributions of the dissertation; Scientometric data; Literature.

Regarding the relevance of the topic - it is known that the anodization of aluminum (anodic aluminum oxide - AAO) allows the creation of matrices of parallel nanopores, located perpendicular to the surface, which are widely used in electronics and communication technologies. This material has very good mechanical properties and thermal stability, which is why it can be used as a basis for catalysts, for the synthesis of nanowires and nanotubes, and also for the creation of some nanomaterials. The structure of the pores (diameter, depth and distance) can be controlled and reproduced using electrochemical and other methods. An

additional advantage of AAO is its compatibility with a large number of materials such as metals, metal oxides, polymers and semiconductors, among which copper occupies a special place due to its extremely suitable characteristics.

A major challenge for these objects is the technology for wiring by means of chemical or electrochemical copper plating while simultaneously preserving the insulating properties of AAO. This would allow the creation of a nanocomposite layer with interesting characteristics – to be conductive perpendicular to the surface and to be an insulator in a parallel direction. The success of such processing would allow the production of conductive images in a layered structure of "conductor / insulator / conductor" type and would help in the obtaining of electronic elements, sensor systems, catalysts and biomedical devices.

From the above, it can be concluded that the chosen topic of the PhD thesis is relevant in view of obtaining nanocomposite materials based on Cu/AAO and layered structures of Al/AAO/Cu. For this purpose, the possibilities for catalyzing the chemical deposition of copper have been studied and new electrolytes for copper plating with neutral or slightly alkaline pH have been proposed. In addition, the most appropriate conditions for high-quality, reproducible and rapid production of nanocomposite materials have been determined.

The extensive literature review made by the PhD student regarding the studied structures clearly demonstrates that Vesselina Milusheva is very well acquainted with the essence of the research problem and has correctly interpreted the available scientific information with a view to the successful implementation of the goals and objectives of her PhD thesis.

Based on this, it can be concluded that the research conducted and the experimental data obtained relate directly to a significant problem, distinguished by a scientific and scientific-applied focus, the relevance of which is beyond doubt.

3. General characteristics of scientific research

As mentioned, the topic of this PhD thesis is related to the study of the possibilities for deposition (chemically and electrochemically) of copper layers on anodized aluminum and the creation of nanocomposite materials based on Cu/AAO and layered structures based on Al/AAO/Cu. Therefore, the goal is reduced, in addition to the production of layered materials based on nanoporous AAO and copper with anisotropic electrical conductivity, also to their characterization in terms of composition, structure and possibilities for application in electronics.

To achieve the goal set, research has been carried out on:

- study of the processes of thinning of the barrier layer at the Al/AAO interface with subsequent chemical or electrochemical growth of copper through the nanopores of AAO and obtaining a composite material with a certain conductivity through the nanocomposite;

- creation of methods for chloride-free activation of AAO and subsequent chemical copper plating;

- obtaining suitable compositions for chemical copper plating in the pH range 4.0 – 9.5 with reduced aggressiveness towards AAO;

- determining the composition and structure of the coatings according to the deposition conditions in view of the possibilities for their application in electronic technologies;

- modifying AAO to increase its chemical resistance and the possibility of selective chemical deposition of copper.

To achieve the tasks set in this PhD thesis, electrolytes for anodizing such as oxalic, sulfuric and phosphoric acid, as well as selected electrochemical and other methods, were used. The newly formed barrier layer was thinned electrochemically (by voltage reduction methods or galvanostatically), and subsequently chemically. The catalysis of AAO was carried out without the presence of chlorides in four ways - deposition of contact copper; sensitization and palladium activation; palladium activation with thermal decomposition; catalysis by photochemical deposition of copper nuclei on AAO functionalized with TiO_2-sol. The chemical deposition of copper on AAO/Al is carried out by three compositions according to the available reducing agent – sodium hypophosphite, phosphorous acid, formaldehyde.

A large number of experimental methods were used to characterize the newly obtained samples, such as: scanning electron (SEM) and energy-dispersive microscopy (EDX); X-ray structural analysis (XRD); photoelectron spectroscopy (XPS); X-ray fluorescence spectroscopy (XRF) as well as software processing of images from optical and scanning electron microscopy.

In my opinion, the experimental compositions and research methods selected and used by the PhD student fully correspond to the set goal and tasks of her thesis. The data obtained as textual and illustrative material are systematized very well. The analysis and comments on the conducted research clearly prove that V. Milusheva is well acquainted with the characteristics of the materials used, as well as with the applied methods. The conclusions and findings show that the educational and scientific goals of the doctoral program have been met successfully and at a very good professional level.

