Session S01: Thin film growth simulation [o01-01]

Prediction of Multisource Sputtering Conditions towards Required Chemical Composition of Thin Films

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Current research effort addressed to development of new materials is partially focused to determination of composition influence onto studied functional properties of the material. In the case of thin films a multisource deposition is one of beneficial techniques for preparation of compositional sample series. Recently, simplified calculation model utilizes basic physicochemical constants of source materials together with reduced number of trial depositions covering basic instrument characteristics (tool-constants) was developed [1].

The above mentioned calculation model is adopted and and experimentally verified for a two-source depositions of optical materials based on the amorphous chalcogenide thin films from Ge-Bi-Se system ($GeSe_2$ – Bi_2Se_3 tie line). The thin films are deposited by radiofrequency (RF) magnetron sputtering from targets with the uttermost compositions of the given tie line. Within the aim of the presented work prepared thin films are characterized namely by means of Energy Dispersive X-Ray Analysis coupled with Scanning Electron Microscope (SEM-EDX) to determine the chemical composition and by Variable Angle Spectroscopic Ellipsometry (VASE) and profilometry to establish film thickness.

Good agreement between results of calculation model and experimentally determined compositions and thicknesses of the co-deposited thin films is achieved for the above-mentioned tie-line. Composition differences of co-sputtered thin films are up to ~ 2 % while thickness differences are up to ~ 10 % compared to required values. Thus the compositional differences are comparable to compositional differences of single source deposited thin films (up to ~ 1 %at for $GeSe_2$ and ~ 4 %at for Bi_2Se_3) within the SEM-EDX technique accuracy.

Acknowledgement

This work was funded with support from the Czech Science Foundation (Project No. 22-05179S), Ministry of Education, Youth and Sports of the Czech Republic (LM2023037 project) and from the CNRS LISOPIC CNRS 80 PRIME (France).

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S01: Thin film growth simulation [o01-02]

Unraveling the nucleation and growth mechanism of {1122} twin in Titanium

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The predictions of mechanical behavior of microelectromechanical (MEMS) materials are essential when it comes to designing and evaluating MEMS devices. Metallic films are often used as an integral part of many MEMS components. The stability of the metallic parts and reliability is a key factor for successful commercialization of MEMS. In order to successfully manufacture MEMS devices, basic physics and operating principles need to be fully understood and appreciated at both a macro and a micro level.

Titanium (Ti) is a promising material for the bulk micromachining of MEMS devices. Titanium metallic layer has been commonly used in the semiconductor industry as an adhesive layer to enhance the bonding strength between metallic film and substrate. Defects in devices and interconnection structure critically depend on the specific process. Twin boundaries are important types of planar crystallographic defects. {1122} Twin is the predominant twinning mode in hcp metals such as Ti, Zr and Mg under <c> axis compression. We analyze the {1122} twin nucleation in Ti by reverse α-ω-α phase transformation. The twin can grow by the migration of the {1122} twin boundary. This migration is mediated by the gliding of line defects with step and dislocation character, i.e. b_I disconnection, along with {1122} twin boundary. Their structure can be interpreted as a pair of disconnections (b and b^*) i.e. dissociated core of b_I disconnection, which contains omega-phase structure inside. These studies reveal the role of ω- phase in the connection with nucleation and growth mechanism of {1122} twin boundary. For the first time b and b^* have been found and analyzed. These results clarify the uncertainties with the growth of the {1122} twins.

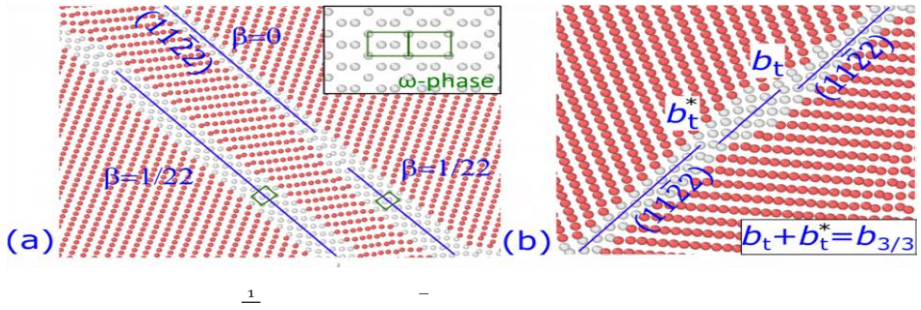

Figure 1. β = 0 and β = segments of {1122} twin boundary. Structure of ω-phase with unit cell marked by green line (Inset). Structure of β = boundary contains half of ω-phase unit cell; (b) Two subsequent b and b^* defects can be interpreted as dissociated b_I disconnection.

Session S01: Thin film growth simulation [o01-03]

Cu-Zr-Al thin film metallic glasses in a wide range of compositions and growth conditions

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Cu-Zr-Al thin film metallic glasses are investigated by a combination of simulations of their atom-byatom growth with magnetron sputtering. We fulfill all requirements which maximize the usefulness of the results: mutual support of calculated and experimental data, simulation algorithm which exactly reproduces what is happening in the experiment, wide compositional range (from pure Cu to pure Zr and from [Al] = 0% to 20%), wide range of growth conditions (energy of arriving atoms, temperature, growth template). We focus on the homogeneity, densification, short-range order (bonding preferences and coordination numbers), medium-range order (common neighbor and network ring statistics) and functional properties. Special attention is paid to the key building blocks of Cu-Zr-Al: not only icosahedral clusters (12 vertices) but also newly identified supraicosahedral clusters (16 vertices). First, we identify crystalline Zr-rich compositions (on any growth template) and Cu-rich compositions (with a strong effect of growth template), and glasses (as homogeneous as what result from a random distribution of atoms) at [Cu] = 20% to 80-85%. Increasing [Cu] in the glassy compositions leads to increasing coordination of both Cu and Zr, packing factor and icosahedron-like medium-range order. Second, increasing [Al] in glassy $Cu_{0.46}Zr_{0.54-x}Al_x$ preserves the homogeneity (at a very low preference to form Al-Al bonds) and once again leads to increasing coordination of all elements, packing factor and concentration of icosahedral clusters (around smaller Cu and Al) and supraicosahedral clusters (around larger Zr). All of that is achievable at low energy delivered into the growing films, while delivering too much energy (by energetic bombardment or by ohmic heating) may be even harmful.

