REVIEW

on PhD thesis for obtaning educational and scientific degree Philosophy Doctor (PhD), Professional Direction 4.2. Chemical Sciences, scientific specialty "Electrochemistry" (including chemical power sources)

Scientific organization: Institute of Physical Chemistry - Bulgarian Academy of Sciences
Author of the PhD thesis: Eng. Vesselina Stefanova Milusheva
Topic of the dissertation: Preparation and characterization of nanostructured layers of copper and anodic aluminum oxide.
Prepared by: Alexander Stefanov Zahariev, Assoc. Prof. PhD Eng. (Technical University - Sofia).

1. Brief biographical data and characteristics of the doctoral student's scientific interests.

Eng. Vesselina Milusheva graduated in 1995 with a master's degree in electrochemistry and corrosion protection, specialty "Inorganic and electrochemical technologies", at the University of Chemical Technology and Metallurgy - Sofia. From 2013 to the present, she holds the positions of chemical technologist and part-time lecturer at the Department of Chemistry at the Technical University - Sofia. From the beginning of 2018 to 2021, she is a part-time PhD student at the Institute of Physical Chemistry "Acad. Rostislav Kaishev" at the Bulgarian Academy of Sciences.

The scientific interests of Eng. Milusheva are in the field of modern nanotechnologies and specifically in the development of chemical and electrochemical methods for forming nanocomposite materials based on porous anodic aluminum oxide (AAO) combined with a copper layer of the Cu/AAO type, as well as layered structures of the conductor/insulator/conductive pattern type based on Al/AAO/Cu.

2. Relevance of the topic of the dissertation

The scientific research of Eng. Milusheva is based on a particularly relevant object, which is porous anodic aluminum oxide, which is distinguished by unique properties and has become the basis of an entire scientific area in materials science. Currently, this oxide is distinguished by an increasingly large-scale study and application, on the one hand as an almost indispensable matrix for synthesizing various nanostructures in its pores - nanowires, nanotubes, etc. from metals, non-metals and various compounds, and on the other - for forming nanocomposite materials with a diverse structure and properties. Devices based on an AAO matrix are increasingly used in electronics, communications, medicine and bioengineering, for the production of microelectromechanical systems (MEMS), for the creation of composite semipermeable membranes, for catalysts and sensors.

The subject of the presented PhD dissertation work is the development of technologies for chemical and electrochemical deposition of copper on anodic aluminum oxide, while preserving the aluminium base and with the aim of creating nanocomposite materials from Cu/AAO, layered structures based on Al/AAO/Cu, as well as conductor/insulator/conductive pattern systems. A method for electrochemical deposition of copper in pores is proposed by removing the barrier layer of the oxide without removing the aluminium substrate, which avoids the use of expensive and insufficiently reliable methods for vacuum evaporation of a metal from the side of the removed layer. Various options for catalyzing the chemical

deposition of copper have also been studied, such as contact deposition of copper, thermal decomposition of palladium salt, two-stage activation with Sn^{2+} and Pd^{2+} ions and photochemical fixation of copper. Two new electrolytes for chemical copper plating with neutral or weakly alkaline pH, with a sodium hypophosphite or phosphorous acid as reducing agents, are proposed. as well as the possibility of enhacing the chemical resistance of AAO, by sol-gel deposition of a layer of TiO_2 on the surface of the anode oxide. This technology allows for the deposition of copper from formaldehyde electrolyte with pH>12. A number of kinetic studies have been conducted to determine the optimal conditions for high-quality and rapid deposition within the framework of the newly developed technologies described.

3. Review of the PhD thesis and analysis of the results.

The thesis is written on 140 pages and contains 48 figures and 12 tables. 163 references are cited. The content is divided into seven sections, as follows - Introduction, Literature review, Methods, materials and experimental conditions and Experimental results, each of them including the relevant subsections. The contributions of the PhD thesis, scientific metrics and the references used are described. A list of abbreviations and symbols used is also attached. In this way, an exceptionally good presentation of the significant volume of publications on the topic, as well as the large number of experimental data and conclusions, has been achieved.

