New Horizons in Coatings and Thin Films
Room Pacific E - Session F1-FrM

Nanomaterial-based Coatings and Structures

Moderators: Dr. Ondrej Kylian, Charles University, Prague, Czechia, **Dr. Vladimir Popok**, Aalborg University, Denmark

8:20am **F1-FrM-2 Giant Actuated Van der Waals Metal/Muscovite Heteroepitaxy***, **Jia-Wei Chen**,* National Yang Ming Chiao Tung University, Taiwan*; Y. Chu,* National Tsing Hua University, Taiwan

A large-response bimorph thermal actuator plays a vital role in the research field of actuation. Various architectures were designed using polymer-based materials with significant differences in thermal expansion. However, polymers' undesirable thermal and chemical instabilities severely hinder their applications. This work achieves a giant thermal actuation via van der Waals heteroepitaxy composed of room-temperature deposited metal and layered muscovite. A maximum bending curvature of 264 m^{-1} at 243 °C can be obtained in the Ag/muscovite heteroepitaxy through uniform heating. Moreover, the outstanding performance of the designed systems in both retention (>10^5 s) and cycling tests (>10^5 cycles) was observed through the electromechanical measurements, delivering the robustness and superior interface quality of the heterostructure. In addition, the robust interface and giant thermal actuation were supported by theoretical calculations and electron microscopy. The electrothermal and photothermal methods were conducted to demonstrate the generality of the control of actuators. This work presents the manufacturable actuator with a giant actuation based on metal/muscovite heteroepitaxy, invoking potential applications in robotic technology and intelligent systems.

8:40am **F1-FrM-3 Brain-Like Behaviour in Percolating Films of Nanoparticles***, **Simon Brown**,* The MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Physical and Chemical Sciences, University of Canterbury, New Zealand **INVITED**

Recent progress in artificial intelligence and machine learning means that humans are now far inferior to computers at playing games like chess and go. However the brain is still far more efficient than even the largest supercomputers at performing some types of tasks, such as pattern or image recognition.

This has motivated a worldwide effort to build brain-like, or "neuromorphic", computers using a number of different approaches. [Note that the focus of neuromorphic computing is on *hardware*, in contrast to the usual *software* approaches to AI.] I will review some of those approaches, which include the use of traditional silicon transistors to emulate neurons and synapses, and new solid-state devices which have synaptic and neuronal functionality.

I will then talk about how my group has attacked a key remaining challenge, which is to achieve truly brain-like networks using self-assembled nano-components. I will show that we have not only been able to build highly complex brain-like networks but that the dynamical signals within those networks are remarkably similar to those of the brain. Further, I will show that stochastic signals from these networks can be used to engineer high quality true random number generators, which have applications in secure information processing, and that the devices can be used to perform classification and time series prediction tasks within a reservoir computing framework.

9:20am **F1-FrM-5 RBS Study of Silver/Copper Diffusions in the Matrix of Amorphous Carbon Coatings Produced by Magnetron Sputtering***, G. Sanzone,* Teer Coatings Ltd, UK*; M. Sharpe, P. Couture, J. England,* University of Surrey, UK*; S. Field, H. Sun, **Jinlong Yin**,* Teer Coatings Ltd, UK

In previous work, we have developed Ag-, Ag/Cu-, and Ag-cluster doped amorphous carbon coatings using magnetron sputtering techniques, for antimicrobial applications in space stations [1]. Inside a spacecraft, the temperature and humidity, suitable for the human crew onboard, also creates an ideal breeding environment for the proliferation of bacteria and fungi; this can present a hazard to human health, and create issues for the safe running of equipment. Utilising the antimicrobial properties of Ag and copper particles, we embedded these particles in a thin film of amorphous carbon and created an antimicrobial solution. These nanocomposite thin films have shown extremely high antimicrobial activities under both terrestrial gravity and micro-gravity conditions [1]. In addition, these thin films are scratch-resistant and wear-resistant with high hardness, providing a long lifetime which is critical for the applications in a space station. The slow diffusion of Ag towards surface from the carbon matrix body can replenish those Ag particles lost over time due to daily wear and tear.

However, the mechanism of Ag diffusion inside the carbon matrix has not been well understood. If the diffusion rate were too fast, the process of losing Ag would be too quick which would inevitably lead to a much shortened antimicrobial lifetime. On the contrary, too slow a diffusion rate would mean those lost Ag particles could not be replenished in time, which would severely impair the coatings' antimicrobial activity. Therefore, it becomes apparent and critical to identify the key factors that influence the Ag diffusion rate in a carbon matrix, and also to understand how they influence it.

In this presentation, we are going to report the latest results on RBS (Rutherford Backscattering Spectrometry) and TOF-ERD (time of flight elastic recoil detection) study of silver and copper diffusion in amorphous carbon coatings. The samples have been annealed at 100°C, 150°C and 200°C, to investigate the temperature influence on the metal species migration. Preliminary results have shown that higher temperature causes a higher diffusion rate, and the addition of copper has slowed down the diffusion rate of silver.

References

[1] G. Sanzone et al.," Antimicrobial and aging properties of Ag-, Ag/Cu- and Ag cluster-doped amorphous carbon coatings produced by magnetron sputtering for space applications", *ACS Appl. Mater. Interfaces* 14 (2022) 10154−10166 (doi.org/10.1021/acsami.2c00263)

9:40am **F1-FrM-6 C:H:N:O Plasma-polymer with Anchored LSPR Active Ag Nanoparticles for Detection of Borrelia Pathogen***, S. Kumar,* University of South Bohemia, Czechia*; H. Maskova,* University of South Bohemia, Biology Centre ASCR, Institute of Parasitology Branisovska, Czechia*; A. Kuzminova,* Charles University, Czechia*; R. Rego,* University of South Bohemia, Biology Centre ASCR, Institute of Parasitology Branisovska, Czechia*; J. Sterba,* University of South Bohemia, Czechia*; O. Kylian,* Charles University, Czechia*; **Vitezslav Stranak**,* University of South Bohemia, Czechia

The contribution focuses on Ag/C:H:N:O nanocomposite acting as a transducer for Localized Surface Plasmon Resonance (LSPR) detection of borrelia pathogen with high selectivity and sensitivity. The nanocomposite composes of gas-phase synthesized Ag nanoparticles (of about 20 nm in diameter) anchored onto/into C:H:N:O plasma-polymer matrix deposited by magnetron sputtering of nylon 6.6 target. The stability of Ag nanoparticles is achieved by the thermal treatment during the deposition process. The produced nanocomposites with plasmonic Ag nanoparticles may detect changes in the distance of several tens of nanometres observed as an LSPR shift of the absorption spectra. Hence, surface changes, e.g. immobilization of pathogens onto the surface, can be easily monitored.

The immobilization of pathogens is achieved by the C:H:N:O surface functionalization done here in a sequence of (i) thin-film plasma polymer deposition for the introduction of $-NH_2$ groups that (ii) enable subsequent immobilization of specific antibodies for (iii) binding of the target agents. Borrelia proteins-specific polyclonal antibody, Borrelia lysate, and live Borrelia were employed as testing target agents. Detailed investigation indicates both a high selectivity for the target agents and high sensitivity with a practical detection limit in the range of 50 Borrelias per sample effective area 0.785 cm^2 causing LSPR red-shift Dl_{50}» 2.2 nm. The proposed concept could be used as a platform for the detection of a wide family of species depending on the suitable surface functionalization.

Acknowledgments: This work was supported by the Czech Science Foundation (Grant Number GACR 19-20168S).

10:00am **F1-FrM-7 Aln Nanostructures for Piezoelectric Nanogenerators***, **Manohar Chirumamilla**, M. Sandager, V. Popok, K. Pedersen,* Aalborg University, Denmark

With recent advancements in bioelectronic devices, self-powered sensors and smart wearables, efficient nanogenerators are required to harvest biomechanical energy. In this respect, aluminium nitride (AlN) is an excellent material choice for nanogenerators due to its piezoelectric nature, high chemical and thermal stability, high thermal conductivity and resistivity, and mechanical strength [1, 2]. Thin films and nanostructures of AlN can be grown using a direct current (DC) reactive magnetron sputtering process.

In this work, c-axis oriented wurtzite AlN nanostructures consisting of a number of laminas grown by sputter deposition on Si substrates are investigated. Ag nanoislands were preliminarily formed acting as a catalyst to initiate the nucleation of individual and separated nitride nanostructures. The quality of the deposited AlN is optimized by utilising ellipsometry, AFM, SEM and XRD, where the nanostructures grown at different conditions, like Ar to N_2 gas ratio, applied bias power, working pressure, substrate temperature, etc., are investigated. By optimizing the AlN growth parameters, well-defined AlN nanostructures with lengths up to 600 nm can be obtained. The piezoelectric behaviour of the structures was investigated using piezoresponse force microscopy (PFM). It was found that piezoelectric coefficients of the grown nanostructures can exceed the values typical for continuous AlN films, thus, forming a good basis for applications towards AlN-based nanogenerators. In this presentation, the AlN structures and their piezoelectric response for various nanofabrication conditions will be discussed.

Acknowledgements

The authors acknowledge the financial support of the Novo Nordisk Foundation under the project “Nanoscale Energy Generators” (grant No. NNF20OC0064735).

References

[1] J. Y. Tsao et al., Adv. Electron. Mater. 4 (2018) 1600501.

[2] L. Algieri et al., ACS Appl. Energy Mater. 1 (2018) 5203.

10:20am **F1-FrM-8 Super-Amphiphobic Nano-Wall Structured Teflon Films Deposited by Microwave Plasma***, **Ta-Chin Wei**,* Chung Yuan Christian University, Taiwan

Super-hydrophobic and oleophobic surfaces have attracted much interest for both fundamental research and practical applications. In this study, Teflon-like fluorocarbon films with nano-wall structure were deposited on various substrates by microwave-generated C4F8/CF4 plasma. The reactor was a long tubular quartz tube with diameter of 5 cm. The substrates were placed in 22 different locations along the flow direction in upstream region, plasma discharge, and afterglow region. It was found that the surface morphology of the deposited film is very location-dependent. As seen in Figure 1, the results are relatively symmetrical to the center of plasma discharge, which reveals the diffusive behavior of the plasma process. The fluorocarbon film is rough with low F/C atomic ratio when substrate is located in the center discharge region (No. 11~15). Fluorocarbon films with nano-wall structure can be deposited on substrates located in the end of upstream region (No. 8) and in the beginning of the afterglow region (No. 18). The F/C ratio of the nano-wall film is 2.0, namely the Teflon structure. It was also found that water contact angle on the Teflon-like nanowall film was above 160° and the CH2I2 contact angle was above 140°. Actinometric OES showed that Teflon-like nanowall film deposited on locations with high CF2 relative intensity. Combining the location dependency and OES result, it is suggested that Teflon-like nanowall film is deposited by soft ion bombardment and abundant CF2 radicals. Finally, by using the same operating parameters, we successfully deposited transparent super-amphiphobic fluorocarbon nanowall film onto various substrates such as glass, copper, polycarbonate, and etc. Moreover, we found that Teflon-like films with nano-wall structure could also be deposited from other fluorocarbon plasmas. We will discuss more details at the conference.

10:40am **F1-FrM-9 Diamond-Based Nanostructured Interfaces for Electrochemical Applications***, **Robert Bogdanowicz**,* Gdańsk University of Technology, Poland

The most common material for electrodes in electrochemical systems is gold or other noble metals, as these can be applied through physical vapor deposition. The recently interesting novel, candidate materials for electrochemical studies are i.e.: (i) boron-doped diamond (BDD) or (ii) diamondized carbon nanowalls (B:CNW), and (iii) composite nanodiamond interfaces. The tailored diamond-rich sensing surfaces are grown by microwave plasma-assisted CVD. The effect of boron incorporation not only enhances the electrical or electrochemical properties but also influences the structure of electrodes by changing it from the maze-like to a heterogeneous distribution of nearly straight walls. B:CNW or BDD could be nanostructured to achieve microelectrodes.

The modification of diamondized boron-doped carbon nanowalls (BCNWs) with an electropolymerized polydopamine/polyzwitterion (PDA|PZ) coating revealing tunable mechanical and electrochemical properties. Zwitterions are codeposited with PDA and noncovalently incorporated into a structure. This approach causes a specific separation of the diffusion fields generated by each nanowall during electrochemical reactions, thus increasing the contribution of the steady-state currents in the amperometric response.

Morevoer, we have manifested also the scalable fabrication of flexible laser-induced graphene (LIG)-boron doped diamondized carbon nanowalls (BCNW) hybrid nanostructures for microsupercapacitors. Direct laser writing on polyimide film is tuned by the presence of BCNW powder where an appreciable absorbance of the BCNWs at the CO2 laser wavelength enhances the local film temperature. The thermal shock due to laser irradiation produces graphitized and amorphous carbon at the diamond grain boundaries which increases the thermal and charge transfer capacity between the LIG–diamond interfaces.

Among numerous materials, functionalized nanodiamonds are specific versatile nanocarbon material attracted ample attention thanks to their exceptional chemical, optical and electronic properties beneficial in the decomposition of harmful organic chemicals. Moreover, the stability of the nanodiamonds in the cocktail media was studied, along with various nature-originated compounds influencing their surface termination, polarity, and charge states. Thanks to the stability and biocompatibility of the nanodiamond, it can be applied in monitoring the condition of i.e. foodstuffs, and in the detection of toxins and pathogens in them.

This research work was supported by the “TEAM-NET” project carried out within the POIR.04.04.00-00-1644/18 program of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.

11:00am **F1-FrM-10 Engineering Nanostructured Metallic Thin Films by Pulsed Laser Deposition with an Outstanding Combination of Mechanical Properties***, **Francesco Bignoli**, D. Faurie,* CNRS, France*; C. Gammer, A. Lassnig,* Austrian Academy of Sciences, Austria*; S. Lee, C. Aguiar Teixeira,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; A. Li Bassi,* Politecnico di Milano, Italy*; M. Ghidelli,* CNRS, France

In recent years, thin metallic films have become object of intense research due to the activation of mechanical size effects enabling a combination of large yield strength (~3 GPa) and ductility (>10%) [1]. However, the correlation between microstructure and mechanical behavior is still not fully grasped and the research on new nanostructures with improved mechanical properties is ongoing. In this context, among the physical vapor deposition techniques, Pulsed Laser Deposition (PLD) have shown a great potential to widely tune the film morphology by simply changing the deposition pressure affecting the growth mechanisms ranging from atom-by-atom to cluster-assembled growth [2]. Nevertheless, very few studies focus on PLD deposited metallic films [3].

Here, I will show the potential of PLD to synthetize two (2) classes of emerging metallic thin films, namely metallic glasses (MGTFs) and high entropy alloys thin films (HEATFs). Firstly, I will cover the results involving the synthesis and the mechanical behavior of $ZrCuAl_x$ MGTFs with different compositions (x = 0,5,8,13 %at.) and morphologies i.e. compact and nanogranular. HRTEM shows a unique self-assembled nanolayered structure with local chemical enrichments alternating ZrCu and Al-rich nanolayers. This leads to a large and tunable elastic modulus and hardness, respectively up to 145 and 9.3 GPa. Furthermore, *in situ* SEM micropillar compression show that compact films have outstanding combination of yield strength (3.2 GPa) and ductility (5.5%), among the highest values reported in literature, while nanogranular films show a fully homogenous deformation (up to 20%) with the suppression of the shear bands process.

In the second case, I will present new results focusing on $Al_xCoCrCuFeNi$ HEATFs deposited by PLD with different compositions (x = 0,9,16 %at.) and morphologies, i.e. compact and nanogranular. HRTEM reveal a unique nanolayered structure with nanoscale Al segregations resulting in a nanocomposite FCC/amorphous structure. This leads to enhanced mechanical properties with hardness up to 11 GPa and an exceptionally large (> 3.5%) onset of crack formation when deformed on polymer substrate.

Overall, the presented results show the potential of PLD to synthetize a novel class of metallic thin films with large and tunable mechanical properties and potential interest as structural coatings.

References:
1. M. Ghidelli et al., Acta Mater., 131, 246, 2017.
2. F. Di Fonzo et al., Nanotechnology, 20, 015604, 2009
3. M. Ghidelli et al., Acta Mater., 213, 116955, 2021.

11:20am **F1-FrM-11 Preparation and Properties of Fluoroalkyl End-Capped Oligomer/Cellulose Nanofiber Composites***, **Hideo Sawada**, Y. Endo, Y. Oikawa,* Hirosaki University, Japan

Cellulose reveals the great sensitivity to water and moisture, quite different from the traditional synthetic organic polymers.[1)] Therefore, the transformation of such hydrophilic materials into hydrophobic, especially superhydrophobic derivatives has been hitherto strongly desirable in order to open a new route to the development of novel cellulose-based materials.[2)] Here we report that sol-gel reaction of fluoroalkyl end-capped vinyltrimethoxysilane oligomer[3)] in the presence of cellulose nanofiber (CNF) under non-catalytic conditions can provide the corresponding fluorinated oligomeric silica/CNF composites. The fluorinated composites thus obtained were applied to the surface modification of poly(ethylene terephthalate) [PET] fabric swatch, affording a superoleophilic/superhydrophobic characteristic on the modified fabric surface. Modified PET fabric swatch was applicable to not only the separation membrane to separate the mixture of oil/water but also the perfect adsorption of oil droplets spread on water interface. In addition, we have prepared the fluorinated oligomeric CNF composites films by casting homogeneous aqueous methanol solutions containing the corresponding composites. Pristine CNF film afforded the superoleophilic property on the surface; however, it was demonstrated that the obtained transparent colorless CNF composite films can supply highly oleophobic characteristic on the surface. The mechanical properties such as Young's modulus, tensile strength and elongation at break of the CNF composite films were superior to those of the pristine CNF film.

References

1) Isogai, A.; Hanninen, T.; Fujisawa, S.; Saito, T. *Prog. Polym. Sci.*, **86**, 122 (2018).

2) Wang, Z.; Zhao, A.; Zhang, W.; Qi, C.; Zhang, S.; Li, J. *Appl. Surf. Sci.*, **478**, 441 (2019).

3) a) Ameduri, B.; Sawada, H. (Eds.), *Fluorinated Polymers*: Volume 1, "Synthesis, Properties, Processing and Simulation", Cambridge, RSC (2016); b) Sawada, H. *Prog. Polym. Sci.*, **32**, 509 (2007); c) Sawada, H. *Chem. Rev.*, **96**, 1779 (1996); d) Sawada, H. *Polym. Chem*., **3**, 46 (2012).

11:40am **F1-FrM-12 Synthesis and Electrical Properties of Single Crystalline Cu_3Ge Nanowires***, **Chang Ting- Hsiang**, L. Bo-Yan, W. Chiu-Yen,* National Taiwan University of Science and Technology, Taiwan

This study reports the synthesis of copper-germanide metal nanowires (NWs). First, the molten Cu_3Ge bulk was homogenized at 450 °C for 12 hours and cooled in the single-zone furnace tube to obtain a smooth and uniform bulk. In order to easily control the composition of Cu_3Ge nanowires, anodic aluminum oxide (AAO) template-assisted hydraulic press die-casting approach is used to obtain a large number of Cu_3Ge nanowires with uniform composition and straight. Second, we used the $H_2Cr_2O_7$ solution to etch and remove the AAO template substrate to obtain Cu_3Ge nanowires. According to the SEM images and EDS analysis, we can further realize the interface and the content information. It can be observed the existence of high-density nanowires, which have a length of more than 10~15 μm and a diameter of about 80~100 nm. In addition, the atomic ratio of copper to germanium is about 3/1. Furthermore, Cu_3Ge nanowires are fabricated into single-nanowire devices with Ti/Pt contacts through electron beam lithography (EBL), electron beam evaporation, and lift-off processes. Lastly, the I-V measurement shows Ohmic behavior. Cu_3Ge nanowires had a resistivity of 106.1 μΩ • cm and a relatively large current density of $6.35x10^7$ A/cm^2 which can be attributed to the massive free electron transport.

Author Index

Bold page numbers indicate presenter

— A —
Aguiar Teixeira, C.: F1-FrM-10, 2
— B —
Bignoli, F.: F1-FrM-10, **2**
Bogdanowicz, R.: F1-FrM-9, **2**
Bo-Yan, L.: F1-FrM-12, 3
Brown, S.: F1-FrM-3, **1**
— C —
Chen, J.: F1-FrM-2, **1**
Chirumamilla, M.: F1-FrM-7, **1**
Chiu-Yen, W.: F1-FrM-12, 3
Chu, Y.: F1-FrM-2, 1
Couture, P.: F1-FrM-5, 1
— E —
Endo, Y.: F1-FrM-11, 3
England, J.: F1-FrM-5, 1
— F —
Faurie, D.: F1-FrM-10, 2
Field, S.: F1-FrM-5, 1
— G —
Gammer, C.: F1-FrM-10, 2
Ghidelli, M.: F1-FrM-10, 2
— K —
Kumar, S.: F1-FrM-6, 1
Kuzminova, A.: F1-FrM-6, 1
Kylian, O.: F1-FrM-6, 1
— L —
Lassnig, A.: F1-FrM-10, 2
Lee, S.: F1-FrM-10, 2
Li Bassi, A.: F1-FrM-10, 2
— M —
Maskova, H.: F1-FrM-6, 1
— O —
Oikawa, Y.: F1-FrM-11, 3
— P —
Pedersen, K.: F1-FrM-7, 1
Popok, V.: F1-FrM-7, 1
— R —
Rego, R.: F1-FrM-6, 1
— S —
Sandager, M.: F1-FrM-7, 1
Sanzone, G.: F1-FrM-5, 1
Sawada, H.: F1-FrM-11, **3**
Sharpe, M.: F1-FrM-5, 1
Sterba, J.: F1-FrM-6, 1
Stranak, V.: F1-FrM-6, **1**
Sun, H.: F1-FrM-5, 1
— T —
Ting- Hsiang, C.: F1-FrM-12, **3**
— W —
Wei, T.: F1-FrM-8, **2**
— Y —
Yin, J.: F1-FrM-5, **1**