While the atomic-scale simulations provide a lot of information not accessible experimentally, they are correlated with and explain experimental data including increasing hardness, Young's modulus, glass transition temperature and crystallization temperature with increasing [Cu]/[Zr] and [Al]/[Zr]. Collectively, the results [1,2] are important for understanding the structures and properties of this class of metallic glasses, and for optimizing their compositions and pathways for their preparation.

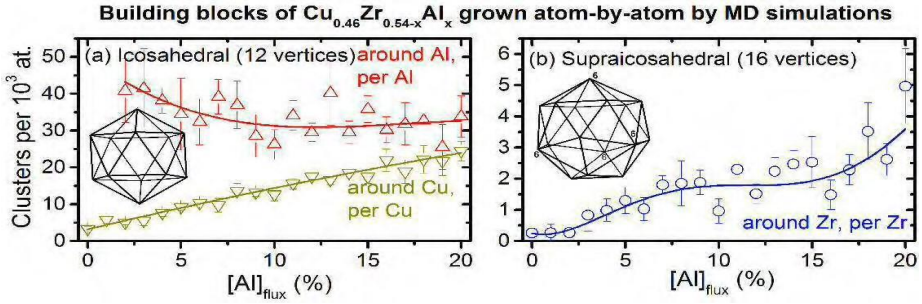

Figure 1. Building blocks of Cu-Zr-Al metallic glasses: icosahedral clusters and supraicosahedral clusters.

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Session S01: Thin Film growth simulation [o01-04]

On-Surface Design of a 2D Co-Organic Network Preserving Large Orbital Magnetic Moment

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One-atom-thick architectures, as thin-film limit, set up challenging scenarios towards the emergence of novel properties. In particular, the design of antiferromagnetic nanomaterials preserving large orbital magnetic moments is important to protect their functionalities against magnetic perturbations[1]. We have recently exploited an archetype H_6HOTP[2] species for conductive metal– organic frameworks to design a Co-HOTP one-atom-thick metal–organic architecture on a Au(111) surface. Our multidisciplinary scanning probe microscopy, X-ray absorption spectroscopy, X-ray linear dichroism, and X-ray magnetic circular dichroism study, combined with density functional theory simulations, reveals the formation of a unique network design based on threefold Co^{+2} coordination with deprotonated ligands, which displays a large orbital magnetic moment with an orbital to effective spin moment ratio of 0.8, an in-plane easy axis of magnetization, and large magnetic anisotropy[3]. Our simulations suggest an antiferromagnetic ground state, which is compatible with the experimental findings. Such a Co-HOTP metal–organic network exemplifies how on-surface chemistry can enable the design of field-robust antiferromagnetic materials.

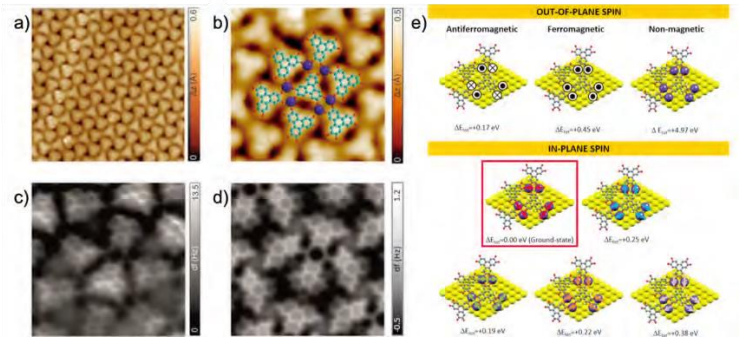

Figure 1. (a) Mid-range STM image, (b) Hi-res STM image (with ball&stick model), (c) nc-AFM (CO-funct. tip), and (d) nc-AFM simulation of the coordinative architecture. (e) Computed spin-configurations.

Acknowledgement
We acknowledge funding from spanish MINECO/MICINN and Comunidad de Madrid (CAM).

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Session S02: Advanced methods for thin film growth [o02-01]

Oxygen plasma treated phenyl silsesquioxane as a scaffold for mesoporous TiO_2 thin film growth.

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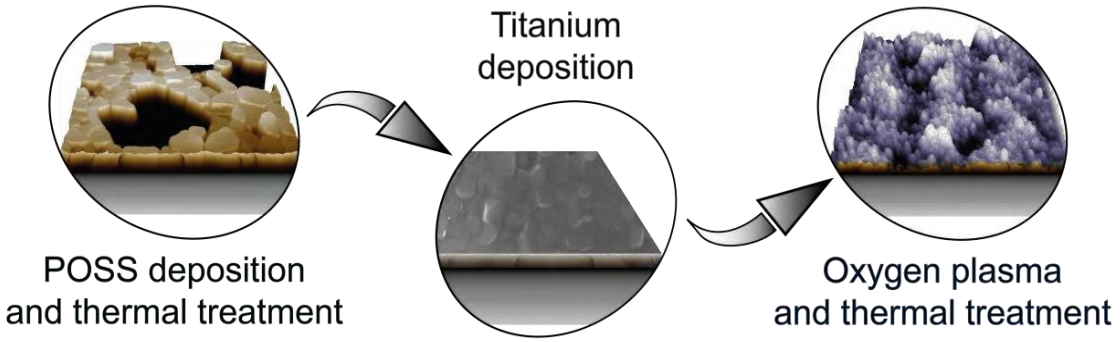
Thin films of titanium oxide polymorphs are of great interest to researchers due to their wide variety of physicochemical properties. These properties change significantly with the structure, from tetragonal anatase and rutile to orthorhombic brookite. As a result, titanium oxide polymorphs are commonly used materials in many branches, as they offer numerous applications. In this study, nanocrystalline TiO_2 thin films were obtained by oxygen plasma-assisted physical vapor deposition on a dodecaphenyl polyhedral oligomeric silsesquioxane (POSS) interphase. Previous research has shown that dodecaphenyl POSS has self-assembling ability, resulting in the formation of a new lamellar structure with alternating silica cages and organic moieties [1], [2]. During the process of plasma treatment, the POSS interface undergoes transformation into structured silica, which forms a scaffold for the mesoporous titania layer. Techniques such as Grazing Incidence X-ray Diffraction, X-Ray Reflectivity, Raman Spectroscopy, Atomic Force Microscopy, and Scanning Electron Microscopy were used to characterize the prepared thin films. Further analysis helped to determine the structure, topography, and chemical composition of the obtained layers. The fabricated multilayers exhibited antireflective properties, which were also investigated.