An abstract is presented, which is written according to the requirements and presents in a well-formulated form the most important experimental results and contributions of the dissertation.

The **first section** gives the most general idea of the state of the research topic and outlines the main directions of research within the thesis.

The **second section** is devoted to a comprehensive and carefully designed literature review. It covers, on one hand, a large part of the research on porous anodic aluminum oxide, examining in detail the main parameters and properties of the oxide, the methods for obtaining conventional and self-organized structures, with special attention paid to the methods for thinning and removing the barrier sublayer. On the other hand, a detailed review of the current state of research on the chemical and electrochemical deposition of copper is compiled, with special attention paid to the features of the formation of copper nanostructures in dielectric porous matrices. Based on the in-depth analysis, the goals and objectives of the dissertation work have been formulated as follows:

1. Investigation of the processes of thinning the barrier oxide layer at the Al/AAO interface and electrochemical or chemical growth of copper from the aluminum base through the nanopores of AAO to obtain a composite with the possibility of electrical conductivity in a direction perpendicular to the aluminum surface (through the nanocomposite).

2. Development of methods for chloride-free activation of AAO, allowing subsequent chemical copper plating of AAO.

3. Development of electrolytes for chemical copper plating with pH in the range of 4-9.5 with reduced aggressiveness towards AAO.

4. Determination of the composition and structure of the coatings depending on the deposition conditions and their potential applicability in electronic technologies.

5. Investigation of the possibility of modifying AAO on aluminum in order to increase its chemical resistance and the possibility of selective chemical copper deposition.

The **third section** describes the experimental methods, materials and conditions used. The described methods for characterizing the obtained materials are suitably selected and

provide quite complete information about the composition, structure and properties of the studied objects. Among the techniques used, one can distinguish Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX), X-Ray Photoelectron Spectroscopy (XPS), X-Ray Fluorescence Spectroscopy (XRF), and measurement of sheet resistance of thin layers using the "four-point probe" method. Various electrochemical methods of analysis were used for the studies. A number of optimal electrolyte compositions for chemical and electrochemical layer deposition and formation of copper nanostructures were developed.

The **fourth section** presents the results of experimental studies within the framework of the presented thesis work. A systematic study of direct electrodeposition of copper in the pores of AAO, with a barrier layer removed electrochemically and chemically, is carried out, which shows that the best results are achieved with electrochemical thinning for a time of about 60 min, with voltage or current control. A significant influence of the preliminary impregnation of anodized aluminum with a removed barrier layer, in an electrolyte containing Cu^{2+}, on the uniformity of filling the pores with copper was established. This influence is expressed in the formation of a very thin layer of contact-deposited copper at the AAO/Al interface and saturation of the solution in the pores with copper ions. Also, a possibly most uniform filling of AAO-pores with copper occurs in a potentiostatic mode, at a potential of -0.45 V vs. SCE, from an electrolyte with a concentration of 0.2 M Cu^{2+}.

A detailed technology for chemical copper plating of AAO from a copper electrolyte with a sodium hypophosphite (NaH_2PO_2) as a reducing agent is presented. It was found that the chemical deposition of copper from an electrolyte with a hypophosphite reducing agent on an ABS copolymer can be carried out with the addition of a small amount of Ni^{2+}, and the highest deposition rate (0.91 mg/h.cm^2) was achieved from a solution with a composition of 10 g/L $CuSO_4.5H_2O$, 30 g/L NaH_2PO_2 at 70°C and pH 9. However, it has been found that copper deposition from hypophosphite electrolyte on AAO requires pH<6. At higher pH values, Cu^{2+} undergoes incomplete reduction and octahedral crystals of Cu_2O predominate in the deposited layer. In the course of these studies, a strong influence of AAO on the composition and morphology of the chemically deposited layers is demonstrated. In studying the catalysis of the chemical deposition of Cu from a hypophosphite electrolyte, it was found that the reaction is successfully catalyzed by palladium, deposited both by ionic activation and by thermal decomposition of a palladium salt, and it is simultaneously shown that the morphology of the AAO has a stronger influence on the structure of the deposited layers from a hypophosphite electrolyte than the method of palladium activation. It was also shown that the resulting layers of chemically deposited copper were a good basis for subsequent electrochemical thickening.

