Workshop on Plasma-Based Synthesis of Nanomaterials

Book of Abstracts

Prague, Czech Republic, February 10-11, 2020

Charles University

Faculty of Mathematics and Physics

Introduction

Workshop "**Plasma-Based Synthesis of Nanomaterials"** is held on February 10 – 11, 2020 in Prague, Czech Republic, Charles University, Faculty of Mathematics and Physics, the Mala Strana campus. The event continues the program of Partner Country Workshops organized in relation to and preceding the International Conference on Plasma Surface Engineering (PSE) held biennially in Garmisch-Partenkirchen, Germany. The biennial PSE conference series is organized by the European Joint Committee on Plasma and Ion Surface Engineering.

With a continuously growing interest in the preceding PSE events, with nearly 800 participants from all over the world in 2018, PSE is a well-established and leading forum in the field of plasma as well as ion- and particle-beam assisted surface modification and thin film technologies.

17th International Conference on Plasma Surface Engineering is organized on September 06 – 11, 2020, in Garmisch-Partenkirchen, Germany with Prof. Jaroslav Vlcek as chairman and the Czech Republic as the partner country. Therefore our Workshop may be viewed as partner country event with the aim to promote the PSE and to increase the interest of Czech companies to employ plasma techniques in their applications. The workshop has 70 participants with 9 invited lectures, 11 oral talks, 23 posters and 5 company communications.
All colleagues from the academia and industry as well as students are warmly welcomed.

Prof. Jaroslav Vlček
PSE Chairman

Prof. Hynek Biederman
Workshop Chairman

Dr. Jan Hanuš
Workshop secretary

Workshop on Plasma-Based Synthesis of Nanomaterials

10th - 11th of February 2020, Prague, Czech Republic

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PROGRAM OVERVIEW

		10.02.2020 Monday			11.02.2020 Tuesday
9:00	9:40	registration	Session 3	chair	V. Straňák
9:40	10:00	Opening - H. Biederman, J. Vlček	9:00	9:40	IN06 - J. Vyskočil
Session 1	chair	J. Benedikt	9:40	10:00	Co01 EurA Ag - R. Förch
10:00	10:40	IN01 - A. R. Gonzáles-Elipe	10:00	10:20	Co02 Kratos - S. Hutton
10:40	11:00	OR01 - T. Košutová	10:20	10:30	Co03 TTS - L. Mikuličková
11:00	11:30	coffee break	10:30	10:40	Co04 Roplass - T. Homola
11:30	11:50	OR02 - A. Chauvin	10:40	11:10	coffee break
11:50	12:30	IN02 - O. Kylián	11:10	11:30	Co05 Hella - P. Tuček
12:30	14:00	lunch	11:30	11:50	OR07 - P. Souček
Session 2	chair	A. Choukourov	11:50	12:30	IN07 - M. Zeuner
14:00	14:40	IN03 - V. Straňák	12:30	14:00	lunch
14:40	15:00	OR03 - M. Mitronika	Session 4	chair	P. Vašina
15:00	15:20	OR04 - P. Sezemský	14:00	14:40	IN08 - V. Matolín
15:20	16:00	IN04 - J. Benedikt	14:40	15:00	OR08 - M. Thukkaram
16:00	17:00	coffee break + poster session	15:00	15:20	OR09 - A. Sergievskaya
17:00	17:20	OR05 - D. Thiry	15:20	15:40	OR10 - J. Čapek
17:20	17:40	OR06 - N. Saito	15:40	16:10	coffee break
17:40	18:20	IN05 - P. Vašina	16:10	16:30	OR11 - V. Prysiazhnyi
			16:30	17:10	IN09 - S. Haviar
			17:10	17:20	Closing

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PROGRAM

February 10th – Monday

9:00 – 9:40 Registration
9:40 – 10:00 Opening: H. Biederman, J. Vlček

Session 1

Chair: Jan Benedikt

10:00 – 10:40 Invited lecture: A. R. González-Elipe: Geometry, Shadow and Sheaths for the Nanostructuration of Thin Films

10:40 – 11:00 T. Košutová: Thermal evolution of heterogeneous silver/plasma polymer nanoparticles studied by X-ray scattering methods

10:00 – 11:30 Coffee break

11:30 – 11:50 A. Chauvin: Synthesis of gold ring-shape nanoparticles using co-sputtering over liquids

11:50 – 12:30 Invited lecture: O. Kylián: Plasma assisted synthesis of nanomaterials: challenges and prospects

12:30 – 14:00 Lunch

Session 2

Chair: Andrei Choukourov

14:00 – 14:40 Invited lecture: V. Straňák:Nanostructured (bio)functional thin films

14:40 – 15:00 M. Mitronika: Hybrid approach coupling Plasma Processes and injection of Colloidal Solutions for customized Nanocomposite thin films

15:00 – 15:20 P. Sezemský: Plasma-assisted deposition of thin ITO film for optical-fibre-based biosensors

15:20 – 16:00 Invited lecture: J. Benedikt: Non-equilibrium atmospheric plasmas for nanomaterials

16:00 – 17:00 Coffee break + **Poster session**

17:00 – 17:20 D. Thiry: The wrinkling concept applied to plasma polymers: an innovative approach for controlling their nano-architecture

17:20 – 17:40 N. Saito: N+-doped Graphene by Solution Plasma

17:40 – 18:20 Invited lecture: P. Vašina: Evolution of ionization fraction of sputtered species in standard, multi-pulse and reactive HiPIMS

Ferbruary 11th – Tuesday

Session 3

Chair: Vítězslav Straňák

9:00 – 9:40 Invited lecture: J. Vyskočil: Nanostructured Coatings in Automotive Industry

9:40 – 10:00 Company presentation: R. Förch, EurAg

10:00 – 10:20 Company presentation: S. Hutton, Kratos

10:20 – 10:30 Company presentation: L. Mikuličková, TTS

10:30 – 10:40 Company presentation: T. Homola, Roplass

10:40 – 11:10 Coffee break

11:10 – 11:30 Company presentation: P. Tuček, Hella Autotechnik Nova

11:30 – 11:50 P. Souček: W-B-C Coatings Prepared by Magnetron Sputtering Utilizing Pulsed Plasma Excitation

11:50 – 12:30 Invited lecture: M. Zeuner: Plasma technologies enabling mobile communication

12:30 – 14:00 Lunch

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Session 4

Chair: Petr Vašina

14:00 – 14:40	**Invited lecture: V. Matolín: PEM Based Ordered Superstructures as a Durable Support for Fuel Cell Catalyst**
14:40 – 15:00	M. Thukkaram: Deposition of antibacterial Ag/a-C:H nanocomposites on titanium substrates using a gas aggregation cluster source
15:00 – 15:20	A. Sergievskaya: Synthesis of nanoparticles by magnetron sputtering of silver and gold onto castor oil
15:20 – 15:40	J. Čapek: Structure and properties of bixbyite-based Ta–O–N films prepared by HiPIMS
15:40 – 16:10	Coffee break
16:10 – 16:30	V. Prysiazhnyi: The utilization of gas aggregated silver nanoparticles for the detection of small molecules for imaging MS
16:30 – 17:10	**Invited lecture: S. Haviar: Nanostructured Materials Based on Thin Films and Nanoclusters for Gas Sensing**
17:10 – 17:20	Closing

INVITED PRESENTATIONS

Workshop on Plasma-Based Synthesis of Nanomaterials

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Geometry, Shadow and Sheaths for the Nanostructuration of Thin Films

A. García-Valenzuela, M. Oliva-Ramírez, A. Palmero, R. Alvarez, A. Borrás, M.C. López, A . R. González-Elipe*,

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In this talk we will discuss the effect of the deposition geometry and the use patterned substrates and template structures to tailor the thin film nanostructure. Basic concepts involved in the nanostructuration mechanisms such as shadowing effects of deposited particles, the occurrence of scattering events in the plasma gas or the preferential impingement of ion species along given directions (1) will be discussed within the frame of various classical thin film growth methodologies, e-beam evaporation, magnetron sputtering and plasma enhanced chemical vapour deposition (2). It will be shown how the modification of experimental conditions and working parameters enable a precise control at the nanoscale of the nanostructure and even the chemistry of the films. Some of these nanostructuration processes will be accounted for by the employ of Monte-Carlo techniques to simulate the film growth. The possibilities of properly controlling shadow, geometry and plasma sheaths to tailor the nanostructure of thin film materials will be illustrated with various application examples in the fields of photonic sensors, optics, electrodes and fuel cells.

Acknowledgements

We acknowledge the financial support of AEI-MINECO and EU-FEDER programs

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2.-a) A. García-Valenzuela, et al. Nanotechnology 2017, 28, 465605. b) A. García-Valenzuela, et al. Appl. Surf. Sci. 2019, 480, 115.

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Plasma assisted synthesis of nanomaterials: challenges and prospects

O. Kylián, J. Hanuš, P. Solař, J. Kousal, R. Štefaníková, D. Nikitin, A. Kuzminova, P. Pleskunov, A. Choukourov, H. Biederman

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Magnetron-based gas aggregation cluster(nanoparticle) sources (GAS) have become very attractive tool for the gas-phase synthesis of nanomaterials of various kinds. The popularity of such sources is given not only by their applicability to produce high purity single or multi-component heterogeneous nanoparticles with tailor-made properties, but also by their compatibility with other vacuum-based deposition techniques that allow for the effective bottom-up fabrication of complex nanostructured or nanocomposite materials. However, in spite of undisputable advances, a wider use of GASes still remains rather limited. The main aim of this presentation is to identify the main obstacles that hinder the applicability of GAS systems. Issues related to the time- and cost-efficiency of the nanoparticle production, insufficient knowledge of the processes that influence their growth and properties, transport of nanoparticles towards the substrate as well as their interaction with the substrate/matrix materials will be discussed on the basis of recent experimental results.