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Session S02 : Advanced methods for thin film Growth [o02-02]

A novel route for the preparation and characterization of active and integrable EuOOH crystalline thin films

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Oxygen-hydrogen compounds (oxyhydrides and oxyhydroxides) have recently attracted an increasing interest because they are versatile materials whose composition can be varied by changing the relative O and H contents, thus endowing them with high potential for functional design.[1] Recent research has been focused on energy storage, while the study of their optical and electrical properties, which show promise for use in optoelectronics applications, has been scarce so far. This is because integration in solid state devices requires the controlled preparation of thin films and nanostructures. However, the usual synthesis routes have been limited to chemical processes that yield materials in bulk or powder configurations and thus, not suitable for integration in functional optoelectronic components that require layered materials, such as LEDs, displays, counterfeiting coding or biological imaging.

In this work we investigate an innovative approach for the preparation and characterization of Europium oxyhydroxide (EuOOH) thin films suitable for optoelectronic luminescent applications. An originality of the present work is that luminescent Eu^{3+} ions are not a dopant of a dielectric matrix; but they are a constituent part of the oxyhydroxide EuOOH structure, which in fact critically determines the luminescent response. Furthermore, we use an isotopic furnace that allows us to analyze the incorporation of O and OH species in the films, by adequately choosing the appropriate isotope. To prepare EuOOH films we have first produced precursor Eu_2O_{3-x} thin films by Pulsed Laser Deposition in vacuum at room temperature using an ArF excimer laser to ablate a high-purity (99.99%) ceramic Eu_2O_3 target. After deposition, precursor films are annealed at temperatures in the 250-300 °C range in different partial pressures of selected oxygen and hydrogen isotopes (O^{18} or D_2O^{18}). Finally, ion beambased techniques (RBS, NRA and ERDA) are used to investigate the effect of the annealing conditions on the O and H content of the films by distinguishing the incorporation of different isotopes,[2] which results in films with different stoichiometries. In the presentation we will discuss the mechanisms of the OH incorporation, as well as the influence of the different obtained compositions in the red emission ($^5D_0 \rightarrow {}^2F_J$ transition) of the Eu^{3+} ions.[3-4]

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Session S02: Advanced methods for thin film growth [o02-03]

Growth and Characterization of GaSb Based Semiconductor Saturable Absorber Mirror

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Ultrafast lasers are widely used in material processing, 3D mapping with light detection and ranging (LiDAR) and detection of hazardous and environmental gases. Semiconductor saturable absorber mirror (SESAM) is the most important component for passive mode-locked ultrafast lasers. The use of ultrafast lasers in the mid-infrared region, which contains the absorption edge of many atmospheric gases, has attracted considerable attention in many research and industrial applications [1]. Therefore, the growth of SESAM for the development of mid-infrared lasers is of particular importance and still a need.

For this purpose, SESAMs consisting of GaSb/AlAsSb distributed Bragg reflector (DBR) and InGaAsSb/AlGaAsSb mid-infrared quantum wells have been designed and grown on GaSb substrate by molecular beam epitaxy (Figure 1). The structural and optical characterization of the epitaxial layers was investigated as a function of the growth conditions. A reflection of over 99% was achieved through linear reflection measurement of the DBR and the operation of SESAM structures in the 2.7 - 3.1 µm range was successfully demonstrated.

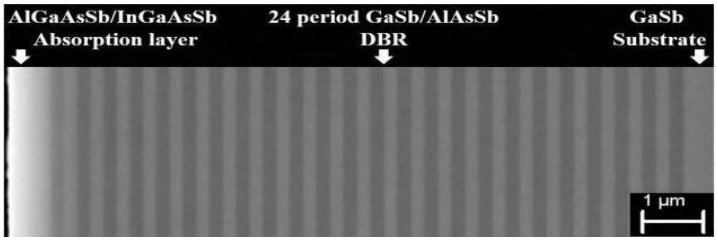

Figure 1. The cross-sectional scanning electron microscopy image of SESAM structure.

Acknowledgement

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Session S02: Advanced methods for thin film growth [o02-04]

Al and Ag porous films prepared by low temperature sputtering

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Black metal thin films with a porous structure have a large surface area and are expected to be applied to gas sensors. In addition to vacuum evaporation, sputtering has also been reported as a method for preparation of black metal thin films[1)]. We have attempted to prepare black Al and Ag thin films by sputtering on the substrate cooled with liquid nitrogen to suppress surface diffusion of atoms. The sputtering power and Ar gas pressure were also changed to obtain the films with porous structure. An RF magnetron sputtering system, in which the substrate can be cooled by liquid nitrogen, was used for the deposition. The films were deposited on glass and Si substrates at room temperature, -80°C, and 170°C with Ar gas pressure of 6.5 - 33.3 Pa and sputtering power of 100 - 150 W at background pressure below 3.3×10^{-5} Pa. The deposited films were characterized by four point probe, SEM, AFM, XRD, XPS, and spectrophotometer.

The Al films obtained at low temperature were black in color. However, metallic luster was observed from the backside of glass substrate. It means that a porous layer was formed after a thin dense layer was formed on the substrate. It was also found that black films formed by deposition at high Ar gas pressures and high RF powers. The light absorption of the films obtained was as high as 80% for the black Al films. The samples had a columnar structure and (100) crystal orientation.

The obtained Ag films were gray and light absorption was about 40%. The density of the film, estimated from the film weight and thickness, was found to be relatively higher than that of black Al films. We expect that more porous and black Ag films might be prepared by further increase in gas pressure or power.

Our results show that black metal films can be obtained by sputtering at low temperatures, high gas pressures and high RF powers.

