



POSITION

on a dissertation for the acquisition of an educational and scientific degree 'Doctor'.

Field: 4.2. Chemical Sciences, Electrochemistry

Author of the dissertation: Eng. Vesselina Stefanova Milusheva, Department of Chemistry, Technical University of Sofia

Dissertation title: Preparation and characterization of nanostructured layers of copper and anodic aluminum oxide

Member of the scientific jury: Assos. Prof. Dr. Eng. Boriana Tzaneva, Technical University of Sofia

1. General characteristics of the research and scientific-applied activities of the candidate

Vesselina Milusheva began her research activity immediately after entering the Technical University of Sofia in 2013 as part of the team at the Department of Chemistry, developing electrochemical technologies for obtaining functional materials with applications in electronics. She was actively involved in studies of technologies for modification of anodic oxide layers on aluminum and their electrochemical filling with metals with high catalytic activity towards methane decomposition aiming to reduce harmful emissions. The acquired experience successfully expanded and developed in her dissertation work.

The research activity of Eng. Milusheva related to the dissertation aims to combine the electrochemical preparation of self-organized nanoporous layers of aluminum oxide and deposition of copper to obtain composite materials. To realize the final structures, Eng. Milusheva put considerable effort both in the analysis of the information available in the literature and in the large-scale experimental work. She carried out on the development of three independent approaches for the deposition of copper in and on anodic aluminum oxide (AAO). Systematically conducted studies on the electrochemical thinning of the barrier layer of AAO and the electrodeposition of copper in the final insulating oxide matrix allowed establishing the optimal parameters for uniform filling of nanopores with copper. Thus, a nanocomposite material with anisotropic electrical conductivity was successfully obtained directly on the aluminum substrate. A similar material was also obtained by chemical filling of the pores with copper, the process being initiated by contact-deposited copper on aluminum at the bottom of the oxide pores. This approach of filling nanopores remains unparalleled in the scientific literature. Another challenge that Eng. Milusheva successfully overcame is chemical deposition of copper from neutral electrolytes. All the processes studied in the development and optimization of the technologies presented in the dissertation, as well as the composite and layered materials obtained from them, have been characterized by appropriate electrochemical and physical methods of analysis.

2. Main scientific and scientific-applied contributions

The main results and contributions of the dissertation work are of a scientific and scientific-applied nature and can be summarized as follows:

- A layered material with anisotropic electrical conductivity of the Al/Cu+AAO/Cu type was obtained by thinning the barrier layer of AAO on aluminum and directly electroless or electrochemical filling the pores with copper.

- New stable solutions for electroless copper plating of nanoporous layers of AAO with phosphorus-containing reductants were developed, from which both metallic copper and Cu₂O can be deposited depending on the conditions. The solutions were used to create the conductor-dielectric-conductor type layered structures based on anodized aluminum and copper. The developed electrolytes enable the production of copper coatings from solutions with a pH of 4.5 to 9.8. Therefore, these solutions are applicable for metallization of materials that are unstable in strongly acidic and strongly alkaline environments.
- Direct selective photochemical catalysis and electroless copper plating of TiO₂-modified anodized aluminum has been achieved. The developed technology significantly improves the resistance of AAO in alkaline solutions and allows direct formation of conductive images on anodized aluminum from a conventional formaldehyde electrolyte for electroless copper plating (pH>12).

3. Reflection of scientific publications of the candidate in Bulgarian and foreign literature

According to the search in Scopus and Web of Science, out of the 8 publications included in the dissertation, four have been cited a total of 5 times. All citations are in renowned international scientific journals such as Electrochimica Acta (Q1), Materials (Q2), Sustainability (Q2), Journal of Electrochemical Science and Technology (Q2), Bulgarian Chemical Communications (Q4).

4. Critical notes and recommendations for the candidate's scientific works

All recommendations that were made by me as supervisor of Eng. Milusheva during the dissertation preparation and its technical design have been taken into account. As a recommendation for the future work of Eng. Vesselina Milusheva, I express my wishes that she does not stop with her scientific work and further develops the many new ideas that did not manage to find a place in the dissertation, such as studying the catalytic properties of the composites of anodic aluminum oxide/Cu₂O created by her and their potential inclusion in sensor systems.

CONCLUSION

During our work together, Eng. Vesselina Milusheva has always shown responsibility, precision and consistency in planning and conducting experiments and analyzing the results. To achieve the goals defined in the dissertation, a large amount of experiments has been carried out, in which various electrochemical methods have been mastered and knowledge has been acquired from the stage of developing electrolytes for copper deposition to synthesizing and fully characterizing the materials obtained from them. I believe that the dissertation aims and tasks have been fulfilled and meet the requirements of the Act on Development of the Academic staff in the Republic of Bulgaria, the Regulations on its Implementation and the Regulations on the Conditions and Order for Acquiring Scientific Degrees in Institute of Physical Chemistry in terms of volume and scientific-applied contributions.

All this gives me reason to confidently vote positively for awarding the **educational and scientific degree "doctor"** in professional field 4.2. Chemical sciences, scientific specialty "Electrochemistry" of **Eng. Vesselina Stefanova Milusheva**.

Sofia, 06.01.2025 r.

Jury member:

/A