Acknowledgements

This work was supported by the grant GACR 17-22016S from the Grant Agency of the Czech Republic and by the student grant of Charles University SVV 260444/2020.

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Nanostructured (bio)functional thin films

V. Stranak[1]*, J. Kratochvil[1,2], V. Prysiazhnyi[1], F. Dyčka[1], Z. Hubicka[3], J. Kousal[2], P. Kus[2], O. Kylian[2]

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Nanostructured materials have gained enormous importance in the last decade because tailoring of the building block size, control of surface geometry, chemistry, and assembly, make it possible to achieve diverse applications. Among them, surfaces with laterally graded physical or chemical properties represent an interesting class of nanomaterials for applied research. Graded surfaces built from nanoparticles (NPs), i.e. from elementary blocks of size in a range from units up to 100 nm, represent structures with high added value. Our work is aimed at the deposition of highly defined 1D and 2D-graded nanostructures. The experiment is supported by a mathematical model. 1D and 2D-graded surfaces were prepared by beam-like deposition of nanoparticles produced by gas aggregated nanoparticle source (GAS); employing so-called Haberland concept. The main benefits of used GAS nanoparticle production are high purity grade, narrow size distribution function, the possibility to tailor the nanoparticle size and subsequently film morphology or chemical composition. For deposition of highly defined 2D-graded, two-metal nanoparticle-based surfaces we used to employ an analytical model which allows us to precisely control (*i*) nanoparticle volume surface density, i.e. the volume of nanoparticles deposited onto a unit surface area, and (*ii*) chemical composition ratio across the surface (*x,y*). The relevance of the proposed method is demonstrated on 2D-graded Ag-Cu nanocomposite film with tunable plasmonic (absorbance) features. The application potential of 1D surfaces is linked with advanced mass spectroscopy (Matrix Assisted Laser Desorption/Ionizations Spectroscopy – MALDI), utilizing the Ag nanoparticles as protonating agent of biological substrates.

Acknowledgments

The work was financially supported by GACR 19-20168S and GACR 18-10897S.

Non-equilibrium atmospheric plasmas for nanomaterials

J. Benedikt, O. Hansen, J. Golda, S. Askari

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Atmospheric non-equilibrium plasmas can generate high densities of reactive species or dissociate effectively precursor gases. Contrary to low-pressure plasmas, the highly collisional conditions prevent ion bombardment and the diffusion is slow, limiting the transport of reactivity towards treated surfaces. On the other hand, energy can be effectively stored in form of excitation energy (metastable atoms, excimers, metastable molecules such as $N_2(A)$) and a convection can be used as an effective transport of reactive species in atmospheric plasma jets. However, the main application of atmospheric plasmas is mainly in surface treatment applications, they are not widely used in applications for thin film generation or etching due to the limited quality of the deposited material, missing ion bombardment and only localized treatment. Their potential for material synthesis is mainly demonstrated in proof of principle experiments [1], where especially interesting is the formation of nanostructured materials [2,3] or nanoparticles [4].

In this contribution, we will discuss the transport of reactive species to the substrate and the effect of recombination reactions on the treatment efficiency. Important effect of highly collisional conditions is that even species with low surface reaction probability contribute very effectively to the surface reactions. As an example, we will report on the use of He/O_2 plasma for the treatment of Cu films at well-defined surface temperature to generate under controlled conditions nanostructured copper oxide layers. Finally, the potentials of atmospheric plasmas for the generation of well-defined semiconductor nanoparticles will be presented.

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Evolution of ionization fraction of sputtered species in standard, multi-pulse and reactive HiPIMS

P. Vašina, M. Fekete, K. Bernátová, P. Klein, J. Hnilica

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High power impulse magnetron sputtering (HiPIMS) attracts the interest of the industry as the coatings deposited by HiPIMS exhibit enhanced properties compared to dc magnetron sputtered (dcMS) coatings. This is caused by very dense plasma generated in HiPIMS, which results in a large fraction of ionized sputtered particles. However, a significant drawback of HiPIMS is a lower deposition rate compared to dcMS, which can be mitigated by operation of HiPIMS in multi-pulse mode (m-HiPIMS). M-HiPIMS further changes the coating structure and resulting properties due to the enhanced ion flux to the substrate. An effective branching fraction method is utilized to study the evolution of the sputtered species ionization fraction derived from the absolute ground state number densities of the sputtered titanium species. Influence of the preceding pulse on the subsequent pulse is examined as a function of delay between them.
In reactive HiPIMS, the hysteresis curve is generally reduced in width and shifted towards lower reactive gas supplies compared to reactive dcMS. We report on the evolutions of the sputtered species ionization fraction in reactive HiPIMS with oxygen, nitrogen and acetylene gases. The sputtered species ionization fraction increases with the partial pressure of the reactive gas, which is attributed to a combination of different effects taking place in HiPIMS plasma. Further, the hysteresis curve shape changes with the change of the repetition frequency. Larger ionization fraction of the sputtered species leads to larger difference in the hysteresis curve shape. The hysteresis behavior is modelled utilizing a modified Berg model, where the back-attraction of the sputtered species to the target is incorporated. The results from simulations prove that the back-attraction of sputtered metal ions is the main effect causing the hysteresis curve reduction and shift in reactive HiPIMS.

Acknowledgements
This research has been supported by project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GACR GA19-00579S funded by the Czech Science Foundation.

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Nanostructured Coatings in Automotive Industry

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Paper reviews nanostructured coatings used in automotive industry and points out expected trends and future visions in coating applications.
Nanostructured coatings prepared by PVD and PACVD are used in automotive industry in several applications mainly in combustion engines to reduce friction and wear and thus to reduce fuel consumption and to increase engine life time. Coatings are applied in different types of sensors, decorative and optical applications on plastics or glass.
New challenges for coating in automotive segment are open in alternative sources of energy, energy storage and electricity generation as well as advanced smart materials like smart anti-corrosion coatings, anti-icing, anti-fouling, self-cleaning and self-healing surfaces.

Plasma technologies enabling mobile communication

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Applications in the production of MEMS (Microelectromechanical Systems) opened up many new applications for plasma and ion beam technologies, especially in manufacturing of assemblies and devices for mobile communication. In the present paper, plasma and ion beam-based manufacturing processes for MEMS based passive high-frequency filters are discussed.

As an essential part of modern mobile communication, high-frequency electronics have developed rapidly. Different information is transmitted on different frequency bands, so that today's mobile phones contain some ten RF frequency filters. The filters use piezoelectric resonators in order to enable of the necessary miniaturization. Dependent on the frequency range and performance criteria, the filters are designed as surface acoustic wave devices (SAW) or bulk acoustic wave devices (BAW). In the filters piezoelectric structures are used to adjust frequency bands exactly based on the geometrical dimension of the device.

The generally simpler designed surface acoustic wave filters (SAW) are built on piezoelectric wafer materials. For the massive wafer material precautions must be taken to compensate for the thermal expansion and a related frequency drift. Using magnetron sputtering, additional temperature compensation films can be applied which at least reduce the temperature-induced frequency drift of the filters.

Magnetron sputtering can also be used to deposit piezoelectric films with high piezoelectric coefficients for volume resonators (BAW). Complex film stacks ensure the decoupling of the resonators from the carrier material, the adjustment of the resonant frequency as well as the passivation of the device. Both functional principles and deposition related properties of these more complex filter components are presented.

In order to establish a volume production of both SAW and, above all, BAW filters cost-effectively, a nearly ideal device yield per wafer must be ensured. Despite optimization of the deposition processes, the achievable film homogeneities clearly fails compared to the necessary accuracy, so that multiple correction processes are inserted during the sequential production of the filters. For this a so called frequency trimming, a focused broad ion beam method gets applied with which wafer specific film thickness

errors are corrected. For this purpose, the pre-measured frequency map or film thickness distribution on the wafer is converted into a dwell time function of the ion beam and gets following applied in the form of a precisely controlled movement of the wafer in front of the ion beam source. In this way, a film thickness error can be corrected with an accuracy in the sub-nm range to the desired homogeneous target value. Ion beam trimming gets applied in various MEMS devices with significant examples presented in the paper.

PEM Based Ordered Superstructures as a Durable Support for Fuel Cell Catalyst

Yurii Yakovlev, Peter Kúš, Jaroslava Nováková, Iva Matolínová, Vladimír Matolín

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Nowadays fuel cell technology is accounted as a viable source of clean energy meeting requirements of carbon-free economy. However, high cost of the technology and limited level of durability are still obstacles on the way of successful commercialization. State of the art fuel cell catalyst layer is based on carbon supported Pt or Pt-based nanoparticles mixed with an ionomer. Despite the acceptable levels of performance this catalyst layer has thickness up to 10 μm, which imposes certain limitation of the reactants/products transport and reduces utilization of the catalyst. Moreover, relatively stable, at working fuel cell potentials, carbon support shows significant degradation at potentials higher than 1.2 V, which limits overall stability of the fuel cell.

On the other hand, employment of the carbon-free ordered nanosupports has already shown a promising stability and high levels of the Pt utilization. In our work we have shown novel approach of preparation of such supports using the etching/deposition treatment of Nafion membrane during magnetron sputtering of CeO2. Treatment of membrane develops deep vertical pores and ionomer nanopillars without a noticeable decrease of membrane thickness. The magnetron sputtering of Pt on these nanostructures leads to the formation of fine nanoclusters with size of about 5 nm. Resulting structures have demonstrated high levels of performance on both sides of the fuel cell. This structure demonstrates high level catalyst utilization on the cathode side reaching up the level of 15 kW/gPt. Membrane electrode assemblies (MEAs) with 20 μg/cm2 on anode and commercial cathode and the all-commercial catalyst assembly exhibit the same level of performance. Accelerated stress test (AST) cycling between potentials 1 – 1.5 V causes only limited degradation with 15 % loss of the initial electrochemical active surface area (ECSA) for the proposed structure, which contrasts to the almost 90% loss for commercial catalyst assembly. At last it worth stress that method proposed in our study allows to prepare efficient catalysts in two steps, which improves reproducibility and decreases cost of the catalyst preparation.

Nanostructured Materials Based on Thin Films and Nanoclusters for Gas Sensing

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Metal oxide semiconductors (MOS) have been investigated for their sensorial activity for more than fifty years. A considerable attention has been paid to nanostructured MOS in the last decades. The main advantages, *i.e.*, tunable electronic properties and an enormous active area, have stimulated a development of a tremendously large variety of methods of synthesis. Usually, these methods are wet-techniques providing a cheap and easy way to prepare a plenty of MOS. However, sometimes the tuning of the nanostructural properties or using the recipes for larger spectrum of materials is complicated or even not possible [1].

Gas aggregation cluster source (GAS) was proved to be a versatile tool for preparing various nanocluster-based materials. Theoretically any sputterable material can be formed (though it is not easy task for most of them) in a form of nanocluster. It is also important and advantageous that the mix of different clusters can be produced as well as the mixed-phase clusters.

In this talk, we will demonstrate the advantages of using clusters produced by GAS utilized as a conductometric gas sensor. The produced clusters are clean, semiconducting and partially crystalline and therefore suitable for gas sensing in an as-deposited state.

We combined CuO and/or WO_x clusters in various architectures to achieve an enhanced sensitivity towards hydrogen. Particularly, the forming of nano-sized *p-n* heterojunctions is demonstrated on a system of CuO nanoclusters and WO_3 thin film [2]. A proper amount of CuO clusters on-top the MOS thin film increases the sensitivity towards hydrogen in comparison with a thin film oxide alone. The improvement is done without any need of using any noble metal.

Finally, an alternative method of forming nanostructured heterojunctions is demonstrated on $CuWO_4/WO_3$ system, where are *n-n* junctions formed in between copper tungstate and tungsten oxide [3]. The nano-sized islands of tungstate were prepared on-top of oxide thin-film by a two-step reactive magnetron sputtering deposition from W and Cu targets, respectively.

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ORAL
PRESENTATIONS

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10th - 11th of February 2020, Prague, Czech Republic

Thermal evolution of heterogeneous silver/plasma polymer nanoparticles studied by X-ray scattering methods

T. Košutová, L. Horák, A. Shelemin, M. Vaidulych, J. Hanuš, H. Biederman, O. Kylián, P. Solař, M. Cieslar, A. Choukourov, M. Dopita

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In presented work we investigated microstructural properties and thermal evolution of nanoparticles composed of silver core and polymeric shell. Studied core@shell nanoparticles were produced by combination of magnetron-based gas aggregation cluster source and simultaneous plasma enhanced chemical vapor deposition of hexamethyldisiloxane (HMDSO). A series of nanoparticles with various HMDSO concentration in the chamber was prepared.

The properties of nanoparticles were investigated by combination of the small angle x-ray scattering, x-ray diffraction, ultraviolet–visible spectroscopy and electron microscopy. Nanoparticles size distribution, shape, inert structure and microstructure was determined and the evolution of these parameters was studied up to 450°C.
Presence of HMDSO in the chamber leads to changes in the size distribution and also in the architecture of prepared nanoparticles. The increasing amount of HMDSO induces the formation of individual core@shell nanoparticles, chains of core@shell nanoparticles and, for the highest concentration of HMDSO, the synthesis of multi-core@shell nanoparticles. The size of crystallites in the silver cores of nanoparticles decreases with addition of HMDSO which prevents further aggregation. Addition of HMDSO was also found to prevent silver cores coalescence up to 300 °C.

Acknowledgements
The authors acknowledge the financial support from the project NanoCent—Nanomaterials Centre for Advanced Applications, Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

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Synthesis of gold ring-shape nanoparticles using co-sputtering over liquids

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The structuration of materials at the nanoscale is of great concern since the properties of a material can be drastically enhanced. Among all structures, nanoparticles are very appealing due to their high surface area.[1] Nowadays, it is possible to produce nanoparticles by chemical or physical ways. However, the chemical way uses toxic reagent and a complex process of purification. Therefore, to avoid these drawbacks, it appears that plasma vapor deposition techniques are an effective alternative.[2] By sputtering a metallic target over a liquid substrate, very small nanoparticles (few nanometers) are created from a wide variety of metal including titanium or silver.[3] In this contribution, we report the synthesis of gold-copper precursor nanoparticles by co-sputtering over liquids. These nanoparticles are further annealed and dealloyed to produce ring-shape nanoparticles. The dealloying process deals, in this case, with the etching of copper from the precursor alloy leading to a ring-shape gold structure. The study involves the characterization by transmission electron microscopy and small-angle X-ray scattering.

Acknowledgements

The authors acknowledge the financial support from the project NanoCent - Nanomaterials Centre for Advanced Applications, Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

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Hybrid approach coupling Plasma Processes and injection of Colloidal Solutions for customized Nanocomposite thin films

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Nowadays, the technological evolution has created a need for faster, smaller and lower energy consuming electronic devices aiming to support the cyber-physical systems and the data exchange. Achieving this often requires new materials and new processes that combine the existing ones. Therefore, in the present work we propose a hybrid approach to prepare nanocomposite NCs thin films by using Plasma Processes in which colloidal solutions are injected. It can be versatile as both the nature of the nanoparticles and the matrix can vary, low in temperature and safer by design. The work focuses in two directions. First, the direct injection [1] of the 5nm anatase TiO_2 nanoparticles in a colloidal solution [2] in the Inductive Coupled Plasma (ICP) O_2 low-pressure plasma and the investigation of the droplet-plasma interactions. The importance of this step is significant for the functionalization and the determination of the film properties. Second, the creation of the nanocomposite by injecting TiO_2 NPs and hexamethyldisiloxane (HMDSO) precursor using an O_2 PECVD system. Film characterization techniques showed a good distribution of the nanoparticles resulting in a homogeneous thin film. The impact of the deposition conditions on the properties of the NC film was monitored through *in situ* ellipsometry.

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Workshop on Plasma-Based Synthesis of Nanomaterials

10th - 11th of February 2020, Prague, Czech Republic

Plasma-assisted deposition of thin ITO film for optical-fibre-based biosensors

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A seek for diagnostics of biomolecules results in the development of new strategies for highly sensitive and efficient sensors. Research of novel nanostructures for sensor design based on an optical fibre covered by a thin indium tin oxide (ITO) film is presented in this contribution. An aim was to tune the plasma discharge towards optimised electrical conductivity, optical transparency in the visible range and refractive index of ITO film - properties necessary for obtaining efficient functional material. Our effort is oriented towards tuneable ITO deposition process, which enables usage of the optical fibre core covered by ITO film to achieve simultaneous electrochemical and optical (lossy-mode resonance) detection. The ITO films on the silica core of multimode optical fibres were prepared by plasma-assisted deposition employing high power impulse magnetron sputtering of ITO target. The special care was paid to optimization of the film crystallography with respect to electrical resistivity and optical transparency. The prepared sensors were used for the study of electropolymerization of isatin and ketoprofen. The biofunctionalisation of the sensor surface by biotin enabled selective detection of avidin.

The wrinkling concept applied to plasma polymers: an innovative approach for controlling their nano-architecture

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Plasma polymerization has become a well-established technique for the synthesis of organic thin film, the so-called plasma polymers films (PPF). Nowadays, despite a highly complex growth mechanism, it is possible to finely control the chemical composition of the PPF by a clever choice of the process parameters. On the other hand, tailoring their morphology at the micro/nano scale is much more challenging limiting further development in the field. In this context, in this work, an innovative strategy allowing the control of both the chemical composition and the architecture of PPF is established. The proposed method is based on the controlled generation of surface instabilities in bilayer systems formed by a mechanically responsive PPF and a stiffer thin film.

As a case study, the mechanical properties of PPF playing a key role in the deformation mechanism are controlled varying the substrate temperature (T_s). It has been shown by means of different AFM-based methods (i.e. approach-retract curves, scratching experiments) that the nature of the PPF is dramatically affected by the thermal conditions of the substrate: from a high viscous liquid ($\eta \sim 10^6$ Pa.s.) to a viscoelastic (E ~ 1 GPa) and finally to a stiffer elastic solid (E ~ 3 GPa) material when increasing T_s from 10°C to 45°C.

In a second step, in view of inducing the morphological reorganization of the material, an aluminium coating is deposited by the magnetron sputtering technique on the top of a mechanically responsive PPF giving rise to the formation of a wrinkled surface with tunable width (i.e. from 0.4 to 5.2 µm) and height (i.e. from 0.4 to 5.2 µm). Finally, the formed pattern is homogenously covered by an additional PPF with the desired functionality.

N^+-doped Graphene by Solution Plasma

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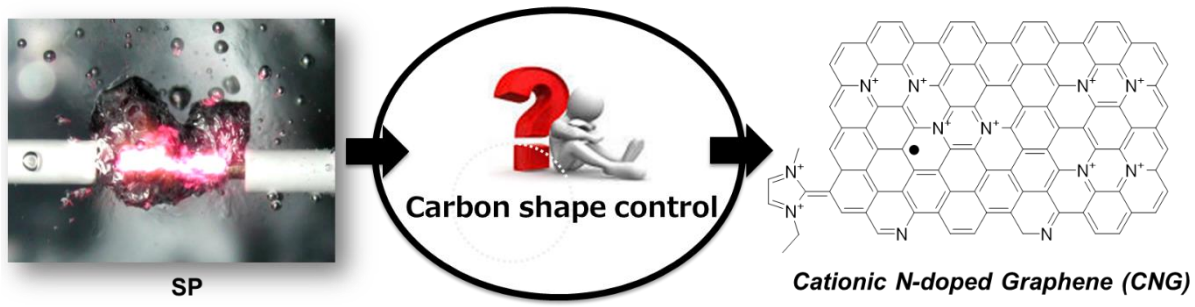
Keywords: solution plasma process, hetero-graphene, cationic nitrogen, excellent electrical properties

Solution plasma (SP) is a cold plasma discharging in solutions, which has a nature of the electron exchange between plasma phase and solution phase. This exchange is driven by plasma potential as same as gamma effect in a glow discharge that can provide oxidization and reduction reactions as in photocatalytic reaction. The difference between SP and photocatalytic reactions is the band gap between valence band and conduction band: ca. 7 eV for SP and ca. 3 eV for photocatalytic reaction. By using analogy of photocatalytic reaction to SP, it is a redox reaction on insulators of 7 eV in bandgap with vacuum ultraviolet light. It becomes difficult to make reaction happen in SP. However, SP has a potential to introduce the new reactions at room temperature and atmospheric pressure by the initiating CH activation reactions[1], which leads to a synthesis of graphene, hydrocarbon conversion such as C1 chemistry, and amino acid synthesis.

Recently, the trend is focusing on hetero-carbons materials, especially nitrogen-doped graphene which has 2-dimensional structure. It has been used as catalyst for oxygen-

reduction reaction (ORR)[2]. However, many researches have been developed on nitrogen-doped carbons, which has much lower performance than nitrogen-doped graphene because of its 3D structure. Thus, our challenge is to develop this kind of material using SP process. Moreover, another crucial factor other than dimensional structure is type of nitrogen atom in carbon framework. There are two major type of N-doping, which are at the edge and in-plane position. The in-plane nitrogen atom is essential to ORR catalytic reaction as active site in term of better electron transfer. To fulfill these condition, cationic N (N^+) is needed. N^+ has sp^2 hybridization that make carbon framework still planar. While, the other in-plane nitrogen type (e.g. graphitic) causes plane to be distorted into 3D structure forming sp^3 hybridization. Thus, N-doped graphene with N^+ can achieve the better performance of excellent electrical properties for advanced electronic devices. Therefore, in study we introduce the route to synthesize cationic N-doped graphene[3,4] by SP and its effect on resistance, semiconductor parameter, and so on.



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We would like to thank all participants for their abstracts.

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Workshop on Plasma-Based Synthesis of Nanomaterials

10th - 11th of February 2020, Prague, Czech Republic

W-B-C Coatings Prepared by Magnetron Sputtering Utilizing Pulsed Plasma Excitation

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Protective coatings are widely used in industry in order to improve the performance and lifetime of the coated tool. New materials are being explored in order to improve the efficiency of the coatings for demanding applications. A system combining tungsten, boron and carbon can be tailored in a way to combine high hardness, stiffness and moderate ductility. This can be due to intermixing of different binary crystalline and/or amorphous phases or due to the formation of a ternary phase. Ab initio calculations predict that crystalline W_2BC should exhibit a bulk to shear modulus (B/G) ratio larger than 1.75 and a positive Cauchy pressure indicating its ductility. However, a considerable drawback of this system is the enthalpy of formation that is negative, however close to zero. Therefore, it will be problematic to prepare this ternary system in a crystalline form.

Two approaches are presented in this contribution. First, a combinatorial approach was used to deposit a total of 182 coatings with a wide composition range using pulsed-DC magnetron sputtering. The coatings were prepared either in conditions, where a comparatively lower energy was delivered onto the growing coating, i.e. at ambient temperature and without applied bias, or in conditions where the coating received higher energy, i.e. at 500 °C with a bias voltage of −100 V, to study the effect of energy flow on the coating structure and mechanical properties. Second, a compound W2BC target was sputtered utilizing HiPIMS at different temperatures up to 750°C to further increase the energy flow to the growing coatings. These were compared to respective coatings prepared by conventional DC magnetron sputtering.

Acknowledgements

This research has been supported by project LM2018097 funded by Ministry of Education, Youth and Sports of Czech Republic, by project GA19-03899S funded by the Czech Science Foundation. and by project TJ01000157 funded by Technology Agency of the Czech Republic.

Deposition of antibacterial Ag/a-C:H nanocomposites on titanium substrates using a gas aggregation cluster source

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The implant-bone interface is the site of competition between microorganisms and cells and thus very crucial in determining the final success of a bone implant. In the past, various strategies have been followed to simultaneously support bony integration and to prevent implant-associated infections. In the present study, we investigated the surface properties, antibacterial activity and biocompatibility of nanocomposite coatings based on an amorphous hydrocarbon (a-C:H) film containing silver nanoparticles (AgNPs). a-C:H deposits with varying silver concentrations were generated on medical-grade titanium discs, using a gas aggregation source (GAS) and a plasma-enhanced chemical vapor deposition (PECVD) process. The obtained results revealed that the surface Ag content increased from 1.3 at% to 5.3 at% by increasing the DC magnetron current in the GAS from 200 to 500 mA. A further increase in Ag content to 11 at% was moreover noticed after O2 etching. A series of in-vitro antibacterial assays indicated that increasing the number of AgNPs in the nanocomposites led to excellent antibacterial activities resulting in a 6-log reduction of E. coli and a 4-log reduction of S. aureus after 24 hours of incubation. MTT assay, fluorescence live/dead staining and SEM microscopy observation of MC3T3 cells showed that increasing the concentration of Ag in the nanocomposites had no significant influence on their cytocompatibility, while improved cell proliferation was mainly observed for nanocomposites possessing a low amount of AgNPs. The fabricated controllable Ag/a-C:H nanocomposites on Ti substrates, which provide a relatively long-term antibacterial ability and a good biocompatibility, can thus have promising applications as orthopedic or other biomedical implants.

Workshop on Plasma-Based Synthesis of Nanomaterials

10th - 11th of February 2020, Prague, Czech Republic

Synthesis of nanoparticles by magnetron sputtering of silver and gold onto castor oil

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Magnetron sputtering of metals onto liquids allows to obtain high purity solutions of nanoparticles (NPs) because this approach does not require the introduction of any reduction and/or stabilizing reagents used in the "classical wet" NP synthesis. Castor oil that withstand vacuum conditions might be a good alternative to ionic liquids and PEG which are widely used in the field of magnetron sputtering onto liquids because this oil has (***i***) low toxicity, (***ii***) good biocompatibility, and (***iii***) low cost.

Here we briefly describe our first results for the systematic study of magnetron sputtering of silver and gold onto castor oil. The effect of following parameters on the formation of NPs has been studied: *(1)* the sputter power; *(2)* the Ar pressure; *(3)* the sputtering time; *(4)* the type of sputtering plasma (DC-MS (Direct Current Magnetron Sputtering) vs HiPIMS (High-Power Impulse Magnetron Sputtering).

In case of DC magnetron sputtering of silver and gold a deep cloud of particles was obtained underneath the castor oil surface. No film formation on the liquid surface was ever observed. The obtained NPs were completely solubilized in the castor oil by mechanical stirring. Stability of the NPs solutions was characterized by UV-vis spectroscopy, the morphology of NPs was monitored using STEM. The concentration of metal in the solutions increases linearly with sputter power and deposition time and decreases exponentially with Ar background pressure.

Sputtering of silver with bipolar HiPIMS power supply leads to the formation of inhomogeneous mixture containing individual Ag NPs and their yellow agglomerates seen with a naked eye while sputtering of gold in the same conditions leads to the formation of homogeneous solutions of Au NPs.

Acknowledgements

This work was supported by the Fonds de la Recherche Scientifique (FNRS - Belgium) under grant n°PDR T.0134.19 - 5/7. SK is Senior Research Associate of the FNRS.

Structure and properties of bixbyite-based Ta–O–N films prepared by HiPIMS

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The Ta–O–N materials are an interesting group of materials that may provide appropriate properties (i.e., band gap width and alignment) for splitting of water into H_2 and O_2 under visible light irradiation (without any external voltage). However, it is still a big challenge to prepare highly crystalline Ta–O–N materials in a form of a thin film mainly due to their very high crystallization temperature (800–900 °C).
In our research we utilize the advantages of high-power impulse magnetron sputtering in combination with film post-annealing in a vacuum furnace to prepare single-phase Ta–O–N thin films. Recently, during our work[1] dealing with monoclinic TaON films, fine-tuning of the elemental composition of the films led to a successful preparation of bixbyite-based Ta_2N_2O films. To the best of our knowledge, this material has not been yet reported. In this work, we present the way of preparation of the films and we investigate their properties with respect to the water splitting application. The optical band gap width of this material is 2.0 eV, allowing absorption of visible light up to 620 nm and the band gap is also well aligned with respect to the water splitting redox potentials (based on the ultraviolet photoelectron spectroscopy data). The electronic structure of this material is further discussed based on data measured by Hard X-ray Photoelectron Spectroscopy (HAXPES) and Hall probe. The explanation of the results is also supported by carried out ab-initio calculations.

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Workshop on Plasma-Based Synthesis of Nanomaterials

10th - 11th of February 2020, Prague, Czech Republic

The utilization of gas aggregated silver nanoparticles for the detection of small molecules for imaging MS

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The utilization of nanoparticles (NP) to enhance the detection of molecules on the surfaces using NP's plasmonic properties is under active investigation for SERS and LDI/ESI MS applications. In this contribution we would like to present the outcomes of our investigations on the utilization of silver nanoparticles for detection of small molecules using nanoparticle assisted laser/desorption ionization mass spectrometry (NALDI MS). The nanoparticles were generated using gas aggregated source. The contribution is going to show the following: preparation/characterization of nanoparticles, investigations of mass spectra of a given set of small molecules and the description of the features for analyte/NP mass spectra, and, finally, preliminary results with imaging MS on the rat and liver cut tissues covered with the silver NPs. The comparison of a conventional LDI MS technique with the so-called MALDI-2 technique (where the additional post-ionization laser is introduced) is also included, which wasn't done for the biomolecule/nanoparcticle systems.

Acknowledgments

Most of the work was done at the facilities of University of South Bohemia, while the imaging samples were prepared at Masaryk University (Dr. Antonin Bednarik) and measured at the University of Munster (with the kind help of Prof. Klaus Dreisewerd, M. Sc. Alexander Potthoff, M. Sc. Tanja Bien, and M. Sc. Christoph Bookmeyer) supported through Erasmus+ staff mobility program.

POSTER

PRESENTATIONS

Workshop on Plasma-Based Synthesis of Nanomaterials

10th - 11th of February 2020, Prague, Czech Republic

Fabrication of nanostructured surfaces by plasma-based sputtering for Raman spectroscopy

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Nowadays, surface-enhanced Raman scattering (SERS) and drop-coating Raman scattering (DCDRS) are highly promising techniques for detection of biomolecules with low analyte concentrations. However, the sensitivity as well as reproducibility of Raman spectra analysis often depends on the surfaces that are used to detect a particular biomolecule. For SERS platforms, nanostructured silver and gold are commonly used materials due to their plasmonic properties that are in the range of optimal enhancement. In case of DCDR, besides of chemical composition, surface roughness and wettability have a crucial effect on the quality of Raman signal. This is connected with the way how the analyte containing droplet dries on the surface. Two situations favorable for DCDR were identified: i) coffee ring or ii) little spot formation where biomolecules are pre-concentrated after the complete liquid evaporation.
In this study different nanostructured surfaces were investigated with aim to test their suitability for DCDR and SERS. The studied surfaces were based on films of metal and/or polymeric nanoparticles prepared by means of gas aggregation source that were overcoated by fluorocarbon thin films. The results showed that the size and amount of nanoparticles in the base layer of nanocomposites influenced their wettability, and, consequently, the dynamics of the droplet drying and Raman signal from methylene blue and riboflavin that were used as model molecules for Raman measurements. A more detailed study of the formed patterns after drying of the analyte on the fabricated surfaces was performed using SiO_2 micro and nanoparticles with different diameter dispersed in water. The resulting patterns of dried silica particles were studied by means of SEM. It was also shown that surfaces with only metal nanoparticles without a top C:F layer were successfully used for SERS.

Acknowledgements
This work was supported by grant GACR 18-10897S from the Grant Agency of the Czech Republic.

Ag@Ti core@shell nanoparticles prepared by *in-flight* Ti coating of Ag nanoparticles

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The core@shell nanoparticles (NPs) combine the advantages of the two different materials. Optical, electrical, chemical and catalytic properties can by tuned by combining specific core and shell materials. Titania (TiO_2) in a form of anatase is well known for its photocatalytic properties and silver exhibits strong plasmon resonance [1,2]. In case of Ag@TiO_2 NPs those two effects can be combined in a way that the photocatalytic properties of the titania are enhanced due to the SPR-mediated electron transfer from the Ag core to the titania shell [3].

In this study, Ag@TiO_2 NPs were produced using a fully plasma-based strategy. The Ag NPs, the served as cores, were fabricated in the gas aggregation source (GAS) of Haberland type. These NPs were subsequently *in-flight* coated by a thin Ti shell in a modification chamber with two DC magnetrons opposing to each other with an axis perpendicular to the beam of NPs. Changes in the magnetron current, distance between magnetrons that were employed for Ti deposition or magnetic field configuration allowed to tune the thickness of the Ti shell. The XPS, EDX, (S)TEM and SAXS analysis confirmed the expected core@shell structure with the shell thickness up to 3.5 nm. According to XPS the Ti shell is fully oxidized and the TiO_x oxide is amorphous as witnessed by XRD. The possibility to convert TiO_x amorphous shell in the TiO_2 anatase will be discussed as well.

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The research was supported by the grant GACR 17-22016S.

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Plasma treatment of poppy seeds in fluidized bed reactor

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Adverse environmental conditions at planting (especially water shortage) can lead to reduced germination rate of seeds. The plasma treatment is one of the possibilities that can solve this problem. Such treatment can increase germination rate of seeds and make germs grow faster due to increased wettability of seeds surface or disrupted seed coat. This could lead to enhanced oxygen and water transport into the seed and improve germination.

Poppy seeds were treated in fluidized bed reactor and discharge power ranging from 10 to 150 W was used. The working gas was air at pressure 100 Pa. Poppy seeds were then planted into petri dishes on 7 layers of filter paper saturated with water and the number of germinated seeds was observed from 3 to 6 days after planting. Every plasma treated sample showed improved germination rate compared to untreated seeds (these have 75.5 %) six days after planting. Samples treated in 150 W discharge had the highest germination rate (86 %). Decreased contact angle of water on treated poppy seeds was observed from 85° (untreated) to 19 – 35° (treated). The changes of wettability were confirmed by changes of chemical composition of seeds surface. These changes were observed by X-ray photoelectron spectroscopy – oxygen and nitrogen content slightly increased. Changes were observed in deconvolution of C 1s peak, increase of C-O component and decrease of C-C component.

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This study was supported by grant UJEP-SGS-2018-53-006-3.

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Sputtered titanium species dynamics in HiPIMS

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High power impulse magnetron sputtering (HiPIMS) is a very attractive physical vapor deposition technique, which has been of great interest over the last two decades. Continuous development of the HiPIMS-based sputtering discharges is tightly related to the more profound understanding of the undergoing physical processes, a crucial factor for the optimization of thin-film growth as well as for further development of sputtering technology in general [1].
In our experiments, various optical diagnostic methods for in-situ characterization of HiPIMS discharges was combined. Special attention was dedicated to the visualization of the ground state titanium neutrals and ions in the discharge volume above the cathode. Their direct imaging is a straightforward way to obtain information about their number density [2]. Two-dimensional time-resolved density mapping of the sputtered species in a HiPIMS plasma was performed utilizing laser-induced fluorescence (LIF) technique. Atomic absorption spectroscopy (AAS) measurements were employed in parallel to LIF to follow the number density evolution of sputtered species. Both methods LIF and AAS were used to investigate the effects such as plasma on-time, plasma off-time, working gas pressure, pulse energy, or oxygen admixture on number density evolution of sputtered species.

Acknowledgements
This research was supported by project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GA19-00579S funded by the Czech Science Foundation.

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Tailor-made nanocomposites with multistage antibacterial action

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Antibacterial coatings find utilization if they are placed on the frequently touched surfaces as handles or surfaces of medical equipment as gauzes, surgery tools, etc. Indeed, the antibacterial surfaces find ultimate applications in implant surgery, because they are able to prevent dangerous biofilm formation. Such biofilms are in many cases caused by highly resistant planktonic bacteria often of genus Staphylococcus. Fortunatelly, the bacteria gets hardly resistant to metal ions, therefore the utilization of antibacterial metals is one of the best ways how to deal with such infections [1]. Here the metal nanoparticles with a large surface volume ratio can provide enough amount of metal ions after reaction with water, while the low amount of relatively harmful material is used. But such small nanoparticles would be able to penetrate through channel proteins (or block them) and cause serious troubles inside human cells, therefore the nanoparticles need to be fixed. Here the plasma polymer matrix, which allows water penetration is ideal for stabilization of such nanoparticles [2]. Furthermore, a suitable plasma polymer matrix can be impregnated by antibiotics [3]. The film storage ability can be then tailored by film thickness or by introducing functional groups to its volume by nitrogen addition to the deposition process [4]. Such antibiotics-immobilized nanocomposite allows the burst release of antibiotics with motivation to kill a large number of bacteria during the first days after surgery, while the antibacterial ions can be slowly released to provide long-term antibacterial action.