Acknowledgement

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Session S02: Advanced methods for thin film growth [o02-05]

Enhancement of properties of magnetron sputtered Cu films by Zr addition

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Nano- and microcrystalline Cu-Zr alloys produced using different techniques exhibit high strength and thermal stability [1-4]. Under certain technological conditions, Zr can form supersaturated solutions in the Cu crystal lattice, two-phase structures with intermetallic particles, and can segregate at the grain boundaries. However, the regularities of the equilibrium grain boundary segregation process and the nature of the alloying element distribution in the volume of the base metal have not been studied sufficiently and require further investigation. In this regard, this study aims to prepare binary Cu-Zr thin-film alloys by magnetron sputtering of Cu and Zr from two separate targets and to study the effect of the Zr content on the structure, phase composition, and properties of these films.

A series of films obtained under the same deposition conditions in the range of Zr contents from ~ 1.0 to 4.4 at. % was examined by X-ray diffraction, scanning electron microscopy, atomic force microscopy, and nanoindentation. It was found that the alloying of Cu films with Zr leads to a significant change in the structure and properties of the studied materials. All investigated films are characterized by an fcc lattice with a strong <111> texture perpendicular to the surface, the degree of which depends non-monotonically on the Zr content reaching a maximum at ~ 1.8 at. % Zr. With increasing Zr content, an increase in the lattice parameter of the films, indicating the formation of a supersaturated solid solution, and a decrease in the size of the coherently diffracted domains were also detected. In addition, the formation of an isotropic granular structure and the appearance of an intermetallic phase were observed at the highest Zr content of 4.4 at. %. The observed evolution of the structure leads to an almost twofold increase in hardness compared to a single-component Cu film, which exceeds even the values for analogous two-component Cu-Zr films reported in the literature [1-4].

The achieved properties are explained by grain boundary hardening caused by a decrease in the size of the structural objects and Zr segregation at their boundaries. Solid-solution hardening is also another contribution.

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Session S02: Advanced methods for thin film growth [o02-06]

Deposition of multi-composite nanoparticle-based thin films for gas sensing

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Working principle of conductometric gas sensors is based on a modulation in electrical conductivity of the sensing material due to adsorption-desorption reactions between the target gas and the sensor surface. Nano-structuring the sensing material increases the effective surface area for interaction between the target gas and the sensing material thereby enhancing the sensorial response. Metal oxide semiconductors (MOS) have shown remarkable sensing performance to oxidizing and reducing gases. Combination of different MOS has often shown to synergistically improve the gas sensing performance via formation of highly sensitive heterojunctions at their interface.

In this work, we deposited thin films composed of nanoparticles (NPs) of p-type CuO_x and n-type WO_x to enhance the effective surface area of the material and to realize the maximum number of nano pn heterojunctions in the material. The films were prepared using the Nanogen-Trio NP source equipped with three 1'' magnetrons, mounted on a custom-built deposition chamber and sputtered by a DC power supply. Depositions were executed in Ar+O_2 gas mixture. As one can see in Fig. 1, the O_2 admixture may significantly enhance the mass flux of NPs, Γ_m. Furthemore, the O_2 admixture allows one to tune the desired stoichiometry of the respective metal oxides. On the other hand, the pronounced hysteresis complicates the deposition of WO_x NPs. The deposition process was controlled using a complex in-house developed software to prepare thin films composing a mixture of NPs with a defined volumetric ratio of the individual materials.

This work demonstrates the versatility of our custom-built gas aggregation source that facilitates the preparation of multi-composite NP-based thin film giving the best sensorial response.

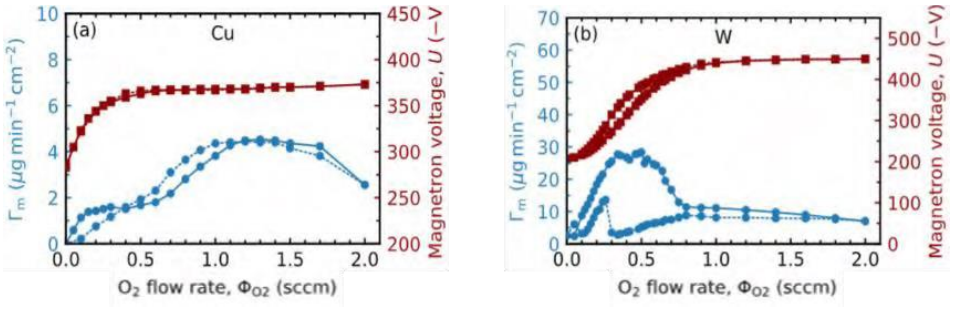

Figure 1. Mass flux of nanoparticles, Γ_m, and magnetron voltage, U, as a function of increasing (solid line) and decreasing (dotted line) flow rate of oxygen, Φ_{O2}, for Cu (a) and W (b) targets.

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Session s02: Advanced methods for thin film growth [o02-07]

The Effect of Ionic Liquids on the Nucleation and Growth of Organic Semiconductor Films

José C. S. Costa[1], Artur F. M. Farinha[1], Ricardo M. Campos[1], Ângela C. M. Castro[1], Gonçalo N. P. Oliveira[2], João P. Araújo[2], Luís M. N. B. F. Santos[1]

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The interfacial behavior of ionic liquids (ILs) significantly impacts a wide range of scientific fields and technologies, particularly under vacuum conditions where these materials exhibit unique characteristics [1-4]. We investigated the use of microdroplets and thin films of imidazolium-based ILs with varying sizes and shapes [1,2] as confining agents to form high-quality thin films of organic semiconductors (OSCs) such as perylene and pentacene through physical vapor deposition (PVD) [3,4]. The role of ILs in controlling the nucleation and crystal growth of OSCs was investigated via sequential and simultaneous depositions of both materials (ILs and OSCs) on an indium tin oxide (ITO) substrate. The deposition of ILs onto the surface of the organic film resulted in the formation of a complete 2D wetting layer, which was followed by island growth. Longer-chain ILs showed higher adhesion and affinity. When the deposition order was inverted, organic microcrystals were grown through ionic liquid droplets, with the nucleation and growth of OSCs enhancing the coalescence mechanisms of the droplets, especially for longer-chain ILs (Figure 1). The wetting process was especially evident for longer-chain ILs. Deposition of OSCs onto ITO surfaces fully covered with coalesced ionic liquid films produced organic films with higher homogeneity due to decreased surface mobility. Co-deposition of OSCs and ILs demonstrated the potential of ILs as crystallization solvents for forming thin organic films with improved crystalline quality without compromising optoelectronic properties [3].