4. Main scientific and scientific-applied contributions of the PhD thesis

As a result of the experiments, nanocomposite materials were obtained by filling nanoporous layers on anodized aluminum with copper after electrochemical thinning of the barrier layer,

followed by chemical dissolution. The optimal thinning conditions were achieved during a 60-minute treatment of the samples, after which preliminary impregnation of AAO (with the barrier layer removed) and potentiostatic mode at a relatively low concentration of copper ions were applied.

The chemical deposition of copper on AAO of a hypophosphite composition was carried out in the presence of small amounts of nickel (to maintain the autocatalytic nature of the process) at pH < 6. It was found that the morphology of AAO has a stronger influence on the structure of the layers than the method of palladium activation. The treatment of AAO in titanium sol increases the chemical resistance of the oxide in strongly alkaline electrolytes. The optimal conditions for deposition in acetate-phosphorus compositions have also been established. The sheet resistance of the layered structures and the solderability of the copper layers have been determined.

In all these experimental data, it can be concluded that the main contributions of the PhD thesis correspond to the set goal and the tasks associated with its implementation, namely:

1/. A layered material Al/Cu+AAO/Cu with electrical conductivity was obtained after thinning the barrier layer of AAO on aluminum and direct filling (chemically or electrochemically) of its pores with copper.

2/. New stable compositions with sodium hypophosphite or phosphorous acid as a reducer have been proposed and tested, which allow for the preparation of Al/AAO/Cu+AAO/Cu layered structures while preserving the insulating properties of AAO and with possibilities for application in electronics.

3/. A new methodology has been created to improve the chemical resistance of AAO, enabling the formation of conductive images on anodized aluminum.

5. Reflection of the candidate's scientific publications in Bulgarian and foreign literature

According to the information submitted, a total of 4 citations have been found so far on the scientific works of V. Milusheva, included in the PhD thesis. This is a very good indicator, taking into account that these articles were published relatively recently, which shows that the presented data are interesting and an increase in the number of citations can be expected in the near future.

In addition, an additional 33 citations were found for the last eight years on the attached article, which is not on the topic of the PhD thesis.

6. Critical remarks, recommendations and questions

I have the following critical remarks:

The present PhD thesis is written at a very good level, but in some places in the text technical omissions or errors are found, such as:

1/. Page 4 – "current density" in chemical deposition is commented on;

2/. Page 8 – the chemical reaction according to equation (3) is not balanced;

3/. Page 9, Figure II.2 – one part of the figure is in Bulgarian, the other – in English; the situation is similar on page 15, Figure II.7, as well as in Table IV.3, etc.

4/. In the part presenting the main ingredients of the chemical copper plating compositions, no information is given about the brighteners (page 31).

5/. On pages 34 and 35, are terms such as "template" and "resist" used?

6/. There is a discrepancy in the number of publications on the topic of the PhD thesis – in the thesis itself and in the attached file of documents, eight articles are listed, and in the Abstract – seven.

Despite these comments, I would like to note that the technical omissions or errors identified and listed by me above do not otherwise change my very good overall impression of the dissertation and of the volume and quality of the research carried out by the PhD student and her scientific supervisors.

I have the following questions for the PhD student:

1/. What is the number of test specimens used for the individual experiments and what is the reproducibility of the presented data?

2/. Why is there no justification given in Part 1.1. for the use of test specimens of different sizes in the interval between 1 and 16 cm^2?

3/. Why is there no homogeneous filling of the pores at the maximum concentration of $CuSO_4$ (Fig. IV.7)?

4/. Have any preliminary studies been conducted on the corrosion resistance of the obtained materials in model test environments, for example those with the presence of chlorine ions?

7. Personal impressions

My personal impressions of the PhD student are very good. I believe that the studies were conducted competently and at a very good professional level, for which both scientific supervisors have undisputed merit. On the other hand, however, I accept that what was done is also to a significant extent her personal work, given her place in the author groups of the scientific publications, as well as the information presented for the oral and poster reports. The analysis of the specialized international literature on the problem and the interpretation of the data obtained, including the presented conclusions and contributions, are logical and well-

founded. Based on this, it is obvious that the efforts of the PhD student have led to noticeable professional growth, which will give an additional impetus to further scientific activity. As a result of the development and formation of her PhD thesis, Vesselina Milusheva has increased her qualification in this topic, which has also achieved the main goal of this type of procedure. The text material from the attached Abstract of the PhD thesis correctly reflects the preliminary concept laid down for implementation, the experiments conducted and the experimental data obtained.

CONCLUSION

Based on the above, as well as on the presented conclusions and contributions of the PhD thesis, its importance in scientific and applied aspects, and also the obviously very good knowledge of the PhD student in the field of Electrochemistry, I propose to the members of the Scientific Jury to vote positively for awarding PhD student Vesselina Stefanova Milusheva the educational and scientific degree "Doctor" in Professional Field 4.2. Chemical Sciences, Scientific Specialty "Electrochemistry".

Sofia, 20.12.2024

Prepared the revie
(