Acknowledgments

The work was financially supported by GACR 19-20168S, and GACR 18-10897S.

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Plasma-assisted growth of polyethylene fractal nano-islands on polyethylene oxide thin films

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Plasma-assisted vapor deposition of $(–CH_2–)_{100}$ macromolecules performed onto polyethylene oxide (PEO) nanolayers leads to formation of two-dimensional 7 nm thick polyethylene (PE) islands of the diverse fractal or dendrite shapes. AFM-infrared nanospectroscopy confirms the phase separation of PE and PEO, and illustrates microscopic details of fractal branches. The nanocalorimetry indicates that crossovers between island shapes may be related to chain dynamics in the PEO underlayer. On ultrathin (< 30 nm) PEO, star-shaped PE dendrites are observed. For thicker (~100 nm) PEO, the PE islands resemble the diffusion-limited aggregation fractals. The segmental mobility in PEO can be controlled by cross-linking which is enhanced under higher discharge power resulting in more linear backbone fractals. The results provide a new physical insight into solvent-free macromolecular diffusion at vacuum-polymer interface and may stimulate the vacuum-compatible development of new functional polymeric structures.

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Effect of nitrogen on sputtered species number densities evolution in reactive HiPIMS

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High Power Impulse Magnetron Sputtering (HiPIMS), one of the promising physical vapor deposition technique studied over the past years, utilizes short voltage pulses with a low duty cycle to produce a high flux of ionized sputtered species [1]. Adding a reactive gas into the HiPIMS process opens up a new alley of producing novel materials with a wide range of different compositions. However, the use of HiPIMS is complicated by the fact that the discharge properties in this kind of a reactive time-dependent process are strongly nonlinearly dependent on the reactive gas supply [2]. Therefore, a deeper understanding of the discharge behavior in reactive HiPIMS is needed to control the deposition process.

The temporal evolution of the absolute number of the sputtered titanium atoms and ions, the ionized density fraction in the target region and the ion flux in the substrate region in reactive HiPIMS process for different partial pressures of the reactive gas are presented in this contribution. A Speedflo Mini fast feedback control system was utilized allowing us to operate within the transition region of the reactive magnetron sputtering hysteresis curve. The non-invasive EBF spectroscopic method based on effective branching fractions is applied to evaluate the density of sputtered species [3]. This study enables us to understand the pulsed sputtering process of the titanium in a nitrogen atmosphere more in detail for possible future applications.

Acknowledgements

This research was supported by project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GA19-00579S funded by the Czech Science Foundation.

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Composite nanoparticles from arrow shaped gas aggregation source

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Composite, specifically core-shell Ni@Ti nanoparticles (NPs) have been formed and deposited using a modified version of Haberland type gas aggregation source. This source utilized two magnetrons in one aggregation chamber placed in an arrow configuration with relative angle 90°, see Figure 1. Such configuration gave the possibility to independently control the power delivered to each magnetron as well as to vary the distances of the magnetrons from the axis of the chamber. It is shown that under optimized conditions this system allows to significantly suppress the formation of single material nanoparticles which are otherwise (in other multi-magnetron systems) commonly formed at the expense of the desired core-shell NPs.

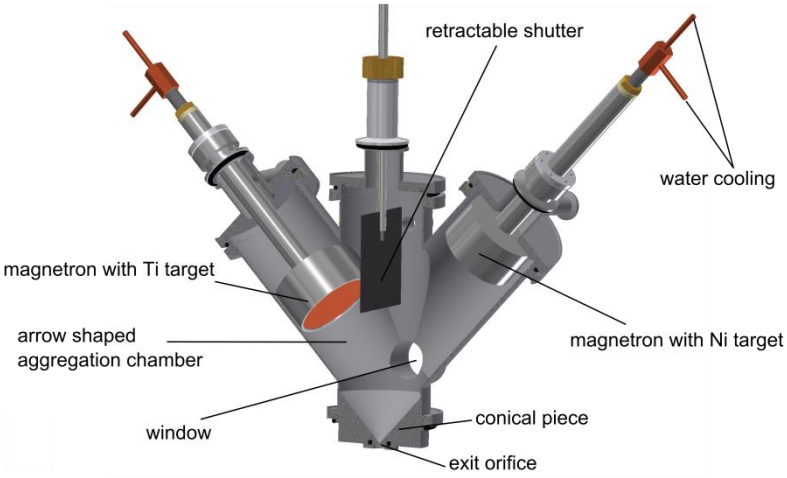

Figure 1: Schematics of the deposition setup

Acknowledgements

This work was supported by grant LTC17062 from the Ministry of Education, Youth and Sports of the Czech Republic.

Time-resolved study of unipolar and bipolar HiPIMS for deposition of Co_3O_4 catalysts

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Reactive high power impulse magnetron sputtering (HiPIMS) of a cobalt cathode in pure argon gas and with different oxygen admixtures was investigated by time-resolved optical emission spectroscopy (OES) and time-integrated energy-resolved mass spectrometry. The HiPIMS discharge was operated with a bipolar pulsed power supply capable of providing a large negative voltage with a typical pulse width of 100 μs followed by a long positive pulse with a pulse width of about 350 μs. The HiPIMS plasma in pure argon is dominated by Co^+ ions. With the addition of oxygen, O^+ ions become the second most prominent positive ion species. OES reveals the presence of Ar I, Co I, O I, and Ar II emission lines. The transition from an Ar^+ to a Co^+ ion sputtering discharge is inferred from time-resolved OES. The enhanced intensity of excited Ar^{+*} ions is explained by simultaneous excitation and ionisation induced by energetic secondary electrons from the cathode. The intensity of violet Ar I lines is drastically reduced during HiPIMS. Intensity of near-infrared Ar I lines resumes during the positive pulse indicating an additional heating mechanism.

Acknowledgements

The work was partly supported by project no. 19-00579S of the Czech Science Foundation and by project no. SOLID21-CZ.02.1.01/0.0/0.0/16_019/0000760 of the Operational Programme Research, Development and Education financed by European Structural and Investment Funds and the Czech Ministry of Education, Youth and Sports.

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Synthesis and surface modification of light emitting silicon nanoparticles using non-thermal plasma techniques

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Silicon nanocrystals (Si-NCs) having room-temperature efficient photoluminescence (PL) have been intensively studied in last two decades. The Si-NCs PL depends on their size [1] and it exhibits a shift towards lower wavelength with a decline in a Si-NC diameter and a transformation of the silicon indirect bandgap towards the direct one in Si-NCs with dimensions below roughly 3 nm due to a quantum confinement and tensile strain has been shown recently [2] making them a good candidate for instance for the integration of optoelectronics on silicon wafer. Recently, an effective glow discharge synthesis of Si-NCs has been developed by Kortshagen [3]. This method enables to synthesis of sufficient amounts of Si-NCs for their systematic exploitation and with a good reproducibility. On the other hand, the plasma synthesis of Si-NC is accompanied by silyl surface termination (especially with SiH3 groups) [4] making them insoluble in water and most probably faster degradation in contrast to Si-NCs prepared by other techniques. Therefore the subsequent Si-NC surface modification is necessary.

Acknowledgements

This work was supported by DAAD grant n. 19-01 and Czech Science Foundation (GAČR project No. 18-05552S).

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Atmospheric pressure plasma engineering of perovskite films for highly-efficient perovskite solar cells

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The demand for low-cost energy source as an alternative for fossil fuels has never been greater and perovskite solar cells (PSCs) are among the most promising candidates. Low-cost fabrication a homogeneous perovskite layer is one of the main obstacles for commercialization of the cheap perovskite solar cells. In this work, atmospheric pressure low-temperature plasma is introduced for the plasm-chemical treatment of perovskite films and can be divided into two different processes:

(i) Plasma treatment of annealed-perovskite films. This plasma is capable of efficiently changing the band-energy alignment of the organic-inorganic halide perovskite film after a short treatment time. Low-temperature plasma enhances the crystallinity of the perovskite film by changing the composition of the surface without damaging the bulk of the film. The results demonstrate that perovskite film becomes homogeneous, with larger grain size, after such plasma treatment.

(ii) Plasma crystallization of perovskite films. Hydrogen plasma is tested as an alternative for thermal annealing. The challenges of time-consuming thermal annealing are avoided by hydrogen plasma treatment of as-deposited perovskite films. Hydrogen plasma is able to transform amorphous film into perovskite phase in a very short period of time. This method may be considered a significant step towards the annealing-free deposition of perovskite films.

Perovskite solar cells were then fabricated to evaluate the effect of plasma on the photovoltaic parameters.

Ionised density fraction of sputtered species in HiPIMS discharge excited in argon/acetylene gas mixture

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High power impulse magnetron sputtering (HiPIMS) technology attracts the interest of the industry as the coatings deposited by HiPIMS demonstrate improved properties compared to conventional dc magnetron sputtered (dcMS) coatings. This is because HiPIMS generates very dense plasma, which results in a large fraction of ionized sputtered particles. We report on the HiPIMS with titanium target in the argon atmosphere with an addition of acetylene gas. Such process can be referred either as hybrid PVD-PECVD [1] or non-saturated reactive process [2].
The non-invasive method called effective branching fraction method is utilized in order to evaluate the absolute ground state number densities of the sputtered titanium species for various flows of acetylene gas. Further, the HiPIMS process is modelled by a modified Berg model. The presented model incorporates the production of thick carbon layer at the target and the back-attraction of the sputtered titanium ions to the target. The simulated trends agree well with the measured ones.

Acknowledgements
This research has been supported by project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GACR GA19-00579S funded by the Czech Science Foundation.

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Plasma modification of Kapton by dielectric barrier discharge in air at atmospheric pressure

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Kapton is widely used in microelectronics, optoelectronics, composites, and optics because of its high heat resistance, high mechanical strength, and good dielectric properties. However, this material has a low surface energy, and therefore poor wettability and low adhesion that limits its use in certain applications.

In this work, the effect of DBD on the Kapton surface was studied. The main attention was devoted to the investigation of changes in surface hydrophilicity, surface composition and surface morphology induced by the atmospheric pressure air plasma treatment as well as to the temporal stability of such changes.

The filamentary plasma was generated between two parallel planar electrodes, one conductive and the other covered with dielectric. Samples were placed on the lower electrode. The upper, moveable electrode was operated at 30 W. The scanning speed was selected so that the processing time when passing in one direction and back corresponded to 1 second. The number of scans ranged from 1 to 20 scans.

It was found that the Kapton film exhibited already after 1 second of plasma treatment much higher hydrophilicity (water contact angle close to 20^o) as compared to untreated film (water contact angle ~ 80^o). Such noticeable change in wettability was found to be connected predominantly with the surface oxidation and formation of new oxygen containing functional groups on the Kapton surface as witnessed by XPS. Furthermore, the plasma treatment caused not only dramatic changes in wettability of Kapton films, but influenced also the dynamics of water droplet drying: whereas for the untreated Kapton three phases drying with significant constant contact angle (CCA) phase was observed, the CCA phase was absent on plasma treated films.

Regarding the ageing, the wettability of Kapton films was found to increase with the storage time and saturated at the value 55 ± 5^o two weeks after the treatment.

Acknowledgements

This work was supported by the grant SVV 260 444/2019 from the Charles University.

Nanostructured $CuWO_4/WO_3$ Bilayers for Hydrogen Gas Sensing

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Nanostructured branched like islands of copper tungstate ($CuWO_4$) and nanocrystalline tungsten trioxide (WO_3) films were prepared by a reactive sputtering technique. It was a two step deposition process in which WO_3 deposition was followed by CuO deposition magnetron sputtering in DC and RF modes, respectively. In order to fabricate $CuWO_4/WO_3$ bilayers the thicknesses of WO_3 and CuO were varied and the nano-junction was formed during the deposition of CuO film on pre-deposited WO_3 at high temperature (400 ^oC).

As-prepared $CuWO_4/WO_3$ bilayers were investigated for sensitivity towards H_2 gas. It was observed that the sensitivity for the pure WO_3 was enhanced by over-layering with $CuWO_4$. The sensitivity specimen 5nm CuO on 20 nm WO_3 ($^5CuO/^{20}WO_3$) was observed maximum (up to 5) [1]. On the basis of SEM, XRD, and sensorial response we propose that the sensing mechanism is based on the formation of the n-n type nano-junction between n-type WO_3 and $CuWO_4$.

1 Submitted to International journal of hydrogen energy

Study of magnetron sputtered SnO_2 films interaction with palladium and methanol

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Stannic oxide is a transparent n-type semiconductor with rutile structure and wide band gap (E_g = 3.6 eV). Due to the stannic oxide electric and catalytic properties, alongside with its high stability toward aggressive chemical environment and low price of the material, made it most widely commercially used transparent conductive oxide.

With vast range of problems in “green” energy field a demand for new more efficient catalysts arise. Stannic oxide with addition of noble metals is a promising catalyst for applications like alcohol fuel cells. However, understanding of catalytic processes on stannic oxide has been obscured by complicity of “real-life” systems and technical limitations.

In this work, we study interaction of stannic oxide films prepared by DC magnetron sputtering with methanol and influence of palladium on the reaction path at near-ambient pressures (NAP). Experiments in this work were conducted by the NAP-X-ray photoelectron spectroscopy (NAP-XPS) technique. NAP-XPS enable us to make measurements in methanol atmosphere in pressure range up to 1 mbar which is not achievable with convenient XPS.

Stannic oxide films has ability to accommodate palladium in its bulk and revealed to be less prone to methanol C-O bond scission reaction than epitaxial stannic oxide nanoparticles on rutile surface. Both, model and system prepared by magnetron sputtering, showed drastic drop in methanol product adsorption when sample temperature was increased in methanol environment.

Embedding carboxylated nanoparticles into poly(ethylene oxide) plasma polymer matrix for tunable attachment of biomolecules

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Over the past few years, immobilization of biomolecules in a controlled way has emerged as a hot topic in biomedicine and surface science. Being beneficial for the development of artificial implants regardless of material or novel drug/gene delivery systems with pH behavioral programming, it also contributes to better understanding of the biomolecule/surface interactions the biocatalysis and biosensing rely on. Herein, we combine plasma polymerization of acrylic acid in the gas aggregation cluster source with already elaborated plasma-assisted vapor-phase deposition technique to fabricate phase-separated plasma polymer nanocomposites. Once immersed into the solutions of lysozymes, these composites are able to accumulate the protein molecules at the sites where poly(acrylic acid) nanoparticles (NPs) reside while the adsorption elsewhere is restrained. The selectivity of the process is given by electrostatic attraction between negative charge of dissociated carboxyls and positively charged lysozyme molecules in conjunction with the biorepellent nature of the poly(ethylene oxide) entities and can be controlled by the number of embedded NPs or the thickness of the capping layer.

Acknowledgements

This work was supported by the grant GAČR-17-12994S from the Grant Agency of the Czech Republic.

Behaviour of spokes in reactive HiPIMS

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Plasma in high-power impulse magnetron sputtering (HiPIMS) discharge, similarly to other discharges utilizing ExB field (Hall thrusters, homopolar devices), undergoes self-organization into the ionization zones rotating in the ExB direction, called spokes [1]. Many studies were conducted focusing on the characterization of their appearance, number, rotational velocity, merging and splitting events in different experimental conditions. Nevertheless, only very little research was conducted in the case of reactive sputtering, where only general spoke characteristics were evaluated [2].
A dual-image fast camera screening was utilized to capture plasma emission on 3" Nb target in a reactive mixture of nitrogen and argon. Spoke characteristics were evaluated while overall pressure and supplied power was kept constant and the ratio of N_2/Ar was varied. The shape, velocity and spoke number were significantly affected by higher ratio of N_2 in the mixture. To distinguish between the effects of the poisoned target and reactive gas present in the plasma on spokes, plasma emission was screened as the Nb target was cleaned in pure Ar atmosphere. Additionally, obtained spoke characteristics were compared to those made on a fully compound NbN target.

Acknowledgements
This research was supported by project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GA19-00579S funded by the Czech Science Foundation.

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Plasma polymer nanoparticles: Do we understand their formation?

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Plasma polymer nanoparticles can be due to their high surface to volume ratio and the ability to covalently bind biomolecules or bioactive substances useful in various applications such as theranostics or smart drug delivery. As it was shown in our recent studies these nanoparticles may be effectively produced by means of gas aggregation sources (GAS) that are based on magnetron sputtering of a polymeric target [1]. However, the dynamics of the formation of nanoparticles, which in turn influences their final physico-chemical properties, is still not fully understood. This represents a serious limitation for further development in the field. To shed light on the formation of NPs inside the GAS we used a source equipped with Nylon target that served as raw material for nanoparticles and run series of experiments focused on both *in situ* and *ex situ* characterization of the deposition process (OES measurements, deposition rate measurements, laser light scattering, SEM and TEM analysis of produced NPs etc.). We observed that the production process is strongly affected by growth induced instabilities and thus the deposition of nanoparticles shows a periodic behaviour. In this contribution we present details of this dusty plasma phenomenon in our system.

Acknowledgements

This work was supported by the grant GACR 17-22016S from the Grant Agency of the Czech Republic. R. Štefaníková also acknowledges support from the Erasmus+ programme for her internship at the Kiel University.

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High-performance Thermochromic VO_2-based Coatings Prepared on Glass by a Low-temperature Scalable Deposition

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Three-layer thermochromic VO_2-based coatings were prepared on soda-lime glass by a low-temperature scalable deposition technique. This deposition technique is based on reactive high-power impulse magnetron sputtering with a pulsed O_2 flow control [1] allowing us to prepare crystalline VO_2 layers of the correct stoichiometry under highly industry-friendly deposition conditions: without any substrate bias at a low substrate temperature of 330 °C. Simultaneous doping of VO_2 by W (resulting in a $V_{1-x}W_xO_2$ composition with x = 0.018 in this work) was performed to reduce the semiconductor-to-metal transition temperature to 20 °C. ZrO_2 antireflection layers both below and above the thermochromic $V_{0.982}W_{0.018}O_2$ layers were deposited at a low substrate temperature (< 100 °C). A coating design utilizing a second-order interference in the ZrO_2 layers [2] was applied to increase both the luminous transmittance, T_{lum}, and the modulation of the solar transmittance, ΔT_{sol}. The crystalline structure of the bottom ZrO_2 layer further improved the VO_2 crystallinity and the process reproducibility. The top ZrO_2 layer provided the mechanical protection and environmental stability of the $V_{0.982}W_{0.018}O_2$ layers. The ZrO_2/ $V_{0.982}W_{0.018}O_2$/ZrO_2 coatings exhibited T_{lum} up to 60% at ΔT_{sol} close to 6% for a $V_{0.982}W_{0.018}O_2$ thickness of 45 nm, and T_{lum} up to 50% at ΔT_{sol} above 10% for a $V_{0.982}W_{0.018}O_2$ thickness of 69 nm. This study provides a new solution for a low-temperature fabrication of high-performance durable thermochromic VO_2-based coatings for energy-saving smart windows.

