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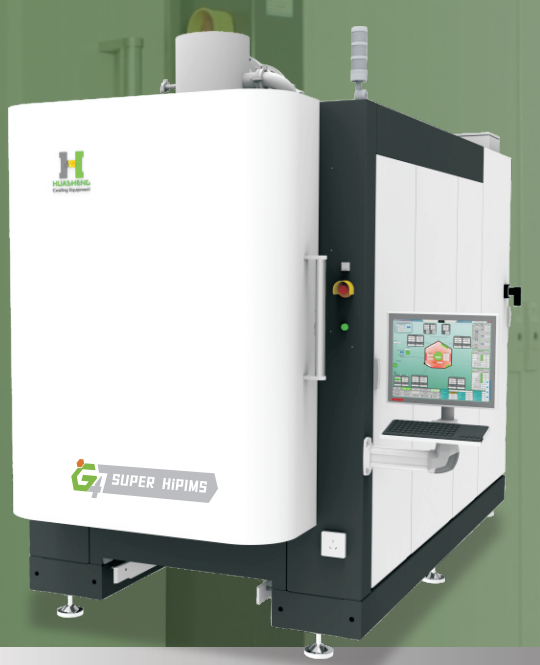

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4th Workshop on Coated Tools & Multifunctional Thin Films Proceedings

Proceedings of 4th Workshop on Coated Tools & Multifunctional Thin Films. Campinas (SP) UNICAMP, 2024.

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Opening 4th Workshop on Coated Tools & Multifunctional Thin Films 2024

August 19-08-2024

Opening - WCTMTF-2024 – 19/08/2024

Prof. Dr. Marcos Cesar de Oliveira – vice director IFGW – UNICAMP
Prof. Fernando Alvarez – IFGW – UNICAMP
Prof. Chegyong Wang - Vice director Guangdong University of Technology,
Prof. Dr. Qimin Wang – Guangdong University of Technology
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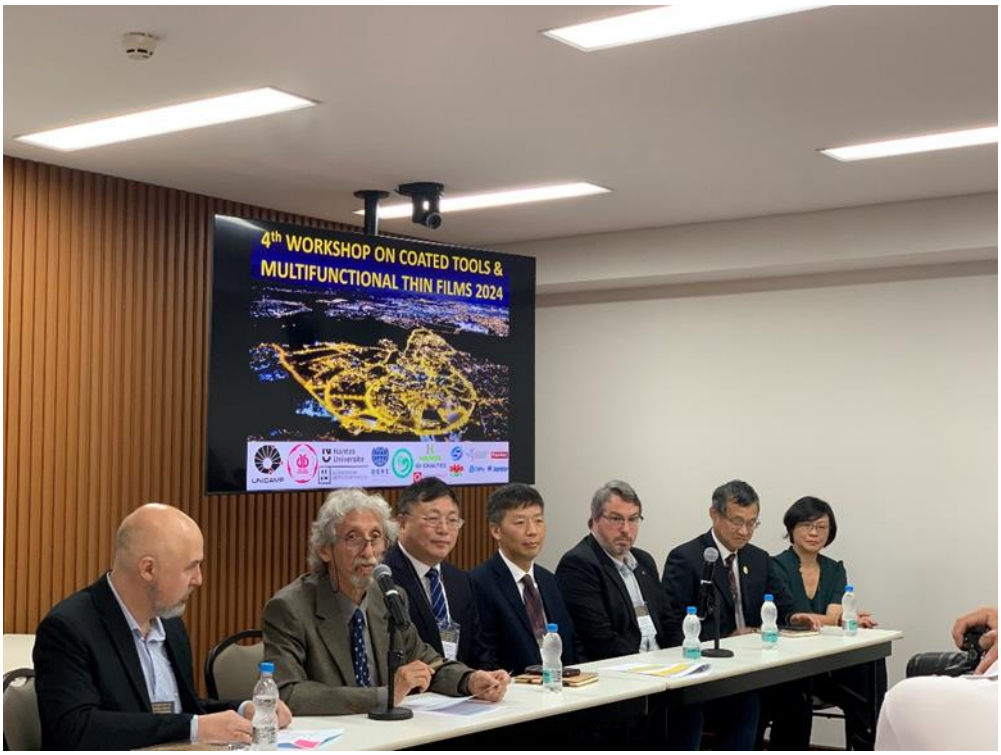

Starting left: Prof. Marcos Cesar de Oliveira, Prof. Fernando Alvarez, Prof. Chegyong Wang, Prof. Qimin Wang, Prof. Rafael de Brito Dias, Prof. Gao Qinxiang, Prof. Lucia Wong-Desbrosses

Prof. Fernando Alvarez:

Good morning, ladies and gentlemen. I am pleased to welcome everyone to the 4th Workshop on Coated Tools & Multifunctional Thin Films 2024, and I have the privilege of opening the scientific activities of the workshop.

This meeting continues the series that began in 2014, organized by Guangdong University and Nantes University. Like the previous meetings, this fourth edition covers the field of

coatings and advanced materials for various applications, with plenary and keynote talks bringing together multidisciplinary scientists such as physicists, chemists, engineers, and materials science specialists.

In this workshop, we will explore broader areas of surface science and engineering, as well as expanding areas of interest. Topics will range from the design and preparation of thin films, hard multi-component and multi-layer coatings, and high-entropy thin films, to the optimization of coatings for various applications such as tribology, 2D materials, sensors, high-speed machining of coated tools, data mining applied to the development of new materials, and virucidal and bactericidal coatings.

This fourth edition of the workshop, taking place in Brazil at UNICAMP, is especially important because it offers the opportunity to bring together scientists from the North and South. Moreover, hosting the workshop at UNICAMP is significant as it allows students and researchers from Latin America to attend lectures on subjects in which they are actively working.

This event was made possible thanks to the logistical and financial support from the Brazilian Research Council (CNPq), the São Paulo Research Foundation (FAPESP), the National Institute of Surface Engineering (INES-CNPq), the Executive International Relations Office (UNICAMP), the Institute of Physics (IFGW, UNICAMP), and the University Development Foundation (FUNCAMP, UNICAMP).

Of course, the role of colleagues from the Guangdong University of Technology, as well as those from the Applied Physics Department (DFA, IFGW), was crucial, and I am deeply grateful for their efforts and generosity in ensuring the workshop's success. This acknowledgment also extends to the members of the Organizing Committee and the Scientific Committee.

Finally, the list of people involved in the workshop's preparation is extensive, and naming each of them would be risky because unintentionally omitting names would be unfair. Nevertheless, I must mention two enthusiastic collaborators who dedicated many hours to organizing this meeting: Dr. Carla D. Boeira and Leonardo M. Leidens, Postdoctoral Fellows.

Thank you very much for your attention and enjoy the workshop!

Fernando Alvarez

ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

PROTECTIVE GRADED COATED FOR HIGH TEMPERATURE APPLICATIONS

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Mechanical parts operating under harsh high temperatures environments have their service life extended and performance enhanced if protected by coatings, contributing to a more sustainable operation. However, the high melting point and high strength of materials that can sustain such an aggressive environment also have been shown to present challenges to be processed particularly by hardfacing. An alternative route to process high strength, high melting point materials is presented using in-situ synthesis of intermetallic alloys during deposition of powder mixtures by Plasma transferred arc. Furthermore, enhanced performance with a good compatibility of metallic substrates is gained by processing graded coatings. Advances on the processing of multilayer nickel intermetallic coatings are discussed as a competitive procedure to achieve high performance high temperature hardfacing coatings. Recent results on Nb silicides graded coatings confirmed the effectiveness of in-situ synthesis of intermetallic hardfacing processing to protect mechanical parts operating in harsh high temperature service conditions.

Keywords: Graded coatings; Hardfacing; Nickel aluminides; Nb silicides

Acknowledgments: This work was supported by CNPq, CAPES, FINEP, CBMM

ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

MICROFLUIDIC E-TONGUE USING METALLIC NITRIDE NANOFILMS FOR SOIL MACRONUTRIENT ANALYSIS

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Electronic tongues are advanced sensors that can greatly enhance precision agriculture by providing quicker evaluations of soil macronutrients, which in turn facilitates improved mapping and decision-making in farming areas [1,2]. In this study, we employ thin films of metallic nitrides, deposited using the Dynamic Glancing Angle Deposition (DGLAD) method, as sensing elements in an impedimetric, microfluidic e-tongue. The use of metallic nitrides enhances the robustness of the sensors, while the DGLAD technique offers precise control over the thickness and porosity of the films, effectively transforming them into molecular sieves [3]. The aim is to improve the sensor's ability to detect specific macronutrients based on their size at the electrode/electrolyte interface. We optimize the sputtering rates to achieve uniform thickness, size, and porosity for four different metallic nitride films (TiN, CrN, BN), each with unique electrical properties that form the device's sensing units. Impedance data is collected by passing samples through the device, with separate measurements taken for ultrapure water, 1 mmol KCl, and 1 mmol NaCl solutions, as well as soil samples with various concentrations of K, which are simply dispersed in ultrapure water at a concentration of 1g/mL. The results showed a higher level of discrimination for K in soil samples, successfully differentiating between all the tested samples. These improvements could facilitate the on-site detection of soil macronutrients, potentially enhancing the device's selectivity for a wider range of applications.