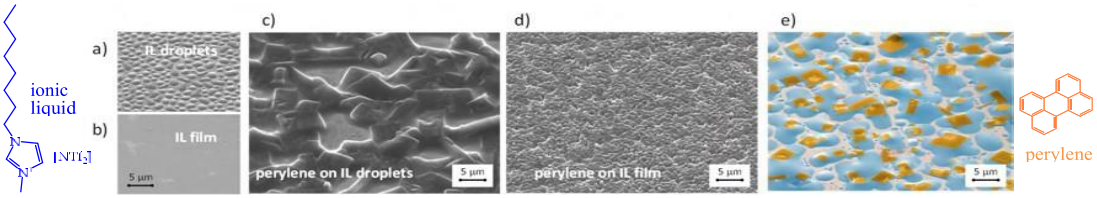

Figure 1. Typical morphology (SEM images) of the ITO surface coated with a nanoscale ionic liquid as micro- and nanodroplets (a) and as a coalesced thin film (b). Morphology of a perylene film deposited onto droplets (c) and a coalesced ionic liquid film (d). Colorized SEM image (e) showing the growth of perylene microcrystals via the ILs droplets (front cover of CrystEngComm, Volume 25, Number 6, 14 February 2023).

Acknowledgment

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Session S02: Advanced Methods for Thin-Film Growth [o02-09]

Controlling the electronic, optical, mechanical, and chemical properties of thin-film alloys via structural disorder

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Crystalline order is typically considered a prerequisite for an ideal material. Disorder is thus commonly perceived as detrimental, even though it is a key advantage in important classes of materials. Structural disorder in amorphous alloys, for example, benefits various macroscopic properties, such as hardness or corrosion resistance, leading to excellent performance as coatings, catalysts, or in advanced electronics [1]. So rather than distracting and detracting from perfection, structural disorder can serve as an ideal design parameter for new corrosion-resistant, hard, and selectively reactive alloys. Typically, crystallinity and amorphicity in alloys are connected to specific stoichiometries, making the effects of structure and composition difficult to disentangle. In the present work, we make use of pulsed laser deposition (PLD) to prepare crystalline and amorphous alloy layers of identical composition by growing thin films under two very different types of conditions, close to and far from equilibrium. We study the structural, mechanical, and electronic properties as well as the surface chemistry of polycrystalline and amorphous films for two selected alloys: CuZr and HfMoNbTiZr. CuZr is a model system for metallic glasses with composition-dependent glass-forming ability [2], whereas the high-entropy alloy (HEA) HfMoNbTiZr has exclusively been observed in its crystalline form [3]. In contrast to literature results, HfMoNbTiZr films grown with PLD at room temperature show no sign of crystallinity in grazing-incidence X-ray diffraction (GI-XRD) and transmission electron microscopy (TEM). Even an increase of the deposition temperature to 700°C is insufficient to induce crystallization, which is observed at 900°C. The liquid-like diffraction features of the amorphous films shift to higher diffraction angles and decrease in width with increasing deposition temperature. This suggests that the packing density in amorphous HEA thin films is tuneable, which could be of interest for their applications as energy storage medium [4]. Nanoindentation studies comparing films of different levels of disorder reveal a clear increase in the hardness of the layers of amorphous nature.

For the binary alloy CuZr, on the other hand, smaller variations in temperature are sufficient to induce crystallization. Room-temperature PLD leads to amorphous layers according to GI-XRD, while films of the same composition are polycrystalline when deposited at 500°C. The first striking effect of disorder is that amorphous CuZr films are partially transparent to visible light, while the crystalline layers are dark and reflective. X-ray photoelectron spectroscopy (XPS) results comparing as-grown and airexposed CuZr films show a remarkable difference in the surface oxidation of the Cu species. Cu is fully metallic for the amorphous film whereas oxide and hydroxide species are observed for crystalline CuZr. Our results demonstrate that the level of structural disorder in thin alloy films can be tuned from polycrystalline to fully amorphous using PLD. This structural disorder significantly influences the surface reactivity and oxidation resistance of the model compound CuZr.

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Session S02: Advanced methods for thin film growth [o02-10]

Structural and Optical Properties of Quaternary Alloy Grown by Molecular Beam Epitaxy

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The antimony-based family has received much attention due to its potential applications in various fields such as infrared sensing, atmospheric pollutant monitoring, and medical identification. Among this family, indium gallium arsenic antimony/aluminum gallium arsenic antimony (InGaAsSb/AlGaAsSb) quantum well (QW) /quantum barrier (QB) structures with having narrow-band gap quaternary compounds are suitable materials for devices operating in the mid-infrared region. In particular, InGaAsSb/AlGaAsSb QW/QB, which operate in the 2-3 µm wavelength range depending on different concentrations are suitable for mid-infrared lasers, laser diodes, photodetectors, and thermophotovoltaic devices [1,2]. In this study, ten periods of InGaAsSb/AlGaAsSb QW/QB structures were grown on Te doped (100) GaSb substrates at different concentrations by molecular beam epitaxy. The effect of As concentration and V/III ratio on the surface defects including crystal quality was investigated. For this purpose, QW/QB layers with different concentrations were grown with or without 1 µm AlAsSb buffer layer grown on GaSb and the comparisons of these samples were made. The crystal quality of the QW/QB layers was analyzed by high-resolution X-ray diffraction (HRXRD) and the surfaces of the samples were analyzed by optical microscopy. In addition, the thicknesses of the layers were determined by cross-sectional scanning electron microscopy and X-ray reflection. As a result, it was observed that the HRXRD FWHM values of the diffraction fringes and the lattice mismatch decreased when the In and As concentrations in the QW were increased indicating an improvement in the crystal quality. It was also observed that surface defects in samples with As concentrations of 14% and above are comparatively less than those in samples with As concentrations of 4%.

Acknowledgment

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Session S02: Advanced methods for thin film growth [o02-11]

Laser processes to generate nitride layers on Nb surfaces

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Niobium nitrides are compounds that exhibit good mechanical properties, in particular, high hardness and toughness and can be considered for use in oxidation protective films. They also exhibit high electrical properties. In a particular stoichiometry, this compound can exhibit a significantly higher superconductor transition temperature than that observed in pure Nb (about 16 K and 9K, respectively).

Standard techniques used to fabricate thin or thick films have been used to obtain niobium nitride layers: chemical vapor deposition, dc and rf sputtering, ion beam assisted deposition, pulsed laser deposition, cathodic arc deposition, magnetron sputtering, vacuum arc deposition or reactive diffusion in N_2 atmosphere. An interesting alternative, explored in this work, entails laser irradiation of a Nb surface in a nitrogen atmosphere.

This work thus explores the use of ns pulsed lasers to generate niobium nitride layers on the surface of a Nb sheet target. Irradiation treatments were performed at room temperature in a nitrogen atmosphere using different laser scanning configurations. In particular, laser line scanning is a relatively novel, scalable configuration where a laser line scans the sample along its perpendicular direction. This configuration can be applied to continuous processing of materials in bulk and/or film configuration. Processing parameters studied include pulse duration and repetition frequency, laser beam scanning rate, sample speed and number of laser line scan process cycles. These laser parameters have been selected in order to achieve ideal zone melting conditions, as well as to avoid surface ablation phenomena that could eliminate the nitride layer generated in previous steps. The appearance of different niobium nitrides has been identified by X-ray diffraction, microhardness and scanning electron microscopy. Evolution of the nitride layer thickness was measured in polished sample cross sections. Results show a continuous diffusion of nitrogen into the Nb surface, showing the following sequence of nitrides upon increasing the number of processing laser steps intensity: Nb_2N, Nb_4N_3 and NbN. Superconducting properties of selected laser treated samples have also been analyzed.

Acknowledgement

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Session S03: Advanced thin film analytical techniques [o03-01]

InCAEM: In-situ correlative facility for advanced energy materials

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In-CAEM will develop a singular infrastructure open to all the scientific community for research in advanced energy materials in order to address the scientific challenges of the European Green Deal. The project started in October 2022 and will have the infrastructure ready by mid 2025. It includes new equipment, infrastructure and staff.
New instruments to be installed in the ALBA premises are a high resolution (scanning) transmission electron microscope for in situ studies in gas and liquid environments and a scanning probe microscopies platform including tip-enhanced Raman spectroscopy capabilities and flexible sample environments. Advanced data infrastructures will be installed both at ALBA and at PIC-IFAE for in situ and ex situ data processing, respectively. In addition, we will carry out the adaptation of existing beamlines to perform correlative experiments, and develop methods and pipelines for multi-modal approaches.

Compatible operando sample environments for complementary characterization tools together with advanced data analysis will provide excellent opportunities for true multi-modal and multi-length scale characterization of functional materials aimed at developing new sustainable materials to be used in batteries, electric vehicles or solar cells, among others. While (S)TEM and scanning probe microscopies offer unsurpassed spatial resolution and a variety of contrast mechanisms, X-ray-based techniques provide highly specific chemical, structural, electronic and magnetic information with high efficiency so that larger fields of view, thicker samples and faster processes can be studied.

The possibility to perform experiments in situ, for example during relevant processes such as reactions, sample growth, thermal treatment or electrochemical cycles, and the correlation of results from different instruments with identical experimental conditions will permit linking the structural, compositional and morphological aspects of the same (nano)structures and of their surroundings for a comprehensive understanding of their structure-function relationship.

We will present the project and the opportunities it will bring for the user community with the help of selected application examples.

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Session S03: Advanced thin film analytical techniques [o03-02]

Probing buried interfaces of SiO_xN_y thin films via ultrafast acoustics: the optimization of transducing layer thickness

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Interfaces are crucial components in many applications, including high-quality optical coating. Controlling the thin film interface is essential with respect to its optical properties and resistance of the coating against high-power laser beams. One of the well-known methods to probe buried interfaces is ultrafast acoustics. It is a pump-probe experiment, where an excitation pulse is absorbed in a thin layer, which serves as an optoacoustic transducer. The excitation pulse, therefore, generates an acoustic wave propagating through the stack of thin films. A delayed probe pulse is able to sense the changes induced by the strain wave localized on the nanometer scale.

We present a thorough study of silicon oxynitride thin films deposited via ion beam sputtering. We deposited thin films with a controlled stoichiometry to cover the entire range from Si_3N_4 up to SiO_2. [1] We used ultrafast acoustics to study the properties of layers and their interface with the Si substrate – see Figure 1A. We observed the variation in acoustic wave propagation and the interlayer formation depending on the layer stoichiometry.

In addition, we studied the effect of varying the optoacoustic transducing Ti layer thickness. The change in the layer thickness led to a significant variation in the features connected to the layersubstrate interface and echo – see Figure 1B. We used a set of Ti layer thicknesses to simulate the optical response, and we demonstrate that the Ti layer thickness of 5-10 nm is the ideal choice to probe the properties of the layer-Si interface. The simulations were carried out for the cases with and without an interlayer providing a distinct signal.

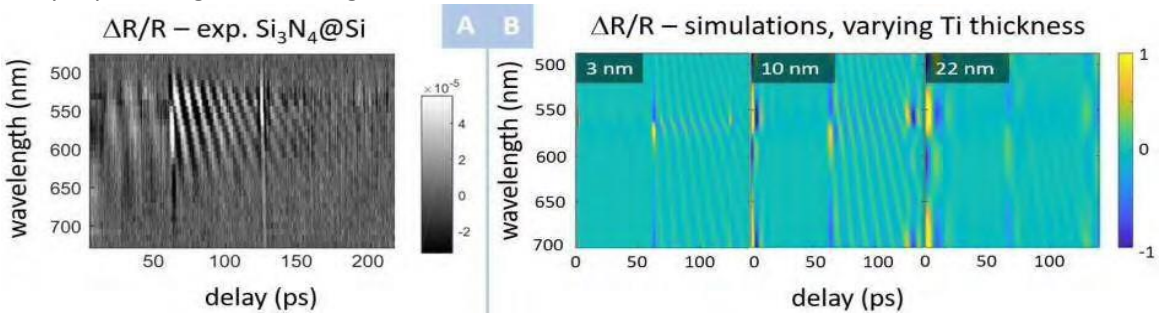

Figure 1. A) Transient reflectivity signal of Ti (10 nm) + Si_3N_4 (620 nm) layers on Si substrate showing Brillouin oscillations from a propagating acoustic wave (1028 nm pump, broadband probe); B) Simulation of the same experiment for a varying Ti layer thickness.

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Session S03: Advanced thin film analytical techniques [o03-03]

In situ depth-resolved compositional, structural and optical characterization of functional thin films at high temperatures

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In addition to classical studies comparing composition, structure and functional properties of thin films before and after high-temperature treatments, new approaches towards the correlation of optical properties, composition and structural changes upon annealing are necessary by using in situ techniques. In situ measurements allow the investigation of the materials in real-time under conditions simulating the intended applications, e.g. high temperatures and defined atmospheres. Intra- and interlayer phase transitions, defect generation and annealing, degradation processes, such as element redistribution and interface mixing, as well as material exchange with the environment can have substantial effects on the material's structure, properties and functionality. All these processes can be studied employing in situ techniques.

In this work, various applications of a cluster tool for depth-resolved compositional, structural and optical characterization of layered materials with thicknesses ranging from sub-nm to 1 µm and for temperatures of -100 to 800 °C are described. [1] The techniques implemented in this setup include Rutherford backscattering spectrometry (RBS), Elastic Recoil Detection (ERD), Raman spectroscopy, Spectroscopic Ellipsometry (SE) and UV-Vis-NIR spectrometry. These in situ techniques allow to identify and to quantify element redistributions, material losses and gains, and the conservation or changes of the optical material properties. Intermixing of the sharp interlayers could also appear at temperatures of up to 800 °C. The onset-temperature of those effects, corresponding to the stability limit, are identified by the in situ measurements. Results of different material systems and processes will be presented including: i) metal-induced crystallization of amorphous carbon in a layer stack of SiO_2/ a-C/ Ni [2]; ii) high-temperature stability tests of a SnO_2:Ta transparent conductive oxide coating [3] and of a WAlSiN-based solar-selective coating [4] as well as iii) diffusion monitoring of an solidlubricant Ag-rich layer sandwiched between two layers of either TiN or TiSiN.

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Session S03: Advanced thin film analytical techniques [o03-04]

Spectroscopic Ellipsometry for the characterization of electrical percolation in thin metallic films

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Spectroscopic ellipsometry is a phase sensitive non-destructive optical measurement technique using polarized light in a broad spectral range from the DUV to the MIR. It is used for the determination of the optical or dielectric constants of materials as well as the thickness of at least semi-transparent single films or multilayer stacks. Spectroscopic ellipsometry is an indirect measurement technique. The measurands are the ellipsometric angles □ (amplitude information) and □ (phase information). An optical model and a fitting procedure are applied for the determination of the parameters of interest, the optical or dielectric constants and film thickness. The accuracy is approximately 0.001 for the optical or dielectric constants and approximately 0.1 nm for the film thickness within a wide thickness range from 0.1 nm to 10 µm.

We are investigating the electrical percolation effects in the growth of thin metallic films of NiCr [1], Au, and Pt by multiple angle spectroscopic ellipsometry. The metallic films were grown in different film thickness from 1 nm to 60 nm on a glass substrate. Thin metallic films form isolated islands, showing low electrical conductivity, and the optical constants resemble dielectric optical behavior. With increasing film thickness the islands are coalescing (electrical percolation) and a free electron gas can form. It causes higher electrical conductivity, and the film shows the optical or dielectric behavior of a metal. The Drude model is used for modeling metallic films. It describes the carrier concentration and mobility allowing to identify the thickness of electrical percolation. Figure 1 shows the carrier concentration vs. film thickness. The points follow curves with different slopes. The intersection of these curves indicates the thickness of electrical percolation.

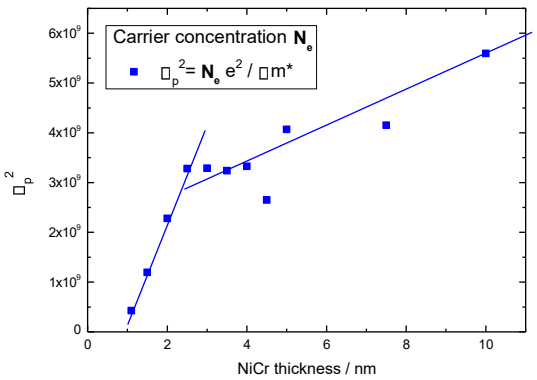

Figure 1. Carrier concentration in NiCr for film thickness from 1 nm to 10 nm. The curve shows two different slopes indicating the film thickness of electrical percolation at their intersection.

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Session S03: Advanced thin film analytical techniques [o03-05]

XPS, APXPS, and HAXPES to Characterize Nano-Structured Materials

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Photoelectron spectroscopy is commonly applied to characterize the composition and morphology of nanostructured materials. A widely used method involves analysis of the inelastically scattered electrons that are always seen on the low kinetic energy side of XPS peaks [1]. In the talk we report on recent advancements of this method. For example, it was recently found that an optimized cross section, that is determined as part of the fitting procedure without any knowledge of the sample composition, can improve the analysis considerably, in particular for cases with stacks of layered materials that have widely different cross sections [2]. We also discuss the application to characterize core-shell nanoparticles (CSNPs) and show that both the shell thickness and its heterogeneity can be accurately determined, and it also correctly proves if the shell material fully encapsulates the core or if part of the core is uncoated [3]. Further, it was recently found that the method can be applied to correct ambient pressure XPS very accurately for the spectral distortion caused by the gas [4]. The method is non-destructive, and the probing depth is considerably larger than the usually quoted 3 IMFP because the inelastically scattered electrons originate from larger depths than the electrons in the peak and it is typically ~8 IMFP but can be ~20 IMFP in cases where the background can be followed over several hundred eV. The latter is often the case with HAXPES where the separation between deep lying peaks can be much larger compared to conventional XPS. With HAXPES, the photo electron energy and thereby the IMFP and the probing depth is also increased and several examples with analysis of structures at > 100 nm depth have been reported [5].
Detailed tutorial videos of several of the examples discussed in the talk are available in [6].

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Session S03: Advanced thin film analytical techniques [o03-06]

A tool for analyzing the electrical properties of composite thin films

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Composite metal/dielectric films consisting of metal inclusions embedded into an oxide or polymer matrix are widely used as attractive materials for research and application. They can have interesting optical, mechanical, and electrical properties. Technologies used for their preparation strongly influence their resulting properties. Especially, the electrical properties are influenced by structural and morphological properties of the composite materials. Therefore, understanding the correlations between morphological and electrical properties is very important for a proper evaluation of the electrical behavior of composite or nanocomposite materials [1]. The paper deals with two-phase composite/nanocomposite films formed typically by conductive particles embedded into a dielectric matrix. Computer experiments which aim is morphological and electrical analysis of both homogeneous and graded composite/nanocomposite films are described. The morphological analysis is the first step and serves to the subsequent analysis of the electrical properties. Efficient methods of mathematical morphology are chosen to describe the morphology of the three-dimensional composite/nanocomposite films. An advanced method of fuzzy clusters has been invented [2] to analyze the electrical properties of the films.

Results of the computer simulations show that at least a partial reconstruction of the threedimensional information from one two-dimensional image is possible using the proper morphological analysis. The morphological analysis can help to derive a right type of the structure. The scalar measure introduced here, gives the possibility to precisely evaluate the disorder degree of the composite structures. The method developed is section-independent. The most interesting conductivity features can be observed near a percolation threshold where the mechanism of the charge transport is changing and the electrical conductivity varies through a large scale. The transport properties are well described and visualized by the fuzzy clusters. The dependence of the conductivity of the composite films below the percolation threshold on their morphological characteristics is discussed in the paper. The electrical and morphological properties of graded nanostructures are shown, too.

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Session S04: Wetting control through thin film and surface functionalization [o04-01]

Omniphobic hierarchical stainless steel surfaces by vacuum and plasma techniques for protective applications

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Most widespread applications of stainless steel (SS) alloys rely lie on their remarkable corrosion resistance when used in a compact configuration. This functionality is preserved upon interaction with the environment and/or a large variety of fluids/external agents, even under chemically aggressive conditions. In order to spam the range of industrial applications of this family of materials, it would be desirable to combine anti-corrosion with other properties (i.e., to achieve multifunctionality). A clear asset in this regard would be the tailored control of the wettability, anti-bacterial and anti-icing response of SS against different liquids under a wide range of environmental conditions. However, the surface of SS materials in massive form present a partially hydrophilic state that is not compatible with antibacterial, waterproof or anti-fouling and anti-icing applications. Key features that can be modified to control the wetting behavior of SS surfaces are the surface topography by combining roughness at different scales and / or their chemical functionalization with hydrophobic groups. [1] This work presents different strategies of nanostructuration of SS surfaces by means of the employment of laser, vacuum and plasma-assisted processes which favors the generation of hydrophobicity without detriment to anti-corrosion capacity. It is shown for example that control of the nanostructure of porous SS films provides a notable antibacterial activity.[2] Moreover, it is also shown that the wetting control through hierarchical SS surfaces combined with fluorinated surface terminations lead to a outstanding protective behavior that, without impairing the anti-corrosive properties, enhances hydrophobicity and provides omniphobicity and an anti-icing response. This is clearly demonstrated upon exposure of these SS surfaces to a variety of liquids (oils, organic fluid simulants, etc,) upon dripping, immersion or under different icing tests at low temperatures.

Figure 1. Hydrophobic SS nanostructured surface.

Acknowledgement

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Session S05: Thin films and surfaces in biological applications [o05-01]

Laser induced periodic asymmetric patterning of TiN thin films for the design of bioelectro-functional surfaces

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Titanium Nitride (TiN) is a reputed electroconductive and stable material with remarkable biocompatibility. It has been intensively explored in microelectronics, as a hard anticorrosive material and as a thin biomaterial film to protect Ti alloys [1]. The objective of our work is to propose new structuring processes allowing to create asymmetric periodic patterns on TiN. These surface structures are at the origin of cell stimulation devices that can combine topographic and electrical stimulation effects.

The TiN thin films were grown on SiO_2/Si structures by reactive magnetron sputtering from high purity Ti targets and Ar to N_2 mixed flows of 9/1. The surface structuring of the TiN thin films was carried out by Laser Induced Periodic Structuring [2]. Irradiation conditions were initially optimized by producing simple linear structures. Selecting ideal conditions, a TiN sample scanning program was designed to obtain the periodic asymmetric patterns. The main effect of the irradiation process was a surface roughening and pinning of the film, which results in a surface tension/wetting contrast. We visualized the passive effect of the patterns on HELA cells cultured for 24h. A fluorescence microscopy and morphometric study allowed confirming that the irradiated areas are biocompatible and antifouling, allowing to concentrate cells on non-irradiated areas (figure 1). Asymmetric motives were observed to be efficient in providing cell niches for cell concentration at irradiated/non-irradiated neighboring areas. Further experiments are in progress to initiate complementary electrostimulation studies.

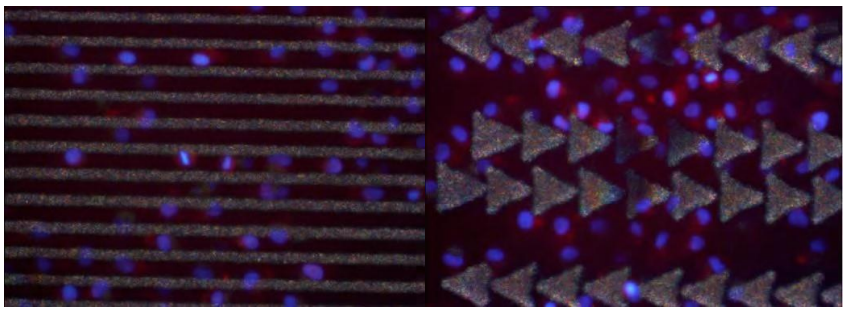

Figