REVIEW

on a procedure for the occupation of the academic position of "Associated Professor" in the professional field 4.1 "Physical Sciences", Scientific specialty ""Condensed Matter Physics ", according to the announcement in the Newspaper of State, issue 35/10.05.2022 г.

Applicant: Dr. Katerina Emilova Lazarova, Assisstent Professor at the Institute of Optical Materials and Technologies (IOMT) -BAS

Reviewer: Prof. DSc. Albena Paskaleva, Inst. Solid State Physics, Bulgarian Academy of Sciences

General description of the materials presented

The only candidate in the competition for the academic position "associate professor" for the needs of the Department "Optical Materials" at IOMT-BAS is the assist. prof. Dr. Katerina Emilova Lazarova. The candidate has submitted all the necessary documents for participation in the competition, required according to the Regulations on the terms and conditions for the acquisition of scientific degrees and for holding academic positions and the specific requirements of IOMT-BAS. The presented documents fully cover the topic of the competition.

Katerina Lazarova graduated with a master's degree in physics from Sofia University "St. K. Ohridski" in 2006. From 2006 to 2013, she worked as a physics and astronomy teacher. In 2015, she received a PhD degree at the Institute of Optical Materials and Technologies (IOMT), BAS. From 2016 up to now, she is working as an assistant professor at IOMT, BAS.

The total number of scientific publications of the candidate is 41, of which 25 articles in journals with impact factor (IF) or impact rank. The total number of noticed citations in the scientific literature is 110, Hirsch index – 6.

K. Lazarova participated in the competition with a total of 20 of her scientific works, which were not used in previous procedures for acquiring scientific degrees and positions. The candidate participates in the competition with the equivalent of a habilitation work (group of indicators B), consisting of 6 publications and with 14 articles, outside of the habilitation work (group of indicators G). All they are in the field of synthesis and research of organic and inorganic materials for optical sensor applications. Of the publications in the habilitation work, 3 are in the Q1 category; 1 - in Q2, 1 - in Q4 and 1 with SJR, with which the candidate collects a total of 117 points. In all these publications, Dr. K. Lazarova is the first author, which is indisputable proof of her leading contribution. Outside the habilitation thesis (group of indicators G), the candidate participates in the competition with 14 articles, of which 6 in the Q1 or Q2 category, 5 in Q4 and 3 peer-reviewed papers published in full text in conference proceedings (journals without IF, with impact rank). From the presented scientific assets under group G indicators, the candidate collects a total of 230 points. In the competition, the candidate participated with 31 citations of her works.

In all indicators, the applicant's points exceed the minimum national requirements for the position of "associate professor".

Dr. K. Lazarova is also actively involved in 19 projects, including being the head of 5 of them and 60 participations in scientific conferences. She holds several awards for the best lecture or poster presentation from scientific conferences, as well as two short-term study grants.

General characteristics of the scientific and applied activities of the applicant

The candidate's activity is aimed at obtaining and researching thin layers of functional materials - both organic (polymers) and inorganic (zeolites, metal oxides), and their application in sensor devices operating on an optical principle. The sol-gel method and spin-coating are mainly used for synthesis of the materials and their deposition as thin layers. The resulting materials are then characterized by structural and optical methods to establish and optimize their properties. Research on the properties of materials is always related to their specific application, with the focus being on optical sensors for humidity or acetone. All studies have a marked interdisciplinary character and were carried out by not very large author teams (between 4 and 7 scientists). The groups are mainly Bulgarian, and the active cooperation with other institutes is impressive - Institute of Polymers, Technical University-Sofia, Inst. of Electrochemistry and Energy Systems, Inst. of General and Inorganic chemistry.

Main scientific and applied contributions

The scientific contributions of Dr. K. Lazarova fall into four main topics.

The articles numbered 1 - 6, presented as a habilitation thesis, fall under the general title: "Thin polymer layers as optical humidity sensors". Polymer layers have been used as humidity sensors because of the advantages they offer – easy application in the form of thin layers; possibility to change their composition and architecture in order to tune the properties in the desired direction and achieve the desired functionality. Optical detection principles, namely the change of color and/or reflectance and/or transmittance of layers under the action of humidity, were chosen because they are relatively easy to apply, do not require operation at high temperatures, and have good sensitivity and accuracy. The polymers are prepared by reduction-oxidation polymerization in an aqueous medium and are spin-coated as thin layers on a suitable substrate. Polymers with different composition and structure were prepared - poly (N, N-dimethylacrylamide) PDMA-copolymers; polyvinyl alcohol PVA - copolymers, and their optical and sensor properties under the influence of humidity were investigated. The change of these properties depending on the composition and architecture of the polymer layers was investigated in order to establish the most suitable combination from the viewpoint of their use as humidity sensors. As more significant results I would list:

- It has been shown that poly (N, N-dimethylacrylamide) – poly(ethylene oxide) (PDMA/PEO) copolymers with different composition and structure change their color under the influence of humidity, as a result of a significant swelling of the layers and a concomitant change in their reflection spectra. This makes PDMA/PEO copolymers very attractive as optical humidity sensors.

- It has been demonstrated that the chemical structure and composition, as well as the macromolecular architecture (star-shaped, triblock or branched) of PDMA-copolymers have a strong impact on their optical behavior and sensor properties. A polymer with a branched macromolecular architecture was shown to have the best humidity sensitivity as well as sensor performance.

- It has been demonstrated that multilayer Bragg structures and thin metal layers coated with a branched poly(N,N-dimethylacrylamide)-based copolymer thin film with optimized thickness can be used as humidity sensors operating in transmission mode. The optimal sensor configuration was found to be a 300 nm polymer film deposited on a 30 nm Au-Pd thin film, where very high sensitivity and resolution were achieved.

- Vinylacetal-modified polyvinyl alcohol (PVA) layers with an optimal acetal content of about 24%, 80 nm thickness and subsequent annealing at 60 °C demonstrate the best sensor characteristics. These characteristics are further improved by adding 20% SiO_2 nanoparticles. The resulting layers respond in the entire dynamic range and show a linear dependence of the measured signal as a function of relative humidity.

- A flexible and transparent polymer-based optical humidity sensor has been developed. The sensor consists of a pre-metallized PET substrate coated with a thin film of poly(vinyl alcohol-co-vinyl acetal). An increase in sensitivity of more than 40% was obtained after bending for RH values higher than 75%; the resolution is also improved - from 0.6% RH to 0.4% RH. It is shown that up to 1000 bending deformations do not affect significantly the surface morphology and optical quality of the sensor.

I would classify the contributions on this topic as scientific (obtaining new and confirming results) and applied (creating sensor devices). Some of the results have been reported for the first time in the scientific literature.

The second topic covers research on zeolite films from the view point of their application in various optical and sensor devices (articles numbered 7, 9, 12, 15, 16, 18). Zeolites are crystalline aluminosilicates that attract particular interest because they possess a porous structure with well-defined pore arrangement, shape, and size. Moreover, they can be obtained in the form of thin layers with different composition, morphology, pore sizes, as well as can be included in the matrix of other materialas. All this allows changing their chemical and physical properties in a very wide range depending on their specific application. As more significant results on this topic, I would point out:

- Thin continuous zeolite layers were obtained by spin-coating deposition from an aqueous dispersion of SiO_2 nanocrystals with a morderite structure (Si-MFI). The possibility to control the optical thickness of the layers by changing the concentration and/or the deposition rate has been demonstrated. It has been shown that these zeolite layers can be used as an antireflection coating in a wide optical range;

- Thin films of oxo-zeolite composites (zeolite crystals with MFI or EMT structure embedded in a SiO_2 or Nb_2O_5 matrix) were deposited by spin coating using pre-synthesized sol-gel suspensions. It is shown that in the case of Nb_2O_5 matrix, the refractive index of the obtained composite can be adjusted in a very wide range (from 2.02 to 1.11) depending on the amount of zeolite;

- Zeolites synthesized from fly ash (FAZ) have been used to deposit thin zeolite or oxo-zeolite composite layers. The potential of these layers for various sensing and catalytic applications depending on their composition and preparation technology has been investigated and some promising results have been obtained. For example, thin layers of FAZ modified with copper oxide have higher catalytic activity due to formation of additional catalytic centers. FAZ-doped Nb_2O_5 thin films demonstrate sensitivity to acetone vapor. It was found that by wet milling of FAZ, the sensing properties of Nb_2O_5 /FAZ nanocomposites can be enhanced and controlled in the desired direction. The technological process was optimized in order to obtain layers with the largest pore volume and specific surface area. These results are of great importance because the utilization of the abundant resources of coal ash in various technologies is an important step towards the realization of zero-emission power plants.