Keywords: E-TONGUE; PRECISION AGRICULTURE; NITRIDE FILMS

Acknowledgments: UNICAMP, FAPESP (#2022/08216-1 and #2023/07552-0), CNPq, INES, INEO.

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ORAL PRESENTATION - 2) COATINGS FOR SPECIFIC APPLICATIONS, INCLUDING (BUT NOT LIMITED TO) TRIBOLOGICAL, HIGHSPEED MACHINING, AND CUTTING TOOLS

FUNDAMENTALS OF NANOTRIBOLOGY AND PHOTOTRIBOLOGY

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The phenomenon of friction is a complex manifestation of nature. Although phenomenological laws can describe the friction force at different scales, the fundamental physical understanding of such a phenomenon has no consensus. In recent decades, various models such as phononic, electronic, magnetic and also electrostatic models were proposed to explain the behavior of friction at the nanoscale. This talk provides a historical and conceptual overview of dissipative friction forces and coupling mechanisms, and then discusses our results about ultra-low friction systems of hydrogenated, deuterated and fluorinated amorphous carbon thin films, including mechanisms. Finally, novel results of the control of friction forces by light in solid and liquid states, which we call phototribology, will be presented.

Keywords: Nanotribology; Phototribology; Friction forces; Light; Mechanism

ORAL PRESENTATION - 2) COATINGS FOR SPECIFIC APPLICATIONS, INCLUDING (BUT NOT LIMITED TO) TRIBOLOGICAL, HIGHSPEED MACHINING, AND CUTTING TOOLS

ANALYSIS OF TOOL WEAR AND CUTTING CHARACTERISTICS IN MILLING BY VARIOUS COATINGS

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Nickel-based superalloys are essential materials for turbine engine components in aerospace applications. However, it is difficult to manufacture nickel-based superalloys with high surface integrity due to the high cutting forces, high cutting temperatures, and severe work hardening, which usually requires cutting tools with good thermal conductivity, superior high-temperature performance, and high abrasion resistance. This study investigates the tool wear mechanism and machined surface integrity of the refractory powder metallurgy nickel-based superalloy FGH 4097 during milling at different speeds, with a special focus on the effect of various coatings (TiAlCrN, TiAlN, and TiAlSiN). The relationship between tool flank wear (VB) and material removal volume (MRV) was studied, and the cutting force signals were analyzed in both the time and frequency domains. This work also examined the influence of tool wear with various coatings on both the surface morphology of machined parts and the distribution of residual stress. Furthermore, the mechanisms of tool wear for different coatings were revealed by analysis using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results demonstrated that the wear characteristics on the three coated tools were similar during milling at a lower speed. However, the TiAlCrN coated tool demonstrated superior performance at high cutting speed. For the identical coated tools, the cutting force and roughness of the surface increased with the elevation of cutting speed when holding an identical amount of MRV. The SEM and EDS analysis revealed that adhesive wear was found to be the dominant mechanism of tool wear for the tested tools, regardless of the coatings used, while the TiAlN-coated tool also exhibited abrasive wear.

Keywords: Varying coatings; Tool wear mechanism; Cutting characteristics; Powder metallurgy nickel-based superalloy

Acknowledgments: This work is financially supported by National Science and Technology Major Project (Y2019-VII-0018-0160).

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

NEW PARADIGMS FOR THE QUANTITATIVE STRUCTURAL AND CHEMICAL CHARACTERIZATION OF NANOMATERIALS BY ADVANCED TEM METHODS

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The field of nanoscience and nanotechnology has induced a surprising rapid progress on instrumentation related to electron microscopesincluding electron optics, automation, reproducibility, and highly performant detectors. During decades, it was usual to consider transmission electronmicroscopy (TEM) as an essential tool but, being mostly only capable of yielding qualitative atom resolutionimaging results in materials science. Here, we will discuss several structural and chemical studies of nanosystems, such as nanoparticles, nanowires, nanotubes, etc. developed atour group; in particular, we will show experimental studies designed to target the assessment of quantitative results both in chemical and structural aspects [1-3]. We have applied different structural refinement procedures based on precession electron diffraction (PED) and electron-diffraction-based pair distribution function (PDF). These research applications aim ofdisplaying the need to change our views onexperiment planning, realization, and subsequent data treatment. It is essential to exploit these advanced tools in association withmeaningful physical phenomena simulations, big data processing to finally derive physical interpretation which has been obtained through quantitative and statistically verified comparison with experimental data.

Keywords: Transmission Electron Microscopy; electron crystallography; precession electron diffraction; nanomaterials

Acknowledgments: This work was supported by CNPq (306513/2017-0, 402676/2021-1,303025/2022-0).

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ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

STRUCTURAL, ELETRONIC, AND MECHANICAL PROPERTIES OF 2D FULLERENE NETWORKS

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The emergence of graphene sparked a revolution in materials science and reignited interest in novel 2D carbon structures. Recently, a novel 2D carbon material, comprised of polymerized C60 fullerenes, was successfully synthesized [1]. This material displayed two distinct configurations: closely packed quasi-hexagonal (qHPC60) and quasi-tetragonal (qTPC60) phases, both exhibiting high crystallinity and robust thermodynamic stability. In this study, we employed Density Functional Theory (DFT) simulations to explore the electronic, structural, and mechanical characteristics of monolayers of qHPC60 [2,3]. These structures demonstrated semiconductor behavior alongside anisotropic mechanical properties, with elastic modulus values ranging between 50 and 62 GPa. Our findings regarding their optical properties suggest their potential as UV absorbers for photon energies up to 5.5 eV, owing to their low reflectivity and refractive index exceeding one. Furthermore, the estimated optical bandgap (1.5-1.6 eV) closely aligns with experimental observations (1.6 eV). Keywords: Fullerene Networks, 2D materials, DFT Acknowledgments: This work was supported in part by the Brazilian Agencies FAPESP and CNPq.

Keywords: Transmission Electron Microscopy; electron crystallography; precession electron diffraction; nanomaterials

Acknowledgments: This work was supported in part by the Brazilian Agencies FAPESP and CNPq.

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

ON THE COLOR EMISSION OF Tb IONS EMBEDDED IN INDIUM TIN OXIDE THIN FILMS

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Advances in optoelectronics devices are often driven by the development or tailoring of multifunctional materials with a unique combination of properties. Thus, transparent conducting oxides (TCOs) have attracted great attention for the development of photonic devices. Among TCOs, indium tin oxide (ITO) has been recently re-assessed for its capability to undergo opto-electronic modulation. The current trend is to embed rare earth (RE) ions into TCO's to dilute luminescent properties. In this work, we assess luminescence activation and tunning of the color emission when introducing terbium (Tb) ions in ITO thin films. Moreover, we also aim to achieve Tb luminescence while keeping the properties of the host material. ITO:Tb films were prepared by RF-magnetron sputtering. Optical bandgap and Urbach energy, were retrieved by means of a fundamental absorption model based on a band fluctuations approach. Electrical characterization was performed by Hall effect in Van Der Pauw configuration measurements, whereas X-ray diffraction revealed the impact of the Tb incorporation in the structure. Samples maintained a high optical transmittance in the ultraviolet and visible spectral regions and showed an electrical resistivity ranging from 10^{-3} to 10^{-1} Ω·cm. Tb-related luminescence was obtained after annealing in air at atmospheric conditions with an unusual red-light emission associated with electric dipole transition $^{5}D4 \rightarrow {}^{7}F2$ [1]. Finally, due to the particular observed branching ratio in the Tb-related emission of ITO:Tb a Crystal-Field analysis and DFT simulations were performed to assess the most probable

sites Tb ions are occupying in the bixbyite structure. The latter confirms that the Tb ions are mainly located in a non-centrosymmetric Crystal-Field of C2 symmetry sites. We believe that this work shed some light on the capabilities to tune the RE-related emission color.

Keywords: ITO; Terbium; Luminescence

Acknowledgments: This research was funded by the Office of Naval Research, Grant No. N62909-21-1-2034. The authors acknowledge the Center for Materials Characterization (CAM) at the PUCP for supporting the development of this work.

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ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

DEVELOPMENT OF Cu-DOPED AZO SENSORS CONNECTED WITH ARTIFICIAL NEURAL NETWORK FOR ORGANIC VOLATILES DETECTION LINKED TO COFFEE QUALITY

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Over the last few decades, electronic nose technology has raised attention to improving the quality control process in the food and beverage industry. While there are several studies to improve the performance of gas sensors, their selectivity, sensitivity, and working temperatures, the integration of artificial intelligence provides an additional way to optimize the capabilities of electronic noses. This work focuses on developing gas sensors based on aluminum-copper co-doped zinc oxide (AZO-Cu) for analysis of organic volatile detection, associated with coffee quality, employing machine learning techniques. The hydrothermal synthesis method used diethanolamine as the oxidizing agent and nitrate salts of zinc, aluminum, and copper as metal precursors. Subsequently, the synthesized oxides were thermally treated at 600°C for 2 hours under an air environment. For the elaboration of the sensors, three layers of AZO-Cu were deposited using a polyethylene glycol suspension over an alumina substrate previously modified with platinum interdigital electrodes. The sensitivity evaluations were carried out at 180°C, using 300 s sampling and 600 s purging cycles for each of the target analytes: vanillin, acetic acid, caramel essence, green apple essence, and red fruit essence. A

multilayer perceptron neural network (MLP), a convolutional neural network (CNN), and random forests (RF) were used to train the electronic nose. The results revealed that the most sensitive sensors presented a selectivity of 99.8% when the MLP network evaluated the analysis. Also, according to the structural characterization, aluminum and copper doping were introduced into the lattice at substitutional positions. While, photoluminescence studies indicated the presence of zinc vacancies and oxygen vacancies, which promote surface active sites in the gas sensors. These findings contribute to the understanding of the parameters to optimize AZO-Cu sensors for coffee quality evaluation and represent an improvement in the training of machine learning algorithms in electronic noses for this application.

Keywords: Semiconductors; Machine Learning; Electronic Nose; Gas sensor; AZO:Cu

Acknowledgments: This work was supported by the Peruvian National Council for Science, Technology, and Technological Innovation (CONCYTEC) for research grant no. 179-2020- FONDECYT. We would like to thank the Research Promotion Directorate (DFI) of the Pontifical Catholic University of Peru for funding the research project no. PI0888-CAP-PUCP2022. The authors acknowledge the Center for Materials Characterization (CAM) at PUCP for supporting the development of this work.

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

ENHANCING ORGANIC VOLATILES GAS SENSING CAPABILITIES BY Cr DOPED AZO THIN FILMS BILAYER SYSTEMS: OPTOELECTRONIC AND STRUCTURAL PROPERTIES

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Transparent conducting oxides (TCOs) are highly versatile materials with tunable optoelectronic properties suitable for diverse electronic applications. They have been employed as gas sensors across multiple domains, but limitations in their current sensitivity have prompted a quest for innovative methods to enhance their performance [1]. In this study, we propose a bilayer gas sensor design based on a n-p homojunction. Our investigation focuses on the preparation, characterization, and sensitivity evaluation of bilayer sensors based on aluminum-doped zinc oxide (AZO) and chromium-aluminum co-doped zinc oxide (AZO:Cr), aiming to elucidate their sensitivity towards volatile biomarker compounds (VBCs), such as acetone. In the long term, this could lead to the optimization of reliable gas sensors for non-invasive diagnostic purposes. The introduction of Al and Cr, from 1 to 3 at. %, into the ZnO host matrix enabled the adjustment of their optical and electrical properties. Two synthesis methods were employed: (1) RF magnetron sputtering and (2) spin-coating. Bilayer sensors were grown with a sputtered layer (p-type) at the bottom and a spin-coated layer (n-type) on top. Post-deposition thermal treatments, within the range of 400°C to 800°C, promoted oxygen vacancies. Bilayer sensors were evaluated to measure their sensitivity at different

temperatures (180°C to 240°C). Our results revealed that their enhanced sensitivity was due to the higher number of active sites on the spin-coated layer, leading to a more stable sensing response to acetone when increasing its thickness. According to Hall Effect measurements, Al dopant concentration and the Cr/Al atomic ratio were responsible for the free charge carrier density and carrier type, respectively. In addition, the evolution of defect states such as oxygen vacancies, studied by photoluminescence (PL), allows us to determine the optimal synthesis conditions to obtain sensitive bilayer n-p structures [2,3].

Keywords: Gas sensor; Radio frequency magnetron sputtering; Spin-coating; Aluminum-doped zinc oxide; Oxygen vacancies

Acknowledgments: This work was funded by the Office of Naval Research, grant no. N62909-21-1-2034 and supported by the Peruvian National Council for Science, Technology, and Technological Innovation (CONCYTEC) grant no. 179-2020-FONDECYT. Further support had been provided by the Pontificia Universidad Católica del Perú (PUCP) vice chancellorship for research (VRI, grant PI0888-CAP-PUCP-2022). The authors acknowledge the Center for Materials Characterization (CAM) at PUCP for supporting the development of this work.

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

2D MATERIALS: ELECTRONIC STRUCTURE AND DOPING

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In this seminar I will present the results obtained in our laboratory over the last 3 years of research into two-dimensional materials. I will present results from strain measurements in twisted graphene bilayers grown by CVD on nickel substrates. Regarding the study of transition metal dichalcogenides (TMDs), results from the introduction of defects, and/or dopants, in WS2 samples grown by CVD treated by cold plasma will be presented. Finally, results from a study of WS2 doping by Gallium will be discussed.

Acknowledgments: This work was partially supported by Brazilian agencies: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Fundação Carlos Chagas de Amparo à Pesquisa no Estado do Rio de Janeiro (FAPERJ) and Instituto Nacional de Engenharia de Superfícies (INCT-INES). The authors are also grateful to fellow colleagues Dr. Cesar Augusto Diaz Mendoza, Dr. Andre do Nascimento Barbosa, Dr. Shuai Zhang, Dr. Neileth Johanna Stand Figueroa for insightful discussions.

Keywords: graphene; TMDs; doping

ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

MOLECULARLY IMPRINTED POLYMER FUNCTIONAL COATING ON ELETROLYTIC TRANSISTORS FOR POINT-OF-CARE SENSING TECHNOLOGIES

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Small molecules play an important role as biomarkers in various diseases and are commonly found in bodily fluids such as urine, blood, and saliva [1]. However, their detection presents challenges due to their presence in complex environments at low concentrations, often in the micro- and nanomolar range. The increasing demand for point-of-care (PoC) devices capable of detecting and analyzing these analytes underscores the importance of developing innovative technologies. Here, aiming to develop innovative PoC technologies, we have developed a platform specifically designed to detect hippuric acid (HA). HA serves as a naturally occurring metabolite in the urine of healthy individuals and acts as a biomarker for several diseases, typically analyzed through expensive and non-PoC methods [2]. In this study, we synergistically combined molecularly imprinted polymers (MIPs) functional coatings with electrolyte-gated transistors (EGTs) based on reduced graphene oxide (rGO). Our MIP-functionalized rGO EGTs exhibited remarkable characteristics and performance, including detection across a wide range of HA concentrations (0.05 to 200 nmol L–1), low operating voltages (<0.5 V), rapid response times (≤10 s), and low limit of detection (LoD) of 39 pmol L–1. Furthermore, the novelty of our study lies in the unprecedented use of machine learning

(ML) on rGO EGT data, enabling a multivariate analysis focused specifically on the device's transfer curves and eliminating arbitrary sensor signal choices. This approach resulted in a 2.5-fold increase in device sensitivity (1.007 μA/nmol L–1) compared to traditional human data analysis (0.388 μA/nmol L–1), along with higher accuracy. Overall, our innovative strategy holds promise for advancing healthcare technologies by enabling accurate and highly sensitive PoC diagnostics for various small-molecule biomarkers found in complex media.

Keywords: Point-of-Care Sensors; Diagnostics, Molecularly Imprinted Polymers; Hippuric Acid; Electrolyte-Gated Transistors; Machine Learning

Acknowledgments: Financial support from the Sao Paulo Research Foundation FAPESP, CNPq, and SisNANO Programme.

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

TRANSIENT ELECTRICAL RESPONSE OF REDUCED GRAPHENE OXIDE LIQUID-GATED TRANSISTOR TOWARDS SYNAPTIC DEVICES

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Machine learning has evolved at an impressive rate in the last decades. Algorithms such as artificial neural networks (ANN) have now demonstrated to surpass humans in multiples tasks, for example, playing chess and handwriting recognition. This increase of applications came with the cost of a high-energy consumption, especially during the training phase of the models. In order to overcome this issue, new forms of information processing have been proposed lately, with great attention given to strategies that mimics the human neural system [1]. Devices that can implement some of the functions that mimic the human brain are called neuromorphic. In this work, we examined the mimetic synaptic capability of electrolyte-gated transistors (EGTs) based on thin film of few-flake reduced graphene oxide (rGO). Specifically, we studied the transient current response of rGO EGTs when a set of squared voltage pulses was applied to the gate. The source-drain current was monitored before and after the stimulus for trains of distinct length (1 - 50 pulses), periods (10ms - 45s), time intervals between each pulse (10ms - 60s) and amplitude (0.1 – 0.8V). For times in the order of ms and low voltage pulses (< 1V), the current variation lies in the range of few seconds. On the contrary, long-term memory (t > 10 min) was achieved when a threshold voltage and a minimum pulse width were applied. Synaptic devices could enable the development of a myriad of applications besides computation, such as (bio)sensing [2] and bioelectronics [3], which makes rGO EGTs versatile electronic devices.

Keywords: Point-of-Care Sensors; Diagnostics, Molecularly Imprinted Polymers; Hippuric Acid; Electrolyte-Gated Transistors; Machine Learning

Acknowledgments: This work was supported by Capes, CNPq and the São Paulo Research Foundation.

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

SIRIUS: TRANSFORMING RESEARCH WITH FOURTH-GENERATION SYNCHROTRON LIGHT

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The use of synchrotron light in interdisciplinary scientific research has surged in the last decades due to the development of brighter light sources and advanced instrumentation. Sirius, a cutting-edge 3-GeV fourth-generation storage ring with an emittance of 0.2 nm rad, is operated by the Brazilian Synchrotron Light Laboratory (LNLS) at the Center for Research in Energy and Materials (CNPEM). This advanced light source significantly improves brightness and coherence, which, combined with advancements in optics, precision mechatronics, detectors, and computing, unlocks new research opportunities at previously inaccessible spatio-temporal scales. Currently, ten beamlines are available for users, with two in the commissioning phase and two under installation. The first phase includes 14 beamlines supporting various scientific programs and experimental techniques, including Coherent Diffraction Imaging (CDI), X-ray Photon Correlation Spectroscopy (XPCS), micro- and nano-Computed Tomography (CT), micro- and nano-X-ray Diffraction (XRD), X-ray Absorption Fine Structure (XAFS), Small Angle X-ray Scattering (SAXS), Angle-Resolved Photoemission Spectroscopy (ARPES), Resonant Inelastic X-ray Scattering (RIXS), Photoemission Electron Microscopy (PEEM), and X-ray Magnetic Circular Dichroism (XMCD). Phase 2 will introduce ten additional beamlines, with four already under development, focusing on programs such as X-ray Instrumentation, High-Energy X-ray Diffraction, Tender X-ray Spectromicroscopy, and Terahertz Spectroscopy. Furthermore, CNPEM is leading the Orion project to establish the first Biosafety Level 4 laboratory in Latin America. This facility will specialize in researching and diagnosing pathogens that threaten epidemiological surveillance systems. The laboratory will feature three X-ray bio-imaging beamlines, allowing scientists to visualize, in three dimensions, the process by which pathogens infect animals and cause diseases, from the cellular level to the entire organism. This presentation will offer an overview of the Sirius light source, highlighting its experimental capabilities and the numerous scientific opportunities it provides with a focus on research in advanced materials.

Keywords: synchrotron; x-ray; diffraction; tomography; Spectroscopy

ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

OPTICAL CHARCTERIZATION OF EXCITONIC ABSORPTION IN METAL TRI-HALIDE PERVOSKITES USING DISPERSION MODELS, A HYDROGEN-POLARON MODEL AND FIRST PRINCIPLES

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Studies of excitonic absorption of metal tri-halide perovskites have depicted several attention due to its high efficiency rates reaching up to 25%. Correct description of excitons in these systems can lead to improvements to solar cell devices based on them. In this work, we present an optical study and characterization that covers modeling of the spectral curves, an effective model and first principles. First, the modeling of the excitonic absorption is studied in terms of a recently proposed model based on the Elliott equation and the band-fluctuations approach [1]. This analytical model is used to fit the absorption of metal tri-halide perovskites with different concentrations $FAPbI_{3-x}Brx$, $MAPbI_{3-x}Br_x$, $CsPbI_{3-x}Brx$ and $MAPbBr_{3-x}Cl_x$. Thus, retrieving information such as bandgap, exciton binding energy and Urbach energy. Secondly, the polar nature of this semiconductors can be modeled in terms of a hydrogen effective model with a potential that mimics the electron-phonon interaction [2]. As a consequence, the exciton-polaron binding energy depends on five parameters. These are the low and high frequency dielectric constant, e_0 and e_{inf}, the effective masses of electron and hole, m_e and m_h, and the LO phonon energy hw_{LO}. These parameters can be estimated from first principle calculations using the independent particle approximation (IPA) for dielectric response, and the finite differences approach for phonon calculations. Thirdly, we perform an study of excitonic absorption based on first principles by solving the Bethe-Salpeter (BS) equation. Here, we use an approach that solves the BS equation using maximal localized Wannier functions

and an analytical screened potential [3]. The advantage of this approach is that it saves computational time up to two order of magnitude so that exciton properties of large systems becomes feasible. As a result, we calculate the exciton absorption evolution of the aforementioned perovskites with different concentrations, for tetragonal and orthorombic phases. The comparison of binding energies and bandgaps of the metal tri-halide perovskites, calculated from our different methods, show the agreement, capabilities and advantages of each approach.

Keywords: Absorption; Binding energy; Electron-phonon interaction; Exciton; Perovskites

Acknowledgments: Absorption, Binding energy, Exciton, Electron-phonon interaction, phonons, Polar, Perovskites, Hydrogen model, DFT, Wannier, BSE.

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ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

LAYER CHARACTERIZATION BY ELLIPSOMETRY OF THIN Ti2CTx AND Ti3C2Tx FILMS PREPARED WITH LOW CONCENTRATED HYDROFLUORIC ACID

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The first MXene was synthesized in 2011 by Naguib et al., [1] from MAX phase powder using concentrated (50wt.%) hydrofluoric acid (HF). Later, the etching conditions were adjusted depending on the structure, stoichiometry, and chemistry of the used MAX phase precursor. Opening a broad field for the development and study of MAX and MXene phases. In the last years, many different etching methods have been reported for MAX phase to MXene transformation [2]. In the present work the focus was put on the preparation of MXenes not based on MAX phase particles but on MAX phase thin films. Therefore, Ti_2AlC and Ti_3AlC_2 thin films were prepared by deposition of multilayers of titanium, aluminium, and carbon on silicon substrates by magnetron sputtering and subsequent rapid thermal processing (RTP) [3]. For the selective etching of the A element low concentrated (1wt.%) HF was used. The etching process for thin films showed certain differences regarding the removing of the Al compared to the powder MAX phases approach. This is mainly due to the different etching directions in both cases. As for thin films the chemical attack only takes place from the top, the results show the formation of MXene on a residual MAX phase. Subsequently, the chemical structure as well as the functional groups of the formed MXene were analyzed by Raman spectroscopy. The optoelectronic properties were analyzed by variable angle ellipsometry. Both, film

thickness, and the modeling of the complex dielectric function as well as the definition of functional groups of thin film MXene are of particular interest to get an understanding of the etching process with low concentrated HF. This study could lead to new applications of these MXenes in electrochemical sensing as well as electrochemical water-splitting among others.

Keywords: Thin film MAX phase; thin film MXene; Ti_2CT_x; $Ti_3C_2T_x$; low concentration HF

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ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

ACTIVE MICRO-ORIGAMI HINGES FOR DYNAMICALLY MORPHING MICROELECTRONICS

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Choreographing the transformation of patterned surfaces into adaptable shapes, to exhibit designable mechanical interactions with their environment, is a complex challenge.[1] We have introduced a new category of strain-engineered dynamic-shape materials that allow for diverse multi-dimensional shape modulation, leading to unprecedentedly adaptive microarchitectures.[2] Using micro-origami tessellation, we can create strategic creases in manifold materials that house actuator micro-hinges. These hinges autonomously reshape upon electrochemical cues. Examples of these novel 4-dimensional (4D) metamaterials include freestanding multifaceted folded structures, auxetic mesosurfaces, and dynamically morphing cages. Such 4D mesostructures are integrated into dual proof-of-concept demonstrations that pave the way for more intelligent shape-changing biomedical technologies, viz. a morphogenetic micro-supercapacitor for high-density energy conversion and storage applications, and a dynamic-shape microelectronic soft implant prototype.[2] These realizations lay the groundwork for designing comprehensive 4D metamaterials, setting a vista to the tangible realization of electronic information-driven morphogenesis.[3]

Keywords: 4D; biomedical implant; energy storage; foldable electronics; intelligent materials

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ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

HIGH-ENTROPY NITRIDE COATINGS DEPOSITED BY MAGNETRON SPUTTERING AS SENSING UNITS IN ENHANCED IMPEDIMETRIC E-TONGUES

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As a physical vapor deposition (PVD) method, magnetron sputtering allows for the controlled deposition of thin films with nanoscale precision. This versatility makes it useful for scientific and technological applications. Recent advancements, such as Dynamic Glancing Angle Deposition (DGLAD) [1], modify hard coatings by controlling substrate motion, resulting in tuning properties like hardness and texture. Magnetron sputtering also enables the deposition of a myriad of high-entropy alloys (HEAs)and thin films. HEAs [2], composed of multiple metallic elements in near-equimolar ratios, offer improved hardness, tensile strength, and ductility. HEN thin films, the nitrogenated form of the HEA coatings, provide enhanced hardness, wear, and corrosion resistance, ideal for protective coatings and advanced sensing. Electronic tongues (e-tongues), inspired by human taste, enable rapid analyte detection [3]. High-entropy nitride thin films as functional coatings produced via magnetron sputtering on sensing units of e-tongues enhance sensitivity, selectivity, and durability. Here, three films were grown on a PCB (printed circuit board) using DGLAD, varying angular positions and nitrogen content. The deposition used a multi-metallic target of Ti, Ta, V, Zr, and Nb. The films with a thickness of approximately 100 nm were deposited onto interdigitated electrodes (IDEs) at room temperature. Preliminary results showed differences in IDEs before and after film

deposition. The sensibility and robustness of the sensor array were improved by adding the coatings. In conclusion, integrating magnetron sputtering with high-entropy nitride thin films advances sensing technologies. This fusion paves the way for next-generation electronic tongues with unparalleled sensitivity and reliability, suitable for environmental monitoring, food quality assessment, and medical diagnostics applications.

Keywords: High entropy coatings; PVD; e-tongues

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

CO-DOPING OF ZINC OXIDE THIN FILMS WITH ALUMINUM AND TERBIUM TO ENGINEER A CONDUCTIVE, TRANSPARENT AND LUMINESCENT MULTIFUNCTIONAL MATERIAL

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Zinc oxide (ZnO) is a semiconductor material with a bandgap of 3.37eV and high exciton binding energy of 60 meV. The electrical conductivity of ZnO can be considerably enhanced by aluminum (Al) doping. Al-doped ZnO (AZO) is a transparent conductive oxide (TCO) with potential and current applications in optoelectronic devices such as, solar cells, LEDs, and gas sensors [1]. Recently, it has been shown that it is possible to dilute luminescence properties on TCOs when embedded with rare earth ions [2]. Among RE ions, terbium (Tb) shows a sharp and well-defined emission line in the green optical region at around 545 nm, attributed to the $^5D4 \rightarrow {}^7F5$ intra-4f electronic transitions. Here, we evaluate the impact of introducing Tb ions into AZO thin films on the host optoelectronic properties, aiming to achieve Tb-related luminescence without compromising its optical and electrical properties. For these, AZO:Tb thin films were grown by radiofrequency magnetron co-sputtering using high purity ZnO, Al and Tb targets. The effect of Tb doping on AZO's properties is investigated for different Tb concentrations. Optical bandgap, Urbach energy, and free exciton bands are assessed by means of optical transmittance and variable angle ellipsometry measurements using recently developed fundamental absorption models. Electrical characterization was

performed by Hall effect measurements in a Van der Pauw configuration as well as by modeling the free carrier absorption. AZO:Tb films show an optical transmittance around 75% in the UV-visible region and an electrical resistivity in the order of 10-2 Ω·cm while the characteristic green light emission related to Tb3+ is observed in photoluminescence measurements for all films in their as-grown state. We believe that these results can help to shed some light on the development of multifunctional materials that combine luminescence, optical transparency, and electrical conductivity.

Keywords: TCO; Luminescence; Rare earths

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

ALUMINUM-DOPED AMORPHOUS SILICON CARBIDE THIN FILMS AS PHOTOCATHODES FOR GREEN AMMONIA PRODUCTION

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Decarbonization of ammonia production via sustainable electrification is of great interest in the 21st century to mitigate climate change. Photoelectrochemical ammonia synthesis emerges as a promising strategy due to its ability to simultaneously convert intermittent solar energy into chemical energy and achieve photo-electroreduction of NOx on suitable photocathodes at low overpotentials. Diverse studies have proposed different photoelectrodes such as CZTS, NiO, Cu_2O, etc. as suitable photocathodes for green ammonia production [1]. However, the high cost and photo-corrosion under PEC conditions prevent their real-world applications. Amorphous silicon carbide (a-SiC) thin films are appealing for their abundance of silicon, corrosion resistance, and tunable band gap (1.8 - 3.1 eV). This makes them ideal for integrating into multi-junction tandem Photovoltaic-Electrochemical cells for optimized spectral utilization and self-sustained operation [2]. Herein, Aluminum-doped amorphous sub-stoichiometric (a-$Si_{1-x}C_x$) thin films were prepared by RF magnetron sputtering on Si substrates. Elemental mapping showed carbon content ranging from 0.25 to 0.71 at. % and aluminum from 1 to 3 at.%. Raman and FTIR spectroscopy revealed varying homonuclear and heteronuclear bond intensities with carbon content, influencing the optoelectronic properties of thin films. The optical transmittance revealed a variation of optical parameters (E_g, n, and k) with varying Si and C concentration. The electrical properties studied by the Van der pauw technique revealed the ohmic nature upon using Aluminum contacts. Photoelectrochemical studies were performed on a-$Si_{1-x}C_x$ thin films to evaluate their

performance as a photocathode in nitrate electroreduction to green ammonia and the results are correlated to the optoelectronic properties to identify the optimal composition of Si and C in a-SiC. Stoichiometric and Si-rich a-SiC emerged as better photocathodes for green ammonia production.

Keywords: Photocathode; Amorphous Silicon Carbide; RF Magnetron Sputtering

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ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

USING AN OFF-AXIS PARABOLIC MIRROR TO INJECT AND COLLECT LIGHT INSIDE AN STM IN UHV

Luiz F. Zagonel

Scanning tunnelling microscopy (STM) is a powerful surface science tool able to map the local density of states with atomic resolution and to locally determine both the density of occupied and unoccupied states. In some materials, the very local tunnel current can act as a local excitation source that may induce light emission. Such luminescence can be due to both elastic processes (for instance, adding minority carriers in a doped direct band gap material) and inelastic processes (such as plasmon excitation by energy transfers). Therefore, an STM can be used to study electronic, morphological and luminesce properties of nanostructured materials.[1] Here, we present a recently developed device that employs a high solid angle off-axis parabolic mirror (72% collection efficiency) to perform optical experiments inside an STM.[2,3] This device is compatible with an adapted UHV Low Temperature STM and can be used to collect the induced Light Emission (STM-LE) when the sample is subjected to tunnel current, also called Scanning Tunnelling Luminescence (STL). The device is also capable of injecting light to perform photoluminescence and Raman Spectroscopy. In a recent application, h-BN monolayer were studied: the band gap was determined, defect states were observed inside the gap, such defects were observed also in images and their light emission was recorded as excited by light (PL) and by electrons (CL).

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ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

UPCONVERSION THIN FILMS BASED ON PHOTONIC STRUCTURES FOR SUNLIGHT CAPTURE

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Conventional photovoltaic materials encounter limitations in converting infrared (IR) radiation into electricity. To circumvent this issue, the use of lanthanide based UpConversion NanoParticles (UCNPs)[1] was proposed due to their ability to capture sub-band gap IR photons and convert them into active visible wavelengths. However, given the low absorption coefficients of these ions, a further concentration of the incoming light has to be considered to enhance the efficiency of the process[2]. The primary goal of this study is to obtain reproducible thin films containing UCNP to integrate them into photonic structures such as metal-insulator-metal (MIM) configurations. β-$NaYF_4$-based UCNPs doped with rare earth ions (Er^{3+}/Yb^{3+}) were synthesized controlling their size and morphology. A comprehensive research into the effects of these parameters is presented for the synthetized UCNPs-polymeric thin films, UCNP@PTF. Thin films were deposited on glass substrates via spin coating, varying the concentration of the polymer solution and the type of solvents. Thickness, homogeneity and emission intensity, of the UCNP@PTF were analyzed in terms of the synthesis conditions and spin coating parameters. The optical response of the UCNP@PTF was studied to obtain 200 nm thick thin films, since this is the optimal thickness according to electromagnetic simulations to enhance the EM field at 980 nm inside MIM structures. We show that the UCNP size is relevant to obtain films with homogeneously distributed luminescent signals at the 10-3 m scale, being the smaller particles (~10 nm) the one more promising for optical applications. Self-assembly of the upconversion nanoparticles was also carried out. By finding the right size and shape, self-assembly of these nanoparticles into a monolayer on gold thin film with a large area was achieved.

Keywords: UPCONVERSION; FILMS; PHOTONIC STRUCTURES; RARE EARTHS

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

MATERIALS SCIENCE-BASED GUIDELINES TO DEVELOP ROBUST HARD COATINGS

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For mechanically dominated load profiles, nitrides are more preferred as the base-material for structural and functional hard coatings, while oxide-based materials provide better protection against high temperature corrosion. Thus, when mechanical and thermal loads are combined, the nitrides used should also provide excellent stability against temperature as well as corrosive attack (such as oxidation). How such nitride materials can be developed to cope with both high mechanical and thermal loads is the focus of this review article. Using transition metal nitride coatings, we discuss important material development guidelines for improved strength, fracture toughness, as well as stability. In particular, the stability (focusing on phase stability with respect to chemistry and temperature, but also against oxidation) of nitrides is an extremely interesting task, since, for example, the face-centered cubic (fcc) structure of TiNz has a relatively wide homogeneity range (TiN even allows the substitution of 66 at% Ti with Al to still crystallize in the fcc structure). In contrast, the preferred fcc structure of other transition metal nitrides (such as MoN_z and TaN_z) is extremely sensitive to small chemical variations, even if only the vacancy concentration changes. Above all, Ta is a particularly versatile alloying element for (Ti,Al)N coatings, which are still the most important protective hard coatings prepared by physical vapor deposition. Tantalum is able to increase not only the strength of (Ti,Al)N, but also its fracture toughness as well as thermal stability and oxidation resistance. Using various superlattice coatings, we further discuss how such nanolamellar microstructures are capable of improving both strength and fracture toughness of hard coating materials. Additionally, we will discuss further concepts to improve the fracture toughness and concentrate on those – especially superlattices, nanocomposites and alloying with Ta, W, and Mo – capable of increasing both, the fracture toughness and hardness. The individual concepts allow materials to be designed to meet the ever-growing demand for coatings tailored with a wide range of excellent properties and outstanding property combinations.

Keywords: PVD coatings; Phase stability; Hardness and toughness; Oxidation resistance; Frictional wear

Acknowledgments: This work was supported by the Austrian Science Fund, the Christian Doppler Laboratory, Plansee and Oerlikon Balzers.

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ORAL PRESENTATION - 2) COATINGS FOR SPECIFIC APPLICATIONS, INCLUDING (BUT NOT LIMITED TO) TRIBOLOGICAL, HIGHSPEED MACHINING, AND CUTTING TOOLS

FABRICATION AND PROPERTIES OF HARD COATINGS FOR HIGH-SPEED MACHINING BY HYBRID PVD METHODS

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To increase the lifetime and performance of cutting tools, there are increasing demands for high performance coatings on tools. Coatings for machining require combinations of properties such as a relatively high hardness, good adhesion, wear and oxidation resistance. To fulfill these requirements, new coating materials and new synthesizing methods are needed to be developed. Due to the excellent mechanical and physical properties, coatings with nanolayered and nanocomposite microstructure are attracting much attention for application on structural applications. Various multi-component nano-layered and nanocomposite coatings were fabricated for obtaining not only superhardness, but also improved oxidation resistance, thermal stability, wear resistance, or low friction coefficient, etc. Among them, some of the coatings were tailored to obtain excellent cutting performance on the high-speed machining tools. In this presentation, some nitride, boride, and oxide hard coatings with nanolayered or nanocomposite microstructure were developed by hybrid PVD coating systems for application on high-speed machining tools. The related coating microstructure, mechanical properties, and cutting performance will be presented. To increase the lifetime and performance of cutting tools, there are increasing demands for high performance coatings on tools. Coatings for machining require combinations of properties such as a relatively high hardness, good adhesion, wear and oxidation resistance. To fulfill these requirements, new coating materials and new synthesizing methods are needed to be developed. Due to the excellent mechanical and physical properties, coatings with nanolayered and nanocomposite microstructure are attracting much attention for application on structural applications. Various multi-component nano-layered and nanocomposite coatings were fabricated for obtaining not only superhardness, but also improved oxidation resistance, thermal stability, wear

resistance, or low friction coefficient, etc. Among them, some of the coatings were tailored to obtain excellent cutting performance on the high-speed machining tools. In this presentation, some nitride, boride, and oxide hard coatings with nanolayered or nanocomposite microstructure were developed by hybrid PVD coating systems for application on high-speed machining tools. The related coating microstructure, mechanical properties, and cutting performance will be presented.

Keywords: Nano coatings; Hybrid PVD techniques; Coating microstructure; Coating properties; Cutting performance.

Acknowledgments: This work was supported by the National Natural Science Foundation of China (Grant No. 52375173) and Guangdong Basic and Applied Basic Research Foundation (Grant No. 2023A1515030198).

ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

TUNING AND MEASUREMENTS OF IONIZATION IN HiPIMS

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Quantification and control of the fraction of ionization of the sputtered species are crucial in magnetron sputtering. This is especially important in high power impulse magnetron sputtering (HiPIMS), since the presence of significant amounts of material ions during film growth has resulted in very smooth and dense films, control over their phase composition and microstructure, as well as enhanced mechanical and electrical properties. In this contribution we show how to extract absolute values of the ionized flux fraction in HiPIMS discharges by using a novel IonMeter, and how the ionized flux fraction varies with with peak discharge current. Using a simple model, we also idenrategtify the physical mechanisms that determine the number of ions reaching the substrate. This analysis identifies ion back-attraction β as a key parameter in the ion balance between the target and the bulk plasma and finally explains why a high ionization probability does not necessarily lead to an equally high ionized flux fraction or ionized density fraction. In the second part we seek to decrease ion back-attraction by exploring the effects of magnetic field strength, pulse length, and working gas pressure on the deposition rate and on the ionized flux fraction when depositing titanium.

Keywords: HiPIMS; Ionmeter; Ionflux fraction

Acknowledgments: This work was supported by Linköping University and Ionautics

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ORAL PRESENTATION - 2) COATINGS FOR SPECIFIC APPLICATIONS, INCLUDING (BUT NOT LIMITED TO) TRIBOLOGICAL, HIGHSPEED MACHINING, AND CUTTING TOOLS

NUMERICAL MODELING OF CONTACT AND RESIDUAL STRESSES OF HARD THIN FILMS

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Modeling is a powerful tool to understand and predict the behavior of thin films and coatings in different applications. Without neglecting the importance of experimental approaches, a series of numerical simulations may, for example, cover a wide range of input parameters at a time (and a cost) usually significantly lower than those of the experimental procedures. Into the wide scope of numerical tools used in the context of thin films and coatings, this work will focus on finite element modeling (FEM) of contact and residual stresses. Mainly, hard thin films produced by Physical Vapor Deposition (PVD) processes will be considered. The use of simulations initially covers indentation problems, to better understand how thin film architectures fail under normal contact loads, and which are the main factors responsible for these failures [1]. The imposition of a lateral displacement to the indenter provides information of system behavior during sliding contacts, such as in scratch tests. Additional topics may be studied with the simulation of scratch tests, such as the effect of growth defects, (e.g. macroparticles) on system behavior [2], and the impact of high contact pressures in the structure of carbon-based films [3]. Residual stresses from thin film deposition play a significant role in the mechanical behavior under contact stresses and this effect may be included in the numerical analyses [1]. The understanding of system failure, under contact and residual stresses may lead to the design of materials, architectures and deposition parameters that provide thin film systems with improved mechanical and tribological behavior.

Keywords: Finite Element Modeling; Thin Films; Indentation; Scratch tests; Residual stresses

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ORAL PRESENTATION - 4) ADVANCED SURFACE SCIENCE AND ENGINEERING, INCLUDING (BUT NOT LIMITED TO) SENSORS, VIRUCIDAL AND BACTERICIDAL MATERIALS, SMART COATINGS, 2D MATERIALS

TUNING DEFECTS AND PORES BY "CHIMIE DOUCE"

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Chimie douce, also known as soft chemistry, offers a land of opportunities for the design of inorganic and hybrid nanomaterials and nanostructures [1]. Functional glasses and ceramics with diverse architectures at the nanoscale can be built at low temperatures in solution imitating the the synthetic pathways employed by living organisms to produce bones or exoesqueletons. Motivated by the need of reducing the contamination present in water, air and soils focus our research on the design of synthetic films and particles based on TiO2 for photocatalysis and removal of cations from e-waste. This presentation summarizes two lines of our group. One concerns the mild synthesis strategies developed for building tunable mesoporous films as an array of nanoreactors for removal of cations present in electronic waste, i.e. Cd(II), Zn(II), Co (III). Our aim is to generate a scaffold for producing optoelectronic devices based on Q-dots with the recovered cations. The second, focused on the synthesis of TiO_2 films with tuned surface defect's density in order to establish the role of defects in the photodegradation of model molecules. The concepts were further applied for the production of self-cleaning tiles [2].

Keywords: sol-gel synthesis; TiO_2 films; mesoporous films; defects in photocatalysis

Acknowledgments: This work was supported by Universidad de Buenos Aires; CONICET; Agencia I+D+I Argentina.

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

DETERMINATION OF INTERNAL STRESS IN CERAMIC COATINGS BY APPLICATION OF THE STONEY FORMULA

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There is an increasing use of coatings to improve the functional performance of materials and components. This can be to protect against damage due to exposure to demanding environments including high stresses and aggressive chemical environments, but can also be to modify many other properties, e.g. thermal conductivity through thermal barrier coatings, friction through low friction coatings, such as diamond like carbon (DLC), and optical reflectivity through coatings with controlled optical properties. Appropriate choice of coatings for particular applications depends on the mechanical and other functional requirements that arise. One factor that can be crucial in determining coating performance and lifetime is the residual stress that is generated by the deposition process and/or by thermal expansion mismatch between the coating and the substrate as the component is cooled from the processing temperature. In this oral report, I will tell the application of a simple experimental technique using the Stoney formula to analyze the coating induced bending of coupons, of known mechanical properties, to determine the residual stress in the coating. Furthermore, according to this principle, our team has developed a film stress tester, which can fast and accurately measure the residual stress of the film. I will briefly describe the principle of this device and some test examples of film stress.

Keywords: Stoney formula; Coating residual stress; Film residual stress; Stress test method; Curvature test

ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

STUDY OF THE RELATIVE HUMIDITY DEPENDENCE ON FILM GROWTH OF SELF-HEALING POLYMERIC SURFACE

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Nanocomposites addressing tailored properties are crucial for technological advancements in organic electronics, soft robotics, sensing, and biosensing. They pave the way for the achievement of multifunctionalities and highly keen features to bring up appealing characteristics that can be easily implemented in many applications, which are often difficult to achieve with isolated matrices. Here, we explore a self-healing polymeric film obtained by the layer-by-layer (LbL) deposition of poly(ethyleneimine) (PEI) and poly(acrylic acid) (PAA) [1]. It is well known the presence of entrapped water in the PEI/PAA structure interferes in the electrical properties of the films [2]. Therefore, it is necessary a detailed study of the electrical characteristics, envisaging a possible use in organic electronics and checking the relationship between the electrical and structural properties with the environmental condition of the growth film. We are studying the growth of (PEI/PAA) films under distinct relative humidity (RH) conditions, with electrical and surface characterizations, and self-healing tests. Impedance tests are performed after each deposited layer during the LbL assembly, carefully controlling the RH in 40%, 67%, 75%, and 96% with saturated salt solutions and (I vs V) test are performed after deposition. The self-healing test is performed after the film deposition with a scalpel and an optic microscope. We have also checked the contact angle in the LbL structures formed. The electrical measurements during film deposition show two different behaviors between the first 15 layers and the last 15 layers, as expected, with the capacitive component of the impedance increasing at higher RH values, followed by a decrease in the resistance component. The IV curves displayed a negative differential resistance (NDR) effect around 1V, which is more pronounced in the LbL films grown at higher RH values, indicating more water molecules trapped in the film structure. The contact angle

was approximately 75° for the 3 lowest humidity values, and 90° for the film grown in the highest RH environmental condition. The self-healing characteristic occurs in all cases. Overall, our findings indicate a stronger NDR effect and distinct surface morphology when the films are grown at higher RH, inducing a new functionality (higher hydrophobicity).

Keywords: Stoney formula; Coating residual stress; Film residual stress; Stress test method; Curvature test

Acknowledgments: UNICAMP, FAPESP, CNPq, Capes, Prof. Bertran from IQ for the contact angle measurements, INEO.

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

REVISITING THE OPTOELECTRONIC CHARACTERIZATION AND BANDGAP NARROWING OF SPUTTERED ALUMINUM-DOPED ZINC OXIDE THIN FILMS

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High electrical conductivity and optical transparency in the visible spectral range make aluminum-doped zinc oxide (AZO) a suitable material for a wide range of optoelectronic applications. Its wide bandgap and large charge carrier density blueshift the optical bandgap by the interplay of the Burstein-Moss shift and renormalization effect. Here, the variation of the optical bandgap as a function of the charge carrier density is systematically investigated to assess the intrinsic bandgap and to estimate the electron and the hole-effective masses. AZO thin films with different aluminum concentrations were grown by radio frequency magnetron sputtering and then annealed at various temperatures in an ultra-high pure argon atmosphere at low pressure. Here we show that the free exciton band remains visible in AZO with low Al concentrations. Thus, we use an Elliot-based dispersion model to accurately determine the optical bandgap, exciton binding energy, and Urbach energy of AZO thin films [1]. We found that while the degenerated character of AZO films blueshifts the optical bandgap, the exciton binding energy is quenched due to the increase of the free electron screening effect. The plasma frequency is retrieved by modeling the free charge carrier absorption and is then

contrasted with charge carrier density values obtained by the Hall effect in the Van der Pauw configuration. An analytical model that describes the nonparabolicity of the conduction band for degenerate semiconductors, is used to determine the zero-density effective electron mass. Finally, the hole-effective mass and intrinsic bandgap of AZO thin films are estimated by modeling the optical bandgap as a function of the charge carrier density in the parabolic and non-parabolic band regimes using random phase and plasmon pole approximations. The strong alignment between the model and the experimental data further validates the effective electron mass data retrieved from the analysis of the free carrier absorption.

Keywords: Effective mass; Excitons; Urbach tail; AZO; Optoelectronic

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ORAL PRESENTATION - 2) COATINGS FOR SPECIFIC APPLICATIONS, INCLUDING (BUT NOT LIMITED TO) TRIBOLOGICAL, HIGHSPEED MACHINING, AND CUTTING TOOLS

ULTRA-THIN FUNCTIONAL COATINGS AND IN SITU MONITORING OF THE GROWTH

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Ultra-thin films are of growing interest by the significant reduction of the material used, the faster deposition process and the significant change of the functional properties of the surface receiving the coating. Physical vapor deposition is still the most popular worldwide and particularly the magnetron technology with all the variety of plasma excitation – direct current (DC), radiofrequency (RF), pulsed, High Power Impulse Magnetron Sputtering (HiPIMS) [1], e-HiPIMS (Electron enhanced – bHiPIMS) [2], etc. After a brief introduction on the magnetron process specificities, two major examples are given to emphasize the importance of ultra-thin films. Drastic change, up to 80%, in the light reflectance of copper have been recorded by covering foils or powders with an amorphous carbon layer (20 to 70 nm thick). A dedicated model describes the light propagation (@ 1 µm wavelength) through this conductive ultra-thin layer. But the experimental observed extinguish of the light can be explained only if one considers the multilayered system, including the interfaces (vacuum/a-C/Cu). The modeling and experimental results are is very good agreement. The direct application is the significant energy reduction when used in copper powder selective laser melting (SLM) or laser welding for industrial processing. Moreover, carbon is intrinsically removed by the laser fusion-induced vapors and other mechanisms when using 25 nm thick films [3]. The in situ monitoring of the plasma growing thin films is still challenging. The most common technique - Reflection High Energy Electron Diffraction (RHEED), which is widely used in Molecular Beam Epitaxy and Pulsed Laser Deposition, is not compatible with magnetron sputtering due to the presence of electromagnetic fields near the substrate. Grazing Incidence Fast Atom Diffraction (GIFAD) [4] has been recently adapted to probe the early stage of ultra-thin film growth. In GIFAD, neutral He atoms with primary energy of 0.2 to 5 keV, are scattered at small angle of incidence (< 1°) from the surface under UHV conditions (below 10^{-6} mbar), to limit degradation of the diffraction signal due to gas phase collisions. We have developed a new high-pressure GIFAD (HP-GIFAD) system that can currently operate at pressures up to ~10^{-2} mbar [5], including a HiPIMS

chamber. This innovation opens new perspectives in monitoring and optimization of the HiPIMS deposition processes.

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ORAL PRESENTATION - 2) COATINGS FOR SPECIFIC APPLICATIONS, INCLUDING (BUT NOT LIMITED TO) TRIBOLOGICAL, HIGHSPEED MACHINING, AND CUTTING TOOLS

REGULATION, AND CUTTING PERFORMANCE OF THE AlCrMoSiN TOOL COATINGS WITH GRADUALLY INCREASING Mo CONCENTRATION

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In the aerospace, national defense, and military industry, the machining efficiency of crucial heated end components is seriously limited because the cutting tool is easy to collapse and wear, and has short service life. However, the superhard tool materials such as ceramics and cubic boron nitride are expensive, have poor toughness and bending strength, and are prone to brittle blade breakage. Applying a high temperature self-lubricating coating on the tool surface is an effective way to solve the above problems. Moreover, the coating must be both hard and tough, and is firmly adhered to the substrate. Lubrication film synthesis induced by elevated tribo-oxidation can improve wear resistance and machining efficiency of coated tools, and reduce interface friction between the tool/chip. A series of AlCrMoSiN coatings with gradual Mo concentration were prepared by high power pulsed magnetron sputtering and pulsed DC magnetron sputtering hybrid technique. By virtue of XRD, SEM, TEM, nanoindentation, scratching, high temperature tribology testing, and vertical machining center, the microstructure and properties of the AlCrMoSiN gradient coatings were characterized and tested. As the gradient rate of Mo concentration on the coating growth direction increased, the hardness and elastic modulus of the coating gradually increased; the critical load, friction coefficient, and wear rate decreased slightly. When the sputtering power of the CrMo target linearly increased from 0.4 kW to 1.2 kW, the hardness and elastic modulus of the resulted AlCrMoSiN gradient coating (Coating C) reached the maximum values of 23.8 GPa and 317.7 GPa, respectively; the critical load was about 57.3 N; the friction coefficient and wear rate were 0.51 and 2.20×10^{-8} $mm3\cdot N^{-1}\cdot mm^{-1}$. Through dry milling hardened mold steel (P20H) test, the service life of AlCrMoSiN gradient coated tool was 24.1 % higher than that of AlCrSiN coated tool. After continuous cutting for 40 minutes, the former cutting temperature is 65.1 ℃ lower than that of the AlCrSiN coated tool.

Keywords: AlCrMoSiN self-lubricating coating; HiPIMS; gradually increasing Mo concentration; tribological behavior; cutting performance

Acknowledgments: This work was supported by the Major Project of Tianjin Multiinvestment Fund (22JCZDJC00670, 22JCYBJC01600).

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ORAL PRESENTATION - 1) DESIGN, PREPARATION, AND CHARACTERIZATION OF THIN AND MULTIFUNCTIONAL, HARD MULTICOMPONENT, HIGH-ENTROPY, AND MULTI-LAYER COATINGS

DLC AND CVD DIAMOND SINGLE CRYSTAL GROWTH DEMANDING A LOT OF HIGH VALUE-ADDED APPLICATIONS

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DLC films and CVD Diamond growth have been in evidence by scientific and technological studies due to their demand in terms of research and a lot of applications. DLC films with its superior properties such as: low coefficient of friction, high chemical inertness, high hardness, high wear resistance, biocompatibility, bactericide, high adhesion on substrates, etc., and CVD Diamond, also with its set of properties that qualifies it for many applications now a days and for near future. So, DLC films and CVD Diamond, obtained by using a modified PECVD (Plasma Enhanced Chemical Vapor Deposition) System and a high power 2.45 GHz MWPECVD (Microwave Plasma Enhanced Chemical Vapor Deposition) plasma discharge, respectively, plays an important role in terms of high P&D&I demand considering features like ease production, low costs and scale up possibilities. In this work, a summary of the last results concerning thin and thick DLC films on substrates of different materials, from metals to polymers at temperature as low as 50 C in a non-collision regime using a modified PECVD pulsed system technique will be presented. This PECVD technique was modified with an Ion Confinement System, providing lower coefficient of friction, lower stress, higher hardness and especially greater adhesion on metallic and nonmetallic substrates. Also, DLC doping with different nano particles, boron and graphene and its final properties will be shown. Concerning CVD Diamond, in this presentation, we will show how to get single crystal by using a high power MWPACVD technique. Pure and doped CVD diamond for many applications, such as jewelry, nuclear batteries, quantum computer devices, etc., will be presented. In addition, optical and nuclear techniques of characterization are used to measure impurities as controlled doping, dislocation, etc., where an AI tools are also used in order to show the best set of parameters of growing when a specific properties are required.

Keywords: DLC Thin and Thick Films; Single Crystal CVD diamond; non collision regime; PECVD pulsed System; High Power 2.45 GHz MWPACVD

ORAL PRESENTATION - 2) COATINGS FOR SPECIFIC APPLICATIONS, INCLUDING (BUT NOT LIMITED TO) TRIBOLOGICAL, HIGHSPEED MACHINING, AND CUTTING TOOLS

UNDERSTANDING COATED TOOL WEAR BEHAVIOR IN SIDE MILLING OF ULTRA-HIGH STRENGTH STEEL UNDER DIFFERENT SUSTAINABLE COOLING STRATEGIES

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Ultra-high strength steel is extensively used in the manufacturing of aircraft components due to its exceptional properties such as high strength, toughness, hardness, and wear resistance. However, these remarkable physical and mechanical characteristics also pose significant challenges for machining ultra-high strength steels. The utilization of coated tools and cooling techniques proves effective in enhancing tool longevity during the processing of difficult-to-cut materials. However, the issue of rapid tool wear hampers machining efficiency and increases production costs. Moreover, the atomization modes of cutting fluid are considered a sustainable and effective method for cooling and lubrication to reduce tool wear. In this study, comparative milling experiments were conducted on ultra-high strength steel using different sustainable cooling strategies, including dry cutting, high pressure air cooling (HPAC), air atomization of cutting fluid (AACF), and ultrasonic atomization of cutting fluid (UACF). The influences of various sustainable cooling conditions on wear behavior of AlTiN coated carbide tools was investigated, focusing on tool life, types of tool wear, and wear mechanisms. Results revealed that the tool life for dry milling, high-pressure air cooling (HPAC), atomized air cooling with coolant fogging (AACF), and ultra-atomized air cooling with coolant fogging (UACF) were 8 min, 3 min, 26 min, and 31 min respectively. HPAC milling exhibited the shortest tool life, suggesting that lubrication ability played a more crucial role than cooling ability in enhancing tool life. Additionally, the reduction of tool wear in UACF could be attributed to the fact that ultrasonic atomization enables the production of small droplet diameters and a uniform distribution, thereby enhancing the droplets' ability to penetrate into the cutting zone. The dominant types of wear observed on the rake face of the tool included abrasion wear, adhesion, and chipping; whereas fracture, adhesion, and coating detachment were primarily observed on the flank face of the tool. The failure mode of AlTiN coated carbide tools was often characterized by severe tool fracture due

to transgranular fracture of WC grains and ductile fracture of Co binder caused by impact cutting forces.

Keywords: Ultra-high strength steel; Coated tool; Cooling strategies; Tool life; Wear type

Acknowledgments: This work was supported by the National Natural Science Foundation of China (Nos. 92160301, and 92060203).

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ORAL PRESENTATION - 2) COATINGS FOR SPECIFIC APPLICATIONS, INCLUDING (BUT NOT LIMITED TO) TRIBOLOGICAL, HIGHSPEED MACHINING, AND CUTTING TOOLS

EFFECT OF Si CONTENT ON MICROSTRUCTURE, MECHANICAL PROPERTIES, AND CUTTING PERFORMANCE OF TiSiN/AlTiN DUAL-LAYER COATING

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$Ti1-_xSi_xN$/AlTiN dual-layer coatings with different Si content were prepared by cathode arc evaporation to study the effect of Si-doping on the coatings. The composition, morphology, and microstructure of the coatings were characterized using SEM, XRD, and XPS. The hardness, elastic modulus, and adhesion strength were measured by nano-indentation and micro-scratch. Results show that coatings all consist of TiN grains and Si3N4 amorphous phases. $Ti1-_xSi_xN$/AlTiN dual-layer coating has the highest hardness of 43.07 GPa at a Si content of 0.19 and the lowest elastic modulus of 314.46 GPa at a Si content of 0.25. High-speed milling of Ti-6Al-4V alloy was performed to evaluate the cutting performance of the coated tools. The value and amplitude of the cutting force were collected to analyze the wear condition of tools. When cutting speed at 120 m/min, the coating with a Si content of 0.19 shows the best cutting performance, having the lowest cutting force and flank wear. The higher silicon content increases the bonding of titanium alloy, influencing the stability during cutting. The lower silicon content reduces the wear resistance of the coating and shorten tool life. Suitable Si content of the coating has been proved effective in improving the cutting performance on Ti-6Al-4V alloy.

Keywords: dual-layer coating; Si content; cutting performance; mechanical properties

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ORAL PRESENTATION - 2) COATINGS FOR SPECIFIC APPLICATIONS, INCLUDING (BUT NOT LIMITED TO) TRIBOLOGICAL, HIGHSPEED MACHINING, AND CUTTING TOOLS

DESIGN AND DEPOSITION OF HARD OXIDE COATINGS WITH IMPROVED HIGH-TEMPERATURE PROPERTIES

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Al_2O_3 coatings have exceptional thermal stability and chemical inertness, making them highly suitable as protective coatings for cutting tools. However, the low-temperature and high-efficiency deposition of dense and wear-resistant Al_2O_3 is still challenging and of great technological significance. This study presents the structure, mechanical, and tribological properties of (Al, Cr)$_2O_3$ coatings deposited by cathode arc evaporation. Compared to conventional AlCrN, the phase structure of (Al, Cr)$_2O_3$ coatings highly depends on the Al content. Also, the substrate bias can noticeably affect the high-temperature wear resistance of oxide coatings. The (Al, Cr)$_2O_3$ coating exhibits superior wear resistance at 600 °C with a wear rate of 2.3×10^{-7} mm^3/N·m due to a high compressive residual stress achieved with an optimum bias potential. Furthermore, a hybrid deposition method combining cathode arc evaporation and high-power impulse magnetron sputtering was employed to deposit Al_2O_3/Cr_2O_3 coatings, showing smooth surfaces with reduced droplet defects. The hybrid oxide coatings exhibit a dominant face-centered cubic structure with a nano-multilayer geometry formed by alternating Al_2O_3 and Cr_2O_3 sublayers. Consequently, the hybrid technique is promising for depositing hard oxide coatings with low surface roughness and high hardness for cutting applications.

Keywords: Oxide coatings, Hybrid physical vapor deposition, Mechanical properties, Wear resistance

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