A technology for chemical copper plating of AAO from electrolytes with phosphorous acid reductant is proposed. The optimal composition of the electrolyte for chemical copper plating, based on $CuSO_4$, is as follows - 40 mM $CuSO_4.5H_2O$, pH 6.5 and temperature 60÷70°C. From this electrolyte, a layer with a thickness of about 0.8÷1 μm is deposited in 30 min. The deposition rate is highest in the first 10 minutes, when the process is concentrated on Pd-catalytic nuclei from the activated surface and gradually decreases as the process progresses. . In addition, a composition of acetate-phosphorus electrolytes is proposed, in which the optimal conditions for deposition are ья одввдуя - 50 mM Cu^{2+}, 0.2 M H_3PO_3, 50°C and pH 7-8. In electrolytes with lower pH, it has been found that AAO has lower chemical stability and after a time of more than 20 minutes, partial destruction of the oxide layer to a state in which it acquires a fibrous structure appears. In general, from electrolytes

containing copper ions with a reducing agent of phosphorous acid, metallic copper is deposited at pH≤5. At pH≥6.5, the layers are entirely composed of well-formed and uniform octahedral Cu_2O crystals.

A number of studies have been conducted in the direction of chemical deposition of copper on AAO, after activation of the surface using a photocatalytic layer. The treatment of AAO in TiO_2 sol and the resulting formation of a thin photocatalytic layer of TiO_2, simultaneously leads to a significant increase in the chemical resistance of AAO in strongly alkaline electrolytes. This TiO_2 layer creates a suitable basis for chemical deposition of copper on AAO, from widely used electrolytes, with formaldehyde as a reducing agent and pH 12.8. The photocatalytic properties of TiO_2 allow for the process of photofixation of Cu (activation) in areas of the surface irradiated with UV light. In this way, copper nuclei are formed, which represent active centers for catalyzing the reaction of chemical copper plating from a strongly alkaline electrolyte, with formaldehyde as a reducing agent. The resulting copper layers are characterized by good conductivity (R_S = 65 mΩ/sq.) and allow soldering using low-melting solders.

4. Main scientific and scientific-applied contributions

From the content of the PhD thesis work of Eng. Milusheva it is clear that as a result of the development of a number of original ideas and hard work, the successful implementation of the set goals and tasks has been achieved. A serious contribution is the preparation of a nanocomposite material with a layered structure of the type Al/Cu+AAO/Cu. This unique material is formed after combined electrochemical/chemical thinning of the barrier layer of AAO, without removing the aluminum substrate. Conditions for the most uniform filling of the pores by electrodeposition of copper are also found and it is established that the formed layered material has electrical conductivity in the direction normal to the aluminum surface.

A significant contribution is also stand out by the development and testing of new stable solutions for chemical copper plating of nanoporous layers of AAO. These solutions use sodium hypophosphite or phosphorous acid as reducing agents, with pH values suitable for maintaining the chemical stability of AAO. This development enables the creation of nanocomposite layered materials of the conductor/dielectric/conductor type. In this particular case, structures of the type Al/AAO/AAO+Cu/Cu were obtained, in which the insulating properties of the anodic aluminum oxide are preserved. The resulting composite material has promising prospects for applications in electronics, e.g. in the production of metal printed circuit boards and MEMS.

A new method for improving the chemical resistance of AAO has been developed and implemented extremely successfully, by sol-gel deposition of a thin layer of TiO_2 on the surface of AAO. This layer, which is known to have photocatalytic properties, determines the subsequent direct selective photochemical catalysis of the dielectric surface. The catalytic centers formed in this way (photochemical fixation) allow for selective chemical copper plating, as a result of which conductive patterns are formed on anodized aluminum. The selective formation of conductive images using the described methodology, which have been shown to have good electrical conductivity and also provide a good basis for soldering with low-melting solders, demonstrates serious scientific and applied potential for the use of this

methodology as part of technologies for the production of various components in electronics and, in particular, in the development of metal printed circuit boards.

5. Description and evaluation of the submitted materials

The thesis is written on the basis of eight publications by Eng. Milusheva and co-authors. The articles have been published in authoritative international journals and in editions of renowned international forums, with an impact factor, SJR, referenced in Scopus and Web of Science and quartiles Q2 and Q4. In a large part of the presented scientific works, the personal contribution of Eng. Milusheva is indisputable, considering that in four of the publications Eng. Milusheva is the first author, and in two of them she is the second author. In addition, Eng. Milusheva is a co-author in six reports, of which one is an oral and five are poster ones. All reports are on the topic of the dissertation and reflect Eng. Milusheva's active participation in specialized Bulgarian and international scientific forums. A publication that is outside the subject of the dissertation, but is published in a journal with a very high impact factor and is currently distinguished by a significant number of citations in well-known international publications, makes a strong impression.

The materials included in the dissertation give reason to believe that the present dissertation work complies to the maximum extent with the Regulations of the Institute of Physical Chemistry-BAS for the acquisition of scientific degrees and occupying academic positions.

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

The presented publications are distinguished by a large number of citations, **a total of 37**, which on one hand is an evidence of the relevance of the developed objects, the originality and innovative approach in the formulation and performance of the research work and the generalization of the results obtained, and on the other - of the great value of the results obtained. Therefore, the significant recognition that the publications of eng. Milusheva receive from the scientific community engaged in issues related to the topic of the dissertation work is obvious.

7. Critical comments and recommendations on the candidate's scientific works.

Given the high quality of the presented scientific production, no significant gaps and shortcomings in the content of the materials have been found. I would only recommend that Eng. Milusheva continue her research in the same scientific field, as I am convinced that based on the serious preparation she already has and the excellent results she has achieved, she will be able to implement many new ideas in this field.

8. Personal impressions of the PhD student.

I have known Eng. Vesselina Milusheva since 2013. During the time we have been working together at the Department of Chemistry at the Technical University - Sofia, I can confidently say that I have gained excellent impressions both from her impeccable organizational and teaching activities, as well as from her versatile competence, thoroughness and innovative approach in developing and researching various chemical and electrochemical processes and obtaining new materials. I would also like to highlight her strong sense of responsibility and self-discipline, as well as the understanding, tolerance and responsiveness with which she invariably treats her colleagues. I would also like to draw attention to the versatile and high-quality work done by Eng. Milusheva, which shows that she already possesses serious knowledge and experience, characteristic of a largely formed researcher and teacher.

CONCLUSION

Considering the excellent results included in the PhD thesis work, characterized by a significant volume and unequivocally distinguished by an innovative approach, it can be concluded that the dissertation work presented by Eng. Milusheva fully meets the requirements of the Regulations of the Institute of Chemical Engineering "Acad. Rostislav Kaishev" - BAS for the acquisition of scientific degrees. This gives me a reason to confidently propose to the Honorable Scientific Jury to award Eng. Vesselina Stefanova Milusheva the educational and scientific degree "Philosophy Doctor", in the professional field 4.2 Chemical Sciences, Scientific specialty 01.05.14 "Electrochemistry" (including chemical sources of current).

Sofia, 06.01.2025 г.

Jury member: