REVIEW

on the competition for occupying the academic position "**professor"** in a professional field 4.2. "Chemical Sciences", specialty "Solid State Chemistry" for the needs of the Institute of General and Inorganic Chemistry at the Bulgarian Academy of Sciences (IGIC-BAS), Laboratory "Electron Spectroscopy of Solid Surfaces", announced in Newspaper of State, issue 46, dated 26.05.2023.

Candidate: *Assoc. Prof. Dr. Ivalina Avramova Avramova, IGIC - BAS*

Reviewer*: Prof. Dr. Violeta Georgieva Koleva, IGIC – BAS*, member of the Scientific Jury, appointed by Order No. RD-09-128/17.07.2023 of the Director of IGIC - BAS

1. General description of the materials presented

The only candidate in the present competition is Assoc. Prof. Dr. Ivalina Avramova Avramova from IGIC-BAS, Laboratory "Electron Spectroscopy of Solid Surfaces".

Assoc. Prof. Dr. I. Avramova has presented all the documents required and specified by the "Law for Development of the Academic Staff in the Republic of Bulgaria (LDASRB), The Regulations for its application and the Terms and Rules for Occupation of Academic Positions" in IGIC-BAS. The materials in the competition include all the needed lists of scientific indicators (papers, citations, participation in scientific forums and projects, etc.), as well as the relevant evidences, so that the authenticity of the materials is beyond doubt.

2. Brief biographical data of the applicant

Ivalina Avramova graduated from the Faculty of Physics of Sofia University "St. Kliment Ohridski" in 1996 with a master's degree in engineering physics. She has a postgraduate qualification in English and as a teacher. In 2003, she finished PhD thesis on "Electronic properties and thermoelectric efficiency of $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ solid solutions" at the Faculty of Physics of the Sofia University. In 2001, she joined the IGIC-BAS as a physicist, where she still works. In the period 2001-2011, she specialized in the Synchrotron Center in Trieste (Italy), Free University in Brussels (Belgium) and Bilken University in Ankara (Turkey), which supports her successful scientific realization and career development, successively holding the academic positions of Assistant (2004), Chief Assistant (2006) and Associate Professor (2012).

3. General characteristics of the candidate's scientific activity

Assoc. Prof. I. Avramova is a recognized specialist in the field of analysis of the surface chemistry of various materials (bulk materials and thin films) by X-ray photoelectron spectroscopy (XPS). The candidate's scientific activity includes 125 scientific works (publications and materials from conferences since 1998 to the present), of which 95 are in journals with an impact factor, 18 without an impact factor and 12 in materials from conferences. A list of a total of 851 independent citations (without self-citations of all authors) on 74 articles of the candidate is presented. According to the Scopus database, the candidate's total number of citations is 858, of which 726 have been acquired after her habilitation as an Associate Professor. The candidate's Hirsch index (H) according to Scopus, based on all publications, is 16 (without self-citations of all authors), which testifies to the relevance and significance of the research conducted with the participation of Assoc. Prof. Avramova.

In the current competition, Assoc. Prof. Avramova participates with 65 scientific works published in the period after her habilitation as an Associate Professor (2013 – 2023), which do not repeat those from previous competitions. I accept all 65 works for review. The high scientific level of the publications is confirmed by their distribution by quartiles of the editions in which they have been published. Nearly half of the publications (49%) are in journals with Q1 and Q2 quartiles (15 articles with Q1 and 17 with Q2), 11 are with Q3 (11%), 6 with Q4 (9%) and 16 with SJR (25%). A large part of the articles are in reputable journals in the field of materials science such as *Applied Surface Science, Surfaces and Interfaces, Thin Solid Films, Journal of Chemical Physics, Superlattices and Microstructures, Materials Chemistry and Physics, International Journal of Applied Ceramic Technology, Materials and Design, CrystEngComm, ACS Omega, Materials,etc.* According to the presented data 341 citations have been received on the articles after the habilitation which proves the international interest in the results obtained by the candidate. All publications are a collective work co-authored by a relatively large number of scientists from various scientific organizations from Bulgaria and abroad (Germany, Turkey, Algeria, France, etc.). In the research carried out, the scientific expertise of Assoc. Prof. Avramova is in the study of various materials provided by other teams, using XPS method. By their nature, these are interdisciplinary studies, including synthesis and complex characterization through various physico-chemical methods, which requires a cooperation between scientists from different fields. This explains the relatively large number of authors in the works - for example 54 papers (about 83%) have between 6 and 13 authors. In 3 of the competition articles, the candidate is the first and corresponding author, in 13 - the second author and in 9 - the third author (a total of 25 papers), from which it can be concluded that the candidate's personal contribution to the joint research is substantial. The review of the candidate's scientific publications shows that they correspond in number and quality to the conditions and the topic of the competition.

The scientific research co-authored with Dr. I. Avramova after her habilitation has been reported at 82 international and national scientific forums as posters (predominant part) and oral reports. A list for participation in 13 projects is presented, of which 8 national, 3 international and 3 bilateral, with provided evidence for 8 of them. It should be noted that in four of the projects funded by NSF, she is the only participant from IGIC as a partner and has attracted funds in the amount of 65 250 BGN, which is a high mark for her scientific qualifications and ability to work in a team. Together with 5 other Bulgarian scientists, the candidate participates in a patent application (No. 113043 of 9.12.2019) on the topic "Method of synthesis of graphene-like phases". Assoc. Prof. Avramova is a co-supervisor of a PhD student, dismissed with the right of defense of the dissertation. Since 2018, she has been a member of the editorial boards of two international journals (Current Smart Materials and Recent Patents on Materials Science). Since 2015, she regularly performs anonymous peer review for reputable international journals in the field of materials science.

4. Compliance with the requirements for occupying the academic position “Professor”

Assoc. Prof. Dr. I. Avramova meets the requirements for occupying the academic position "Professor" in IGIC - BAS, according to the Law on the Development of the Academic Staff in the Republic of Bulgaria and the Regulations for its application and the Terms and Rules for Occupation of Academic Positions” in IGIC - BAS.

- According to the Nacional Center for Information and Documentation (NACID) (https://ras.nacid.bg/dissertation-preview/26779) Ivalina A. Avramova has acquired a “Doctoral

degree" and academic rank "Associate Professor" in the professional field 4.2. "Chemical Sciences";

- Her experience as Associated Professor at IGIC-BAS is over 10 years, i.e. more than five years term required;
- The publications and citations submitted for the competition do not repeat the ones submitted for the degree "Doctor" and for the academic position "Associate Professor";
- The report on the scientific activity of Assoc. Prof. Dr. Avramova shows that according to all indicators **she fulfills and exceeds (in some groups significantly) the national minimum requirements as well as the enhanced criteria of the Bulgarian Academy of Sciences and additional ones of IGIC for occupation of the academic position "Professor" in the professional field 4.2. "Chemical Sciences".** The science-metric indicators are as follows: indicator "B" - 185 points are achieved at minimum 100; indicator "G" - 942 points at minimum 220; indicator "D" - 682 points (minimum 120); indicator "E" - 193 points (minimum 150) and additional for IGIC indicator (J) – 160 points (minimum 120). **Thus, in total for all groups of indicators Assoc. Prof. Dr. I. Avramova has achieved 2212 points *vs* minimum of 760 required.**
- The professional qualification and the thematic scope of the scientific activity of Assoc. Prof. I. Avramova fully correspond to the specialty of the announced competition in professional field 4.2. "Chemical Sciences";
- There is no evidence of plagiarism in the scientific works submitted to the competition;

5. Main scientific achievements

The main competence of the candidate in research is in the use of X-ray photoelectron spectroscopy to study the chemical features of the surface of various materials (bulk materials and thin layers), which in combination with the data from other characterization methods, helps to explain their properties, and hence for their subsequent optimization, as well as to create new materials.

5.1. Achievements in the frame of the Habilitation work (papers from group "B")

The habilitation work includes 10 articles that thematically comprise research on carbon-based materials such as graphene, graphene-like phases, graphite and carbon black. The results of these studies have been published in 3 journals with Q1 (30%), 2 with Q2 (20%), 4 with Q3 (40%) and 1 with SJR (10%). Research on this class of materials is undoubtedly topical in view of the unique properties of graphene and graphene-like materials determining their versatile application in various fields. In these studies, the personal contribution of the candidate is clearly declared and it is in the analysis of the carbon chemistry by the XPS method. For a more detailed description of the carbon state, a complex analysis of the C1s photoelectron line along with the heteroatomic spectral regions such as O1s, S2p and N1s has been carried out. The significant role of the candidate in these studies is evident from the distribution of authors. In two of the publications the candidate is the first and corresponding author, and in 6 of them she is the second author. The most important specific scientific contributions of these studies can be summarized as follows:

- Based on the determined relative amount of sp2 and sp3 carbon atoms from the XPS spectra, it is shown that the carbon layers deposited by sublimation of pyrolytic graphite on Si and SiO_2/Si substrates are amorphous, while on DLC (diamond-like type carbon) substrates + SiO_2 a combination of predominantly single-layered graphene on the SiO_2 regions and of few layers of

polygraphene and sp2 and sp3 hybridized carbon/hydrocarbon species on the DLC islands is obtained;

- The influence of low-energy Ar+ plasma irradiation on layers deposited on SiO_2 and DLC and on highly oriented pyrolytic graphite (HOPG) has been studied. In the layers deposited on SiO_2 and DLC, breaking of C–C bonds from sp2 carbon atoms, formation of carbon vacancies, increased content of sp3-carbon atoms, accompanied by an increased amount of C=O functional groups have been found. The irradiation changes the structure of the HOPG layers as well, associated with a surface transformation to multilayer defective graphene. A thinning of the carbon layer occurs, an increase in the sp3/sp2 ratio with increasing treatment time, as well as a preferential formation of C=O bonds over C–O bonds;
- The deposition of graphene layers on various substrates such as Ni, μ-metal, SS304 and Si, by thermal decomposition of acetone using the CVD method has been confirmed by XPS analysis. High-quality three- or five-layer folded graphene is deposited on the μ -metal substrates, while few-layer (1–3 layers) defective graphene is deposited on the SS 304 substrates. Based on the changes in the C1s photoelectron spectra after exfoliation of the layers from the supports, a hypothesis has been proposed that the sp3-bonded carbon occupies the interface region between the supports and the layer(s), which mainly consist of sp2-bonded carbon. On a Si substrate, the deposition of both single-layer and up to few layers of defective graphene on two types of interlayers has been demonstrated. The one represents a mixture of sp2-hybridized pyrolytic graphite and a small amount of C70 and C60 fullerenes, and the second one is dominated by a diamond-like mixture of sp3- and sp2-hybridized carbon, SiC, SiO_2 and a small amount of C60 and C70 fullerenes;
- In order to control the process of deposition of thin carbon films on different substrates by pulsed laser deposition, the influence of the regime (continuous and pulsed) has been examined in details. It has been found that in continuous mode, nanoscale multilayer graphene with a thickness of about 25–30 nm is deposited, while pulsed deposition favors the formation of an extremely thin and high-quality graphene layer (from 0.5 to 1.2 nm), which is characterized by low resistance, similarly to that for pure graphene with good crystallinity;
- The possibility of obtaining graphene-like phases (defective graphene, graphene oxide and reduced graphene oxide) as fine suspensions by applying a novel pulsed laser ablation (PLA) approach in flow mode as well as the modification of two types of graphite and carbon black by acetone, toluene and phenol have been studied.

5.2. Achievements in the papers from group "G"

The publications included in group "G" are 55 in number and cover a great variety of research objects, with different nature, composition and state, predetermined by the field of application such as catalysts and photocatalysts, protective anti-corrosion coatings, in microelectronics, medicine and others. Prof. Avramova has divided these studies into 8 thematic groups depending on the application of the objects, their nature or method of preparation. I would summarize them in 5 directions and highlight the following as the most important scientific contributions:

5.2.1. Studies on catalysts and photocatalysts (14 papers)

- In general, valuable information (new or confirmatory) about the chemical composition, stoichiometry and oxidation state of the elements in photocatalysts/catalysts with different applications has been obtained by XPS analysis;

- A number of photocatalysts for the degradation of different dyes have been investigated by XPS: ZnO doped with Ag, Mn, Cu, Co and Ni, boron and nitrogen doped TiO_2 nanotubes, $CaTiO_3$ obtained by a combination of hydrothermal method with mechanical grinding, and spinel-type oxides such as $Ni_{1-x}Cu_xAl_2O_4$, $CuCr_2O_4$ and $CdFe_2O_4$, etc. The doping of ZnO with the metals is found to result in a defective samples with the generation of oxygen vacancies and complex defects, which accounts for the very good photocatalytic activity for dye degradation as well as almost 100% catalytic activity towards ozone oxidation. The XPS analysis proves the incorporation of boron and nitrogen mainly in the interstitial positions in the TiO_2 nanotube framework, accompanied by the reduction of Ti(IV) to Ti(III), which improves the photocatalytic activity for the degradation of methyl orange. The enhanced phoroactivity of the $CuCr_2O_4/SnO_2$ system toward the degradation of crystal violet dye is shown to be due to electron transfer from the $CuCr_2O_4$-conductive zone of the sunlight-activated sensitizer to the SnO_2-conductive zone;
- Dynamic X-ray photoelectron spectroscopy has been applied to determine the oxidation state of cerium in CeO_x/Al_2O_3 thin films electrochemically deposited on stainless steel substrates. At low cerium content, the main part of the surface is $CeAlO_3$ phase, while at high cerium content, CeO_2 and $CeAlO_3$ phases dispersed on Al_2O_3 have been recorded;
- $Zn_{1-x}Cu_xAl_2O_4$ and Fe-doped ZrO_2 have been investigated as photocatalysts for Cr(VI) reduction under light irradiation. The XPS analysis provides evidence for a moderate Lewis acid character and pronounced anionic character of the $Zn_{1-x}Cu_xAl_2O_4$ surface;
- Lanthanum and cerium oxides deposited on gamma-aluminum oxide in order to neutralize nitrogen oxides have been characterized by XPS.

5.2.2. Studies on carbon materials and their modifications (15 papers)

- A series of papers report results on the preparation of reduced graphene oxide (rGO), most often mixed with different carbon phases (defective graphene, graphene-like phases, GO, amorphous carbon, etc.), by laser ablation of a graphite target in water medium at different wavelengths. A significant increase in the amount of oxygen-containing radicals has been found as a function of laser fluence. It has been shown that by changing the laser wavelength and fluence it is possible to control the content of the different types of carbon.
- A mechanism for the two-dimensional polymerization of 1,3,5-trihydroxybenzene to graphene oxide (GO) has been proposed based on XPS;
- Results for the modification of nano-sized graphene and thin graphene-like layers under the influence of UVc light are presented, and the effect of the direction of irradiation (perpendicular and parallel) is also evaluated;
- The thermal modifications of carbon black pretreated with acetone have been studied. The treatment with acetone increases the content of oxygen-containing radicals, and heat treatment at 1080 °C stabilizes 2D graphene-like phases, while at 1150 °C 3D nano-graphite is formed;
- By means of XPS the deposition of carbon films by sublimation of modified carbon blacks on SiO_2/Si substrates and graphene layers on copper surfaces, as well as the influence of low-temperature thermal annealing on the phase formation in thin layers of TiO_2 doped with carbon, have been investigated.

5.2.3. Studies on thin coatings obtained by atomic layer deposition (11 papers)

- The conditions for the deposition of AlN thin films on different substrates such as Si(100), Si(111), Si/SiO2, graphene and SiC have been established and their stoichiometry has been

investigated depending on the experimental parameters. XPS analysis shows that when deposited on graphene, incomplete coverage with randomly distributed nano-sized islands of AlN is observed;

- The chemical composition and oxidation state of the elements of ZnO layers doped with Al, Co, Fe and Ni have been determined and their structural, morphological, optical and magnetic properties have been investigated. An increase in oxygen vacancies has been observed as a result of the doping. Iron-doped ZnO is particularly promising as it exhibits ferroelectric behavior.
- The atomic layer deposition process of amorphous Al_2O_3 layers on Si and graphene/Cu substrates has been optimized. The effect of temperature on the stoichiometry of the Al_2O_3 layers has been established by means of XPS.

5.2.4. Studies on glasses and glass-ceramics (6 papers)

- Multicomponent glasses with different compositions, containing modifying elements such as Ti, Fe, B, Mn, as well as glass-ceramics based on barium and strontium titanate, have been studied.
- Data have been obtained on the oxidation state of the elements. Iron is mainly in the form of Fe^{3+} ions in tetrahedral coordination as a glass matrix stabilizer or in octahedral coordination as a network modifier, but heat treatment leads to an increasing amount of Fe^{2+} ions. Titanium is found only as Ti^{4+} and is present in tetrahedral and octahedral coordination in glass and glass-ceramics, while Ba^{2+} ions are found in different environments depending on the time of crystallization. The behavior of the non-bridging oxygen bonds as a function of the crystallization time has also been monitored.

5.2.5. Studies on corrosion protective coatings, organic and other materials (9 papers)

- XPS measurements have been carried out by means of a specially developed tantalum screen and the changes occurring as a result of a corrosive media in the chemical composition and state of the elements in electrochemically deposited CeO_2-Ce_2O_3 films on stainless steel have been examined. Interesting and valuable information has been obtained, indicating for the self-healing abilities of these films, namely, the formation of secondary passivating oxide/hydroxide films has been observed on the steel surface, which serve as a barrier preventing the corrosion processes.
- The effects of the transition elements Mo, V and Zr on the phosphate sealing of cerium oxide primer layers deposited on an aircraft alloy have been evaluated. XPS studies of the bi-layer coatings suggest that these elements are successfully incorporated into the phosphate-sealing layer causing oxidation of Ce(III) to Ce(IV). Thus, doped sealed coatings show unsatisfactory protective capabilities in a corrosive environment.
- The comparative study on the impact of the anodization of aircraft alloy in HCl, HNO_3, H_2SO_4 and H_3PO_4 on the samples' surface morphology and chemical composition reveals that the monoprotonic acids have a deep destructive effect due to dissolution of the alloy components, whereas the polyprotonic ones possess either indistinguishable influence, or surface film formation like $AlPO_4$.
- It has been shown that $(CeO_2)_x(Al_2O_3)_{1-x}$ mixed layers show better corrosion protection in nitric acid compared to pure Al_2O_3 or Ce_2O_3, CeO_2 layers, which improves with increasing cerium oxide concentration.
- XPS method has also been applied: to determine the surface composition of multilayer coatings of chitosan and xanthan with a view to their use for drug deliver; to study the anti-bioadhesion behavior of four types of superhydrophobic carbon black coatings towards Pseudomonas bacteria; to characterize Ag-doped alumina coatings with antimicrobial properties; to

study the sintering processes of B_4C in the presence of WC and W_2B_5 as well as to synthesize tungsten diselenide flakes and layers.

In summary, the scientific contributions of the candidate are with experimental and scientific-fundamental character in the field of solid state chemistry, mainly related to the enrichment of knowledge and the establishment of new spectral data on the chemistry of the surface of various materials by means of X-ray photoelectron spectroscopy.

CONCLUSION

Assoc. Prof. Dr. Ivalina Avramova is well-recognized scientist with high qualification in the analysis of the chemistry of the surface of materials with different nature and applications, with valuable research and achievements in the field of experimental X-ray photoelectron spectroscopy, with a significant amount and internationally recognized scientific work. The science-metric indicators of the candidate fully meet and exceed the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the additional requirements of IGIC- BAS for occupation of the academic position of "Professor". Based on the above, **I give my positive evaluation and convincingly vote "YES" Associate Professor Dr. Ivalina Avramova to take the academic position "Professor"** in the professional field 4.2. "Chemical Sciences", specialty "Solid State Chemistry" at the Institute of General and Inorganic Chemistry – BAS.

Sofia, 04.09.2023 Reviewer:

(Violeta Koleva, Prof., Dr., IGIC - BAS)