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Review Report on PhD Thesis

Faculty: **Central European Institute of Technology Brno University of Technology in Brno** Academic year: **2020/2021**

Student: **Ing. Tomas Lednicky**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **Dr. techn. Ing. Maria Bendova**

Reviewer**:** **Prof. dr. hab. Grzegorz Sulka**

PhD thesis title: **Utilization of porous anodic alumina for fabrication of nanostructured layers and their photoelectrochemical and optical applications**

Topicality of doctoral thesis:

In recent decades, anodic aluminum oxide (AAO) has received significant attention due to its unique chemical and physical properties that make it promising material for various applications in nanotechnology. A specific nature of porous oxide formed during controlled anodization of aluminum is extremely attractive for fabricating nanomaterials using AAO template-assisted methods as well as development of diverse nanodevices such as quantum-dot structures, polarizers, photonic crystals, and magnetic memory structures. Particularly on basis of porous AAO templates with a precisely arranged pore cells and controlled dimensions of nanopores, an inexpensive formation of periodically ordered structures, including highly ordered and close-packed nanopores, nanodots, nanotubes, nanowires, and nanoparticles has been widely reported.

Exploitation of nanomaterials for practical applications is frequently limited by relatively high cost of their fabrication. Therefore, research efforts have been recently focused on development simple and inexpensive methods for the synthesis of diverse nanomaterials. Among numerous strategies reported in the literature, a popular method is based on anodic oxidation (anodization) of thin Al or Al/Ti layers deposited on Si substrates. In the presence of the undelaying Ti layer, the anodization of aluminum can result in the formation of TiO_2 nanocolumn arrays with inter-column distances controlled by initially formed AAO. The obtained TiO_2 nanocolumns can be further used for photoelectrochemical water splitting, which is an attractive technological solution to harvest solar energy and generate hydrogen in a clean and sustainable manner.

For these reasons, the dissertation of Mr. Tomáš Lednický is an interesting proposal and responds to current research challenges of material engineering and nanotechnology. The ideas formulated and developed in this dissertation and the results presented in the thesis are a perfect response to current needs of the scientific community.

Meeting the goals set

The doctoral thesis consists of two separate research topics and each part has different research goals.

In the first part of the thesis, devoted to synthesis of TiO_2 nanocolumn arrays by anodization of the aluminum layer deposited on titanium-based substrates, the optimization of procedures for obtaining mechanically stable and freestanding titanium oxide nanocolumns on Si substrate can be treated as a successfully met goal. The electrochemical characterization of fabricated nanocolumn arrays formed on substrates of different nitrogen contents proved semiconducting properties of formed nanostructures. However, photoelectrochemical performance of perfectly stable nanostructures formed at the optimized conditions was not studied due to a limited time span of the PhD research. Although this research goal was not fully achieved, it was demonstrated that TiO_2-based layers, obtained at non-optimized etching conditions, could be used as photoanodes for photoelectrochemical water splitting.

The second part of the PhD thesis covers the issue of AAO-assisted fabrication of Au nanoparticle arrays, which can be transferred to transparent substrates, and then used as a Localize Surface Plasmon Resonance (LSPR) sensor. All purposes important for the development of this technology were achieved, and the Author of the thesis demonstrated that the proposed method of synthesis of Au nanoparticles based on solid-state dewetting, occurring during thermal treatment of the Au layer deposited on Al concaves, provides a uniformed distribution of Au nanoparticles over the whole sample. Moreover, it was proved that the dimensions of Au nanoparticles could be controlled by synthesis conditions. The fabricated Au nanoparticles distributed at the surface of the dielectric substrates (polymer or SiO_2) were used successfully as sensors for plasmonic detection of DNA. The performed studies showed in a convincing way that proposed procedures allow fabricating Au nanoparticles over various substrates in the controlled manner and used them for sensor applications.

Problem solving and dissertation results:

In general, the doctoral dissertation discusses two different ways of using anodization of aluminum for fabrication of nanostructured materials. Actually, two types of dissimilar materials were fabricated in the course of this research, and a common element linking them is the same process (anodization of Al) used to obtain nanostructured materials. Consequently, the PhD thesis was divided in two separate parts. In my opinion, the reviewed doctoral dissertation is written very clearly, and the rich literature sections (to both parts of the thesis) very accurately introduces all important research aspects.

The literature introduction to the first part of the thesis covers such topics as photoelectrochemical water splitting at semiconductor electrodes, process efficiency, titanium oxide photocatalysts, porous anodic aluminum oxide growth and morphology, and anodic oxidation of superimposed metallic Al/Ti layers. It is worth emphasizing that the content of the literature part is a real compendium of scientific knowledge presented in an accessible and professional manner, which I read with great interest, and a large number of literature sources indicates a good knowledge of the latest trends in the synthesis, characterization, and studies of photoelectrochemical properties of semiconductors.

The experimental results obtained during the formation of titanium oxide nanocolumn arrays by anodization of the Al layer deposited on the Ti, Ti-Nb or Ti-N substrates are discussed in the first part of the thesis. This specific anodization process results in TiO_2 nanocolumns partially embedded in remaining aluminum oxide. The freestanding nanocolumn arrays can be obtained by chemical etching of aluminum oxide. However, the etching process worsened mechanical stability of nanocolumns and, consequently, their photoelectrochemical performance as anodes for water splitting.

It worth mentioning that each preparation stage of TiO_2 nanocolumn arrays (e.g. anodization, chemical etching) required a detailed optimization of the experimental conditions. It is not easy task and extremely time consuming. The Author of the thesis has faced serious problems with mechanical stability of obtained nanocolumns and their porous/hollow morphology, but he always has found a proper solution by modifying anodizing conditions (electrolyte temperature, re-anodizing time, etc.). In my opinion, this issue is the most important contribution to the theory and practice of anodization of metallic Al/Ti bilayers. This subject has not been widely reported in the literature before.

Since TiO_2 absorbs mainly UV light, one of the challenges is to shift its photoresponse to the visible light region by e.g., doping with nitrogen. In this context, the Author of the thesis investigated formation of TiO_2 nanocolumns from Ti-N substrates of various chemical compositions. As could be expected, heat treatment of anodic layers at different conditions (in air or vacuum) resulted in a phase transformation (from an amorphous anodic titanium oxide to the anatase phase), higher conductivity, and increased donor density. Surprisingly, formed TiO_2 nanocolumns possessed poor photoelectrochemical activity when compared to the samples without nanocolumns due to much higher photoresponse from the thermal oxide layer formed during annealing. These results suggest that it will be rather difficult to apply this type of nanostructured materials for effective water splitting, especially when taking into account the complex and multi-stage preparation procedure of these materials.

In the second part of the thesis, the theoretical introduction briefly discusses solid-state dewetting of thin metallic films, localized surface plasmon resonance (LSPR), surface plasmon coupling effect, and state of the art within the field of plasmonic nanostructures used as LSPR sensors and their applications for bio-sensing purposes. The literature part has been prepared carefully and harmoniously, and the Author of the dissertation discussed the current state of knowledge in the areas of research important in the context of the research plan being carried out.

A second, reported in this thesis, strategy exploiting of aluminum anodization for the fabrication of nanomaterials is based on the use of the Al template left after oxide removal. In this approach, the anodic oxide layer was removed by wet chemical etching, and the remaining Al substrate with the ordered array of concaves was used as a template for formation of ordered Au nanoparticles. The solid-state de-wetting of a thin gold film deposited over the aluminum template, occurring during thermal treatment, was exploit for obtaining Au nanoparticles. As a significant part of the research, the influence of many factors on the formation of nanoparticles was investigated including: technique used for the deposition of the thin Au layer (magnetron sputtering in two different chambers and evaporation), type of the Al template (different inter-concave distances and concave depths), rate of Au deposition, Au film thickness, annealing temperature after deposition, and presence of the native oxide layer or hydrocarbon contaminations at the surface of the Al template. In this aspect, the scope of the research was very broad and required a large number of experiments to be conducted. A significant contribution of the thesis with respect to the formation of Au nanoparticles by solid-state de-wetting is a strict control of their distribution and size. The latter one was controllable, among others, by depositing the appropriate thickness of the Au layer and subsequent (after annealing) sequential repeated depositions. To the best of my knowledge, this type of study was not performed before and, therefore, the obtained results provide a novel valuable insight in the solid-state de-wetting process occurring on nanostructured surfaces.

In the next step of the research, the Author showed an interesting set of data related with the transferring Au nanoparticles from the Al substrate to an electrically non-conductive and optically transparent substrate. In this regard, experimental tests included different substrates such as polydimethylsiloxane (PDMS), polymethyl methacrylate (PMMA), epoxy resin, and sandwich structure of the top evaporated thin SiO_2 layer with epoxy support. In the final step toward the fabrication of efficient LSPR sensors, reactive ion etching was used for removal of the transparent substrate around Au nanoparticles in order to increase sensitivity of sensors and accessibility of the gold surface for DNA hybridization. The best sensing properties were observed for the sensor based on Au nanoparticles on the SiO_2 substrate.

To summarize this part of the thesis, the most important strength is that it has provided a valuable evaluation of the possible procedures for the formation of Au nanoparticles over the Al templates and their transfer to transparent substrates in the way preserving the ordered arrangement of nanoparticles. This complex approach to the studied subject has to be emphasized, because provides valuable experimental data from initial stages of nanoparticles synthesis up to the final fabrication of the efficient LSPR sensor for DNA detection.

Importance for practice or development of the discipline:

The data presented in the PhD thesis completes the knowledge on the template-assisted synthesis of nanostructured materials for potential photoelectrochemical and plasmonic sensing applications. The anodic layers of TiO_2 layers obtained by anodization of Al deposited on Ti, Ti-N and Ti-Nb substrates fill the existing gaps in research and understanding which factors play an the most important role in the formation of freestanding and mechanically stable TiO_2 nanocolumn arrays. On the other hand, the results obtained in the scope of the solid-state de-wetting process, occurring on Al templates covered with a thin Au layers, complete the available literature data on precise design and control of ordered metal nanoparticle arrays. In addition, the performed studies allowed to establish dependencies between the synthesis conditions and properties (electrochemical, photoelectrochemical, optical etc.) of fabricated nanostructured materials and, consequently, understanding the processes which take place during each step of the material processing. The received nanomaterials can be a good starting point for further research devoted to new nanomaterials for photoelectrochemical water splitting, photocatalysis, and high-quality nanostructured LSPR sensors.

Formal adjustment of the thesis and language level:

It is worth mentioning that the PhD thesis was written very carefully, however, as typical for such an extensive study, there are minor linguistic errors, typos, missing subscripts in chemical formulas (e.g. page 162, ref. 55), missing or excessive words, spaces and commas, or even a non-necessary temperature unit (page 147, line 4 below table 5.8), and doubled some paragraphs on pages 21 - 24. I have noticed also a lack of consistency in using British or American English and both spellings are used, i.e., anodisation (page 25, caption to Fig. 1.5) or anodization (arrow description in Fig. 1.5). I am not going to list all these minor shortcomings here, because they do not detract from the great value of this work. It is worth emphasizing that all graphics and layout are refined in every detail.

Questions and comments:

This thesis, of course, represents a good example how the scientific work should be done. The Author presented carefully obtained results, supplementing them with in-depth analysis and critical discussion. In cases where the obtained results were unsatisfactory or unexpectedly, he was looking for a solution to the problem and did not leave the results without showing reasons of deviations or failures. The short summaries at the end of extensive chapters improve significantly and systematize the discussed knowledge. The conclusions presented in the thesis are insightful, so they can be particularly useful in further research studies. The Author presents significant contributions to the knowledge on utilization of Al anodization for the template-assisted fabrication of nanomaterials, and therefore, the overall assessment of this thesis is extremely positive.

However, some issues should be raised:

1. Equation 1.2 on page 17 is incorrect.
2. It is not clear what the Author mean by suggesting that the larger sample can be anodized (page 42, "*This setup allows larger samples with up to 50 cm compared to 0.4 cm for…*"). The provided unit does not characterize unequivocally the sample size. Is it about cm^2?
3. The Author of the thesis used different annealing temperatures for heat treatment of amorphous TiO_2 samples obtained after anodizations. For example, 600 °C is provided on page 60, but 500 °C is stated on page 68. Moreover, 550 °C was used for the thermally oxidized sample. What was the reason for using different annealing temperatures? It is common known that the annealing temperature influences the anatase/rutile transition and, thus, the phase composition of TiO_2 (J. Phys. Chem. C 119 (2015) 24182–24191).

Did the Author quantitatively determined (e.g., by Raman spectroscopy) the anatase content in the studied samples? On the other hand, the phase composition of TiO_2, and in particular the anatase content, significantly affects the photocatalytic and photoelectrochemical properties, and consequently, the generated photocurrents during photoelectrochemical water splitting.

4. From the Mott-Schottky analyses donor densities were estimated. Knowing the flat band potentials (from the same analyses) it quite easy to determine the conduction band edge, and construct the energy diagrams for the studied materials. Can the Author explain what made it impossible?
5. The IPCE measurements are presented in the thesis on pages 76-8). Why the Author did not try to determine a band gap of studied materials from those measurements? The possible differences in band gaps could provide some information on the N-doping effect.

Conclusion:

To sum up, this is a convincingly documented PhD thesis, which provides very interesting and valuable results of high quality. The Author of the thesis showed all necessary practical skills (all experiments were well arranged and measurement techniques and methods were correctly applied), theoretical knowledge, and high motivation for research work. The discussion of results and explanations of problems, which arise are suitable and focused on the relevant topics.

In my opinion, the reviewed thesis fulfill all requirements posed on theses aimed for obtaining PhD degree. This thesis is ready to be defended orally, in front of respective committee.

In Krakow, 12th July 2021

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Prof. dr. hab. Grzegorz Sulka