I would classify the contributions on this topic as scientific, related to obtaining new data on the physical and chemical properties of zeolites and their nanocomposites, and applied, related to their possible practical applications.

The third thematic area in which the candidate's research is focused is related to the development of photonic crystals based on metal oxides and nanocomposites. Nb_2O_5, Ta_2O_5 or V_2O_5 deposited by the sol-gel method were used. The parameters of the deposition process are optimized in order to achieve control over the thickness of the layer, its refractive index and absorption coefficient. The main results on this topic are:

- It is shown that precise control of Nb_2O_5 film thickness can be achieved by controlling the sol concentration; by annealing in a temperature range of 60-650 °C, a change of n in a relatively wide range from 1.82 to 2.20 was achieved. The influence of Nb sol aging on the optical properties and thickness of the films was also investigated; technology for preparing porous layers by using a Pluronic copolymer as an organic template is developed. Bragg multilayer structures of alternating dense and porous thin Nb_2O_5 layers with a thickness of a quarter wavelength have been developed. 7-layer structures demonstrate a more than 10-fold increase in sensitivity to acetone vapor compared to monolayers. It has been shown that a further increase in sensitivity can be achieved by introducing a defect layer with an optical thickness of about $3\lambda/4$.

- Technology based on sol-gel method and spin deposition is optimized to obtain thin, transparent layers of V_2O_5 with high refractive index and good optical quality. These layers as well as their combinations with zeolite have been demonstrated to be sensitive to acetone vapor and can be used as optical sensors.

- Thin Ta_2O_5 layers were obtained with a mesostructure achieved by using organic templates of four Pluronic polymers. A modulation of the refractive index ranging from 1.94 to 1.48 was achieved depending on the type and concentration of the polymer. The sensor response of these materials to acetone vapor was also investigated and the optimal composition of the layers, with the largest sensitivity, was established.

I would classify the contributions on this topic mainly as applied, related to the development of technology and application of materials in sensor devices.

The last topic covers three articles (numbers 11, 17, 19 of the author's reference) and is devoted to the study of ZrO_2 layers - pure and doped with Sm^{3+}.

- A technology based on the sol-gel method was developed, by which transparent and homogeneous layers were obtained. ZrO_2 layers with different additives (HNO_3, AcAc, AcAc-PEG) were investigated in order to improve the properties of the layers.

- Sm^{3+} doped ZrO_2 layers with high optical quality were obtained. The effectiveness of ZrO_2 as a matrix to enhance emission from Sm^{3+} is demonstrated and an optimal Sm^{3+} concentration at which maximum emission is obtained is found. Doping with Sm^{3+} was found to increase the photoluminescence intensity and it causes a red-shift of the photoluminescence peak.

Reflection of the candidate's publications in scientific literature

Katerina Lazarova's works have received a good international recognition, with a total of 110 independent citations, and a Hirsch index of 6. A total of 31 citations of two papers were submitted for participation in the competition. These papers, however, are not contained in the author list submitted for the competition. Subsequently, the applicant presented a list of citations of the papers participating in the contest, which contained a total of 41 citations. This is enough to cover the minimum requirements. The most cited paper (Materials 13, 9 (2020)) has 13 citations in the scientific literature.

Personal impressions, questions and critical remarks

I do not know the candidate personally. I have no critical remarks. I have a few questions for the candidate.

- The drying of the layers and their high-temperature annealing (if any) is carried out in air. Doesn't this introduce unwanted polluting elements?

- Some of the layers being investigated as humidity sensors show hysteresis, with the curve at decreasing concentration being below the curve at increasing concentration. This is contrary to expectations, as recovery generally takes longer than sensor response. Do you have an explanation for this effect?

- You have studied several different pentoxides (Nb_2O_5, Ta_2O_5 or V2O5) and they all demonstrate sensitivity to acetone. In your opinion, which of these oxides has the best properties from the view point of its application as acetone sensor.

The above facts allow me to conclude that Dr. Katerina Emilova Lazarova satisfies all the requirements of the national Regulations for the occupation of the academic position of

"Associated Professor". The submitted scientific assets to the competition and the contributions mentioned give me a reason to strongly recommend to the respected Scientific Jury to support the application and to propose to the Scientific Council of IOMT-BAS to award Dr. Katerina Emilova Lazarova the academic position of " Associated Professor " in the professional field 4.1 "Physical Sciences "

07.09.2022

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Sofia

Prof. DSc. Albena Paskaleva