REVIEW

by Prof. Dr. Plamen Kirilov Stefanov
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regarding a competition for the occupation of the academic position "Professor", for the needs of laboratory "Electron Spectroscopy of Solid Surfaces" at IGIC-BAS under professional field 4.2 "Chemical sciences", scientific specialty "Solid State Chemistry", ”, announced in the "State Gazette", issue. no. 46 of 26.05.2023

For participation in the announced competition, only one candidate, Assoc. Prof. Dr. Ivalina Avramova from IONH - BAS has submitted the respective documents

1. General presentation of the received materials

Assoc. Prof. Ivalina Avramova has submitted the necessary documents: CV, copy of diploma for awarded PhD degree, diploma for Associate Professor; extended habilitation reference in Bulgarian and English, general list of publications, general list of citations, list of publications for participation in the competition, list of participation in scientific forums after habilitation, certificate of fulfillment of the minimum and additional requirements of BAS and IGIC-BAS. The documents contain the full texts of publications and evidences of participation in scientific forums and research projects.

Assoc. Prof. Avramova has published a total of 125 scientific works, and for participation in the present competition she submitted 65 scientific publications, which do not repeat those presented in other competitions for holding academic positions and acquiring scientific degrees, and all of them fall within the field of the competition and this reason are subject to review. Prof. Avramova and I have two publications in common, marked AR1 and AR6 in the list of articles included in the competition materials and therefore will not be considered in the review

2. Brief biographical data about the candidate

Ivalina Avramova graduated from higher education in 1996 at the Faculty of Physics of the University of St. Kliment Ohridski", as a master's degree in "Engineering Physics" and defends a diploma thesis on the topic: "Partially coherent interaction of rays in a two-layer system". In 2003, she defended PhD thesis on the topic: "Electronic properties and thermoelectric efficiency of Ge1-xAgx/2Bix/2Te solid solutions" at the Faculty of Physics of the Sofia University of St. Kliment Ohridski" . Ivalina Avramova's scientific career developed mainly at the IONH-BAS where she held the following academic positions: physicist (2001-2004); Assistant (2004-2006); Assistant Professor (2006-2012) and Associate Professor (2012-present) in the "Electron Spectroscopy of Solid Surfaces" laboratory, which is indicative of her upward professional development. She completed a postdoctoral specialization at Free University, Brussels (2006-2007) and a postdoctoral specialization at Bilkent University, Ankara (2009-2011).

3. General characteristics of scientific research and applied science

The detailed review of the results summarized by the candidate, reflected in the Habilitation Thesis and the Author's Reference and the relevant publications, outline a certain

orientation of her scientific research activity towards clarifying the fundamental and applied aspects of synthesis, studying the properties and application of new innovative materials.

Assoc. Prof. Avramova's Habilitation thesis summarizes research on obtaining graphene and graphene-like phases with different methods and its functionalization. Graphene and its analogues are potential candidates in various applications, such as photovoltaics, catalysis, fuel cells, sensors and batteries. But a detailed understanding of graphene needs accurate surface characterization, which can only be provided by the specific capabilities of X-ray photoelectron spectroscopy (XPS). This determines the candidate's main role in conducting research, namely the detailed characterization with XPS of deposited graphene and graphene-like phases on different substrates. In 8 of the publications included in the Habilitation report, she is in first or second place in the author team, which is indicative of her essential role in the conducted research and the processing of the obtained results.

The candidate's summarized results, reflected in the Author's Reference of Contributions and related publications, outline a focus on the study of innovative materials with potential applications, such as catalysts and photocatalysts, protective anti-corrosion coatings, in microelectronics, medicine and others.

The results presented by Assoc. Prof. Avramova are up-to-date and of interest, both from a fundamental and from a scientific-applied point of view, and correspond to the theme of the announced competition.

4. Evaluation of the presented materials

Associate Professor Dr. Ivalina Avramova is the author of 125 publications, of which 95 are in publications referenced and indexed in the global WEB OF SCIENCE and SCOPUS databases. In the current competition, 65 of these articles are involved, distributed among journals by quartiles as follows: Q1-15; Q2-17; Q3-11 and Q4-6 articles and 16 articles with SJR without IF. Among those presented for the competition are articles in the authoritative Applied Surface Science JCR-IF (Web of Science):5.155, Surface and Interfaces JCR-IF (Web of Science):3.724, Journal of Alloys and Compounds JCR-IF (Web of Science):4.65 and others. In 18 of these articles, she is in first or second place in the author's team, which is indicative of her leading role in the conducted research and the shaping of the obtained results. The number of citations noticed on all the candidate's publications is 851, of which 341 are on publications included in the contest. Some of the research results have been presented at 85 national and international scientific forums at home and abroad. The H-index of the candidate, evaluated by SCOPUS, is 16. Assoc. Prof. Avramova has participated in 13 scientific projects, co-authored 1 patent, which is indicative of her active participation in research and applied science. She was the supervisor of a doctoral student who was dismissed with the right of defense. Recognition of her competence in the relevant scientific field is the membership in two international editorial boards, as well as the large number of reviews of publications for renowned international journals.

The presented report on the minimum requirements for the scientific activity of candidates for the academic position of "Professor" shows that for all groups of indicators, the points completed by Assoc. Prof. Avramova correspond to the required ones, namely for indicator B (Habilitation thesis) with a required minimum of 100, 185 were declared, and in group D (scientific publications in publications referenced in WoS or Scopus) for the required 220 points, 942 were fulfilled. In group D, referring to citations in scientific publications referenced and indexed in the WoS or Scopus databases, at the requirement of 120 points, 682 points are met. For indicator group E with a required minimum of 150 points, the candidate scores 193 points. The total number of points from all indicators is 2214 and significantly exceeds the minimum requirements of the IGIC for occupying the academic position "Professor" .

5. Main scientific and scientific-applied contributions.

The research activity of the candidate Assoc. Prof. Avramova, the results of which are included in publications submitted for participation in the competition, can be thematically systematized in 5 main directions:

1. Characterization of graphene and carbon allotropes and phases deposited on different supports
2. Research of catalysts and photocatalysts with XPS
3. Study of protective coatings with XPS
4. Examination of glasses and glass-ceramics with XPS
5. Study of different thin films obtained by laser ablation

The main scientific and scientific-applied contributions of the candidate enrich the existing knowledge and theories and show a serious potential for application in practice. They will be highlighted, in the order of the formulated main topics:

Characterization of graphene and carbon allotropes and phases deposited on different supports

Carbon materials are widely used in various technological applications such as energy storage, catalysis, and sensors, etc., making them the subject of significant interest.

The research included in the first direction occupies the most essential part of Assoc. Prof. Avramova's scientific work and is summarized in 10 main publications of the Habilitation work, as well as 15 outside it, which are related thematically. The object of the research summarized in the Habilitation reference is the search for an approach for the deposition of graphene and graphene-like phases that would ensure high reliability and relatively high quality. For this purpose, methods such as sublimation of pyrolytic graphite, pulsed laser deposition,chemical deposition from gas phase of acetylene have been used. Since the surface properties of materials are governed by the atomic structure and composition of the outermost layer on the surface of the material, it is necessary to use appropriate surface analysis techniques for its characterization. X-ray photoelectron spectroscopy (XPS) is a key surface analysis technique that is widely used to characterize carbon materials.

As indicated in the Habilitation report, it is the XPS results obtained in the course of research that determine the candidate's main contributions to solving the set goals and are an essential part of the results presented in the relevant publications. The identification of the type of deposited carbon layers is mainly based on a detailed analysis of the photoelectron C1s peak. The main approach used by the candidate in the conducted XPS studies is the application of the decomposition procedure of the C1s peak, which allows to extract information about the type of sp^2- to sp^3-hybridized carbon and to establish the presence of types of carbon phases such as graphene, graphite, graphene oxide, fullerene etc. Another approach used to determine the sp^3/sp^2 ratio in graphene layers is through the so-called D-parameter, which is based on the first derivative of the carbon Auger KLL line. The differential shape of the spectrum allows the energy separation of the most intense bipolar deviations to be estimated, as a measure of the ratio of hybridized sp^3 and sp^2 type carbon. In the case of the presence of different functional groups on the surface of carbon materials and the photoelectron peaks of other elements such as O1s, S2p and N 1s were used to clarify their nature. With the help of the mentioned methodology, a detailed analysis of the synthesized carbon materials was made, and the importance and contribution of the candidate's research can be summarized as follows:

Carbon layers were deposited by sublimation of pyrolytic graphite in an Ar gas stream on Si- substrates (types Si, SiO_2/Si and (DCL (diamond-like carbon) + SiO_2). By deconvolution of the photoelectron C1s peak into two components, corresponding to sp^2 hybridization and sp^3 hybridization, it was determined that the graphene film was 60.7% of the total amount of carbon, and that of other hydrocarbon groups is 12.6 at.%, and it is concluded that the layer can

be defined as "polygraphene" (mainly a single-layer graphene film consisting of mutually non-oriented zones.

A study of deposition of carbon films by sublimation of carbon from modified carbon black on SiO_2/Si substrates at a temperature of about 1050-1060°C was carried out. The transformations of the film as a function of the deposition time were followed by X-ray photoelectron spectroscopy. In the first few nanometers, the deposited film is amorphous and enriched in sp^3-hybridized carbon, followed by the deposition of multilayer defective graphene, then a continuous carbon layer is formed, and finally a continuous layer, a mixture of nano-sized graphite and graphene.

The possibility of deposition of graphene and graphene-like phases on (001)Si substrate, using a chemical vapor deposition (CVD) method by acetone decomposition was studied. By XPS analysis, it was found that the deposition takes place as two types of interlayers: i) the first consists of a mixture of sp^2-hybridized highly oriented pyrolytic graphite (HOPG) and amorphous carbon, also containing some sp^3-hybridized carbon as well as a small amount of C_{70} and C_{60} fullerenes; ii) the second is dominated by a diamond-like carbon (DLC) mixture of sp^3- and sp^2-hybridized carbon, some cubic SiC, and a small amount of C_{60} and C_{70} fullerenes.

Thin layers of graphene were deposited on silicon substrates by means of laser ablation with two different deposition modes: continuous and pulsed. With XPS, it was found that in continuous mode the sp^3/sp^2 ratio decreased with increasing deposition time, forming thicker films. Accordingly, when the number of deposited layers increases, the structure acquires a pronounced sp^2 character. In pulsed mode, XPS analysis shows a predominant sp^2 structure of the deposited film, with their thickness ranging from monolayer to multi-layer graphene. The results of the conducted experiments show that in the continuous mode the thickness of the deposited layers can vary in the range from 1 to 180 nm, while the pulse deposition mode is more promising when the goal is the deposition of thin and high-quality graphene layers.

An original approach was used to synthesize graphene oxide (GO) by two-dimensional polymerization. The transformation process of the precursor to GO was followed by analyzing the C 1s and O 1s peaks, characterizing carbon atoms in different functional groups such as C of the type (C-C), C in C-O and bonds (C-OH), carbonyl C (C=O) and carboxyl carbon bonds (O=C-OH). Using the C/O intensity ratios, the degree of graphenization of the layers is estimated.

Experiments were carried out with laser irradiation of a fine suspension obtained from a solution of microcrystalline graphite in doubly distilled water in order to obtain graphene and graphene-like phases (defective graphene, graphene oxide and reduced graphene oxide). With XPS the composition of the obtained carbon phases was determined and it was found that the obtained colloids mainly contain reduced graphene oxide-rGO, but in some of them graphene oxide-GO, graphite microparticles similar to graphene and some amorphous carbon phases were also found and polymers.

In practical aspect, these studies has contributed to the development of a patent for a method of obtaining graphene-like phases by laser ablation.

In order to functionalize graphene layers, a low-energy Ar^+ plasma treatment was used. In order to determine the changes that occurred, as a consequence of the treatment with argon plasma and subsequent heating, all layers were examined with XPS. An improvement in the structural quality of the layers, thinning and surface transformation to multilayer defective graphene was found.

In order to modify nanoscale graphene, irradiation with 254-nm UVc light was performed and an increase in sp^3 hybridized carbon in the layer was found.

Investigation of catalysts and photocatalysts with XPS

X-ray photoelectron spectroscopy is a valuable method for characterizing the composition, chemical state of atoms, and electronic structure of various materials. In this capacity, XPS has been used by the candidate in a number of studies for the characterization of catalysts and photocatalysts.

A detailed XPS study of activated ZnO powder doped with Mn, Co, Ni, Cu and Ag for photocatalytic applications was carried out. From the photoelectron O1s spectrum of oxygen, a significant increase in the ratio of oxygen attributed to defective ZnO to total oxygen in the doped samples was found for the various elements in the order: (Ni)<(Cu)<(Co)<(Ag). Doped, preactivated ZnO with these elements exhibits enhanced photocatalytic activity in the reaction of the model pollutant RB5 dye compared to pure zinc oxide.

In a XPS study of a ZnO catalyst doped with Cu for ozone conversion, the formation of defects due to the inclusion of Cu^{2+} ions in the ZnO lattice was found. This is manifested in an increase in the peak in the O1s spectrum attributed to an oxygen-deficient region in the ZnO matrix. The formation of this defective structure significantly increases the catalytic activity, reaching 100% ozone conversion at 70°C

In the hydrothermal synthesis of zinc oxide for photovoltaic material, different precursors have been used with the aim of obtaining different types of porosity and surface particles on ZnO. With XPS, the ratio of oxygen belonging to defects (oxygen vacancies) to the total amount of oxygen on the surface was determined, which gives information that a catalyst having a greater number of defects has a correspondingly higher activity in the reaction of the azo dye Reactive black 5 (RB5).

The XPS study of N and B doped TiO_2 nanotubes (TNTA) can be considered as a significant contribution. X-ray photoelectron spectroscopy studies demonstrate successful incorporation of N and B in predominantly interstitial positions, with N and B promoting reduction of Ti(IV) to Ti(III) during calcination. As a result of B,N-doping, remarkable photocurrent enhancement and better photocatalytic activity for methyl orange (MO) dye degradation were observed due to the synergistic effects of B,N-co-doping and lower electron-hole pair recombination rates.

A series of studies on spinel photocatalysts have been carried out, with the main contribution of XPS being the determination of the stoichiometry and acid-base properties of the surface. In this aspect, a study of spinel catalysts of the $Zn_{(1-x)}Ni_xAl_2O_4$ (x = 0.0-1.0) was conducted, in which the oxide state of the constituent elements and their surface concentration were determined. By determining the ratio of the sum of the fractions of Al^{3+}, Zn^{2+}, Ni^{2+} and that of oxygen for two compositions (x =0.2 and 0.8), respectively 0.75 and 0.69, it was found that the surface has a moderately acidic character of Lewis and pronounced anionic character, which is a prerequisite for interesting catalytic and electrochemical properties for these materials.

In a similar experiment, XPS was used to investigate the elemental composition, surface state, bonding nature, and acid-base properties of $Zn_{(1-x)}Cu_xAl_2O_4$ ($0.0 \leq x \leq 1.0$) photocatalysts for Cr(VI) reduction in daylight . It was found that the surface has a moderate Lewis acid character and a pronounced anionic character, which is a prerequisite for high photocatalytic activity.

As a continuation of the search for an active catalyst for the photocatalytic reduction of the toxic chromate Cr(VI), Fe-doped ZrO_2 was investigated. The surface compositions of $Zr_{1-x}Fe_xO_{2-x/2}$ (x=0.0 and 0.5) and the chemical states of the constituent elements were determined by XPS, and it was found that the introduction of Fe^{3+} cation into the ZrO_2 lattice favors the formation of oxygen vacancies, which is reflected in a larger number of surface active sites.

For the first time, optical, electrochemical and photoelectrochemical characteristics of Gd_2CuO_4 were investigated with a view to its use as a photocatalyst for the removal of various inorganic and organic pollutants. The stoichiometry and states of the constituent elements of Gd_2CuO_4 were analyzed by XPS. Two types of oxygen defects in Gd_2O_3 have been identified, related to oxygen deficiency and excess. A similar study was carried out for spinel $CdFe_2O_4$ nanoparticles synthesized in nitrate solutions. The stoichiometry and states of the constituent elements of $CdFe_2O_4$ were analyzed by XPS. Good chemical stability and suitable optical properties were found, i.e. absorption in a wide visible range due to the nanometric size of the particles, due to which a high efficiency was obtained for the degradation of Methyl Green Dye (MGD).

A study was conducted with different methods of forming spinel solid solutions of the type $Ni_{(1-x)}Cu_xAl_2O_4$ (x = 0.0–1.0) as effective photocatalysts for the daylight degradation of Congo red-azo dye. The use of XPS provides clear evidence for the formation of spinels and for harmonic replacement of Ni^{2+} by Cu^{2+}. The intensity of the Cu2p peaks for Cu^{2+} decreases as the Ni^{2+} content increases and simultaneously the intensity of the Ni2p peak increases. As a consequence of the established substitution, Cu-substituted $NiAl_2O_4$ has been shown to absorb more photons and generate more electrons and holes, which favors higher photocatalytic activity compared to unsubstituted compounds ($NiAl_2O_4$, $CuAl_2O_4$).

Investigation of protective coatings with XPS

In this direction, the main emphasis in the contributions is the use of XPS in the characterization of coatings to protect the surface of materials. The main role of XPS is in the analysis of the composition of various types of coatings that are actively investigated for corrosion protection, as well as post-corrosion analysis, which provides sufficient information to understand the mechanism of corrosion protection.

Detailed deposition studies, investigation and evaluation of the corrosion protection ability of mixed model layers in nitric acid corrosion media as a function of changing ratio between CeO_2, $CeAlO_3$ and Al_2O_3 on a modified steel surface were carried out. The changes in the surface composition and states of the constituent elements of the electrodeposited on steel/mixed Al-Ce oxide layers, depending on the concentration ratio of Al^{3+} and Ce^{3+} ions in the working electrolyte, were investigated by XPS. In this way, the stoichiometry described by the formula $(CeO_2)_x(Al_2O_3)_{1-x}$ was determined, where the value of x depends on the ratio between the concentrations of Al^{3+} and Ce^{3+} ions in the working electrolyte.

A practical contribution is the investigation of the possibility of incorporating transition elements in a layer of $CePO_4$ deposited on an AA2024-T3 aircraft type alloy. The XPS data show that the cerium in the pure cerium phosphate coating is mostly in the Ce^{3+} state, while doping with Mo, V, Zr leads to its oxidation to Ce^{4+}. The obtained results show a successful incorporation of these elements into the phosphate protective layer. A similar practical contribution is a systematic study and comparison of the effect of acidic anions from HCl, HNO_3, H_2SO_4 and H_3PO_4 solutions on the morphology, chemical composition and distribution of elements on the metal surface of aircraft type AA2024-T3 alloy, as a result of anodic polarization . The XPS studies show aluminum oxide formation as a result of the anodization process. For anodization proceeding in H_3PO_4 solution, formation of an additional layer of $AlPO_4$ on the surface of the anodized metal alloy is assumed, and in H_2SO_4 solution formation of $Al_2(SO_4)_3$ thin layer, which contribute to suppressing the dissolution of the protective Al_2O_3 layer.

Investigation of glasses and glass-ceramics with XPS

XPS is a valuable method for the study of glasses and glass-ceramics, providing accurate information on the surface concentrations of elements and their chemical state.

Several of the studies in this direction are devoted to the synthesis and characterization of the phase composition of glasses of the type $20.1Na_2O/23.1BaO/23.0TiO_2/7.6B_2O_3/17.4SiO_2/3Al_2O_3/5.8Fe_2O_3$ at different treatment temperatures. The XPS study shows that the titanium is only in the Ti^{4+} state, and the iron mainly as Fe^{3+} and forming BaTiO3. Information about the valence state of iron is important because it is decisive for the stability of the formed glass, since the ability to form glass is due to the different type of incorporation of Fe^{3+} in the glass, it is either in tetrahedral coordination, as a stabilizer of the glass network or in octahedral coordination, as a network modifier. It has also been shown that Ti^{4+} and Fe^{3+} ions are present in tetrahedral and octahedral coordination in glass and glass-ceramics, and Ba^{2+} ions occur in different environments, depending on the time of crystallization.

X-ray photoelectron spectroscopy study of glass-ceramic materials with a composition of the type $(23.1- z)Na_2O/17.1BaO/6SrO/23TiO_2/17.4SiO_2/7.6B_2O_3/5.8Fe_2O_3/zAl_2O_3$,, z = 0 and 3 mol %. shows that in both compositions, crystalline phases containing Ba^{2+} and $Sr^{2+,}$ ions are present in the form of a perovskite structure. Also, from the deconvolution of the O1s peak, the appearance of Si-O-Si bonds, which lead to the stabilization of the glass network, was established. Another object of research are glasses from the system $(100 - x)(0.16Na_2O/0.10MnO/0.74SiO_2)/xFe_2O_3$, (x = 15 and 25 mol %), for which XPS found that Mn is in the oxidation state Mn^{2+} in the glass, while Fe occurs mostly as $Fe^{3+,}$ and some Fe^{2+}.The heat treatment leads to a change in the chemical state of Fe from mainly Fe^{3+} to a mixture of Fe^{3+} and an increasing amount of Fe^{2+} and to the appearance of very small particles of $MnFe_2O_4$.

Investigation of various thin films produced by atomic deposition

A series of investigations have been carried out on the deposition of thin films on various substrates by chemical phase atomic deposition. The main role of XPS is in stoichiometry analysis of different types of coatings. Formation of AlN layers during deposition on Si(100), Si(111) and Si/SiO_2 graphene and SiC has been demonstrated by XPS. ZnO layers doped with Co, Fe or Ni have been deposited for electronic, magnetic or optical applications. Formation of ZnO was detected by XPS, but only Ni^{2+} was detected in the layer, while Co and Fe were not detected. By analyzing the O1s peak, an increase in the amount of oxygen vacancies was found, suggesting the incorporation (at least in very small amounts) of Co and Fe in ZnO films.

6. Critical notes and recommendations to the candidate's scientific works.

I have technical remarks about the candidate. I believe that it is more correct that the names and abbreviations of the various synthesis and analysis methods in the Habilitation and Author's reference should be written in Bulgarian, which will be more understandable when reading the text by non-specialists. It would also be better to avoid detailed technical details. These notes refer to the formatting of the text in the Habilitation and Author reference, but do not detract from the quality of the candidate's scientific achievements and contributions.

7. Personal impressions of the candidate.

I know Assoc. Prof. Ivalina Avramova personally since she joined the Laboratory "Electron Spectroscopy of Solid Surfaces" at the IGIC-BAS in 2001. Over the years, she has grown as a competent specialist in the application of XPS in studing the chemistry of the surface of innovative materials, which maked her in demand partner for participation in numerous research projects.

CONCLUSION

The presented materials for the publication activity and the obtained results fully correspond to the theme of the announced competition and exceed all the required indicators according to LDAS, the Regulations for its application, the relevant Regulations of the BAS, as well as the specific requirements of the Regulations of the IGIC-BAS for occupying the academic position "Professor". Upon their review, the impression remains that Associate Professor Dr. Ivalina Avramova is a scientist with significant contributions in her scientific field. This gives me the reason to give my positive assessment and to propose to the respected members of the Scientific Jury and the Scientific Council of IGIC-BAS to support the candidacy of Associate Professor Dr. Ivalina Avramova and vote for awarding the academic position "Professor" in professional direction 4.2 "Chemical sciences" and scientific specialty "Solid state Chemistry".

20/09/2023 Reviewer:

Prof. Dr. Plamen Stefanov