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Quantitative Structure-Activity Relationship for Carbons prepared by Solution Plasma

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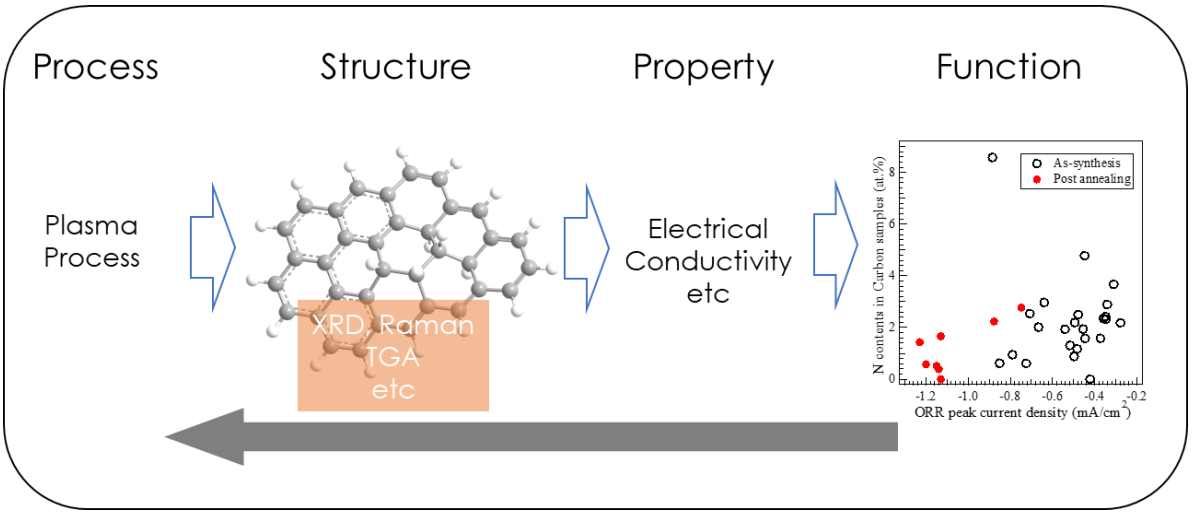
Keywords: QSAR, Solution Plasma, Carbon

The carbon material is a promising material for a Li-ion battery (LIB). In the case of the application to LIB cathode, the pathways of electron and ion are required, i.e., the electrical conductivity and capacity. When they fabricated a new LIB system, they must arrange the conditions or property of carbon again. Even for the property of carbon to the structure, a clear correlation cannot be seen if not a causal relationship. The ambiguity originates from the diversity of carbon structures composed of sp3 and sp2 chemical bonding states and the impurity. Carbon includes an amorphous part, which provides us the difficulties when it is identified.

Cluster and neural network analyses (CA and NNA) can find out and indicate the hidden relationship, moreover, quantitative relationship. In this study, we investigate the quantitative structure-activity relationship among the conventional carbons and the ones synthesized by solution plasma.

The carbons materials are evaluated by X-ray diffraction (XRD), Raman spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and four-point probe (FPP) measurement. The characterized values were extracted from the results. The extracted values were analyzed by CA and NNA with JMP software.



Plasma diagnostics in hybrid reactive pulsed HiPIMS magnetron sputtering system

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Low temperature hybrid plasma sources are recently very popular tools for technological applications in thin film depositions. These plasma sources are very flexible and plasma parameters can be tuned in a wide range. A reactive hybrid high power impulse magnetron sputtering (r-HiPIMS) system combined with a radio frequency electron cyclotron wave resonance (ECWR) plasma source was investigated as a tool for technological processes as deposition of thin films for WO_3 and WO_{3-x}, working as semiconductor photoanodes in water splitting applications. One great benefit of this plasma system is the possibility to operate the process at very low pressures ≈ 10^{-2} Pa. These conditions are very suitable for low temperature crystallization of deposited semiconductor thin films and are able to obtain interesting semiconductor properties. The plasma is generated in the gas mixture of $Ar+O_2$ and metallic magnetron target made of W is reactively sputtered in HiPIMS+ECWR plasma. The non-stationary pulsing plasma was analyzed in the position of the substrate by a planar fast sweep high frequency time resolved Langmuir probe working with the voltage frequency 350 kHz. The time evolution of ion concentration and electron temperature were obtained during the pulsing cycle. Higher electron temperature was found during the active discharge pulse in case of hybrid HiPIMS+ECWR in comparison with the pure HiPIMS system. This phenomenon influences the degree of ionization of sputtered particles in the discharge plasma.

The plasma hydrogenation of hedgehog-like ZnO nanopowder

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Due to a high surface-to-volume ratio and related size effects, ZnO nanostructures are a perspective for energy conversion or sensing applications such as solar cells, light emitting diodes high performance electrochemical capacitors, biosensors, gas sensors, or highly efficient nanoscintillators. We have developed the technology of hydrothermal growth of hedgehog-like nanostructured ZnO powder from Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$) and shown that the surface composition drastically changes upon the exposure to plasma treatments. The plasma hydrogenation is done in a novel inductively coupled plasma (ICP) quartz reactor developed in the cooperation with SVCS Process Innovation, s.r.o. The reactor operates at the radio frequency 13.56 MHz, 10-200 W discharge power, gas pressure 2-100 Pa and gas flow 1-100 sccm. Prior the plasma hydrogenation, the powder was pressed into pellets. The photoluminescence in near UV region (peak at 380 nm) has been enhanced whereas the deep defect related yellow PL (broad band 550-600 nm) has been significantly decreased after plasma hydrogenation. We explain the observed phenomena by passivation of defects at grain boundaries that significantly prolongs the lifetime of excitons.

Acknowledgements

This work was supported by the Czech Science Foundation project 19-02858J and by the Operational Programme Research, Development and Education project SOLID21 - CZ.02.1.01/0.0/0.0/16_019/0000760.

Stability and composition of thin PLA-like films

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Some polymers, like polylactic acid (PLA) have biodegradable properties and undergo a hydrolysis process in water. In this work, thin PLA-like plasma polymer films were prepared using plasma-assisted vapour thermal deposition (PAVTD) from powders of polymer precursor prepared by classical chemistry and heated in a crucible under low pressure. The auxiliary RF plasma power was 0-120 W.

It was found that the PLA structure is still preserved after repolymerisation, with some aliphatic hydrocarbon-rich segments. Using a combination of XPS and NMR data, an approximate chemical structure of the plasma polymers was obtained.

The properties of the films after immersion in water were found to strongly change at the RF plasma power around 30 W. The sample prepared in weaker plasma had properties of a hydrogel. The samples prepared above 30 W of plasma power did not dissolve or swell in water significantly. Since the transition is not fully abrupt, stability and other properties of the films can be tailored, as was demonstrated on the permeation properties of the films for selected model molecules.

This work was supported by the grant 17-10813S of the Czech Science Foundation.

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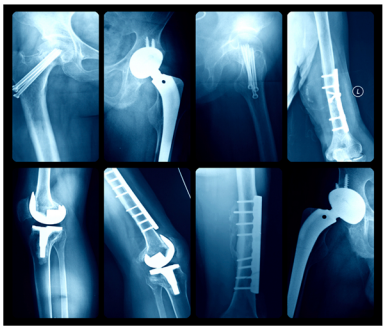
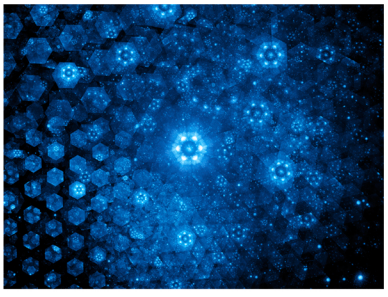


Biomaterials

Tungsten Oxide Nanorods: An Efficient Nanoplatform for Tumor CT Imaging and Photothermal Therapy
Zhiguo Zhou, Bin Kong, Chao Yu, Xiangyang Shi, Mingwei Wang, Wei Liu, Yanan Sun, Yingjian Zhang, Hong Yang and Shiping Yang.
Scientific Reports 4, Article number: 3653.

Thin films & coatings

Transparent Conductive Two-Dimensional Titanium Carbide Epitaxial Thin Films
Joseph Halim, Maria R. Lukatskaya, Kevin M. Cook, Jun Lu, Cole R. Smith, Lars-Åke Näslund, Steven J. May, Lars Hultman, Yury Gogotsi, Per Eklund and Michel W. Barsoum.
Chem. Mater., 26, 2014, 2374–2381.



Nanomaterials

Building an appropriate active-site motif into a hydrogen-evolution catalyst with thiomolybdate [Mo3S13]2– clusters
Jakob Kibsgaar, Thomas F. Jaramillo and Flemming Besenbacher.
Nature Chemistry, 6, 2014, 248–253.

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