REVIEW

on the defense of the dissertation **"Preparation and Characterization of Nano-Structured Layers of Copper and Anodized Aluminum Oxide"**, presented by **eng. Veselina Milusheva Stefanova** for the award of the educational and scientific degree "Philosophical Doctor", Field 4.2., Chemical Sciences, Specialty: 01.05.14 "Electrochemistry"

Member of the Scientific Jury: assoc. prof. eng. Christian Assenov Girginov, PhD

1. General Characteristics of the Candidate's Research and Applied Scientific Work

The dissertation comprises 140 printed pages, includes 69 figures and 19 tables, and cites 163 literature sources. It is based on **seven published works**:

Three publications in journals with impact factor (IF): *Catalysis Science & Technology - Q2* (1) and *Bulgarian Chemical Communications - Q4* (2).

One publication in a journal without IF: *Nanoscience & Nanotechnology*.

Three full-text conference papers: (*HiTech 2018*, IEEE), (*12th National Conference with International Participation "Electronica 2021"*), and (*31st International Scientific Conference Electronics, ET 2022*).

The dissertation is logically structured, written in clear scientific language, and well-formatted and illustrated, which significantly aids the reader.

The conducted research is planned based on an extensive literature review that systematically organizes data on the preparation, properties, and application of copper-containing composite coatings. Based on this review, the dissertation's objectives are clearly defined and strictly limited to the following main activities:

- Electrochemical formation of porous anodized aluminum oxides (AAO) using various contact electrolytes: aqueous solutions of sulfuric, oxalic, and phosphoric acids. Investigation of chemical and electrochemical processes to thin the barrier oxide sublayer at the Al/AAO interface. Copper was deposited through the AAO nanopores formed on the aluminum substrate using electrochemical and chemical processes. Composites of the type Al/AAO/(Cu+AAO)/Cu with good electrical conductivity were created.
- Development of chloride-free activation methods for AAO matrices to enable subsequent efficient chemical copper deposition. Design of chemical copper deposition electrolytes (pH range 4–9.5) that are non-aggressive toward aluminum and the AAO layers formed on its surface. Investigation of the possibilities for modifying the AAO porous matrices to form composites through copper incorporation.
- Systematic characterization of the composition and structure of the coatings formed, depending on deposition conditions (electrolyte nature, concentration, complexing agent, stabilizer, process duration). Various instrumental techniques were used: Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS), and X-ray Diffraction Analysis (XRD).
- Analysis of the obtained results and evaluation of the potential applications of the composite materials in various electronic technologies.

2. Key Scientific and Applied Contributions

The scientific contributions of the dissertation are timely and significant, summarized as follows:

- Composite materials with the composition Al/AAO/(Cu+AAO)/Cu were formed. A procedure was developed for thinning the barrier sublayer of electrochemically formed AAO. Copper was directly incorporated (chemically or electrochemically) into the AAO films' pores. Materials produced by this procedure possess good electrical conductivity.
- Systematic studies were conducted on the chemical copper deposition process for the formed nanoporous AAO layers. New stable solutions (pH 4.2÷9.5) were developed and tested using sodium hypophosphite and phosphorous acid as reducing agents. These solutions enabled the effective formation of composite Al/AAO/(AAO+Cu)/Cu structures of the conductor/dielectric/conductor type. Notably, the designed solutions are non-aggressive toward aluminum and AAO, preserving their properties. The composite materials have strong potential for applications in electronics (electronic components, printed circuit boards, micro-electromechanical systems, etc.).
- A methodology for improving the chemical stability of AAO was developed, allowing direct selective photochemical catalysis and chemical copper deposition. This enables the formation of conductive images on anodized aluminum surfaces.

The dissertation's scientific contributions are of theoretical and applied importance, achieved through substantial research on complex systems and phenomena. The results have significant potential for addressing various practical tasks in electronics.

3. Impact of the Candidate's Scientific Publications

Two of the publications included in the dissertation have been cited three times in specialized literature. One of the conference papers has also been cited.

4. Critical Remarks and Recommendations

I have no direct impressions of eng. Stefanova's research activities. However, the presented materials convincingly demonstrate that she is a researcher with a broad range of interests and high competence in forming composite materials combining dielectric and conductive substrates. Regarding the dissertation's research and results, I have no substantive criticisms. I do have one recommendation: eng. Stefanova could expand her studies of the obtained composite materials by determining some surface properties such as hydrophobicity, optical characteristics, and color parameters.

CONCLUSION

In conclusion, the topic of the dissertation presented by eng. Stefanova is leading and promising in science and technology. The formation and study of functional coatings based on nanoporous anodized aluminum oxide (AAO) and embedded copper open broad opportunities for fundamental research. Additionally, the materials obtained through the research have increasing practical applications. The combination of the dielectric AAO layer with conductive copper creates

composites with unique properties, suitable for applications in electronic components, micro-electromechanical systems, semipermeable membranes, catalysts, sensors, and more.

The doctoral candidate has mastered advanced physical methods and specific experimental techniques for obtaining and studying composite materials based on AAO with incorporated copper. With this dissertation, Eng. Stefanova demonstrates her ability to identify and solve critical problems in this significant area of materials science.

The research included in the dissertation, in terms of scope, quality, and significance of the results, fully meets the requirements for a successful defense. Therefore, I confidently recommend that the esteemed members of the Scientific Jury vote to award the educational and scientific degree "Philosophical Doctor" in professional field 4.2. Chemical Sciences, specialty 01.05.14 "Electrochemistry" to **eng. Veselina Milusheva Stefanova**.

09.12.2024

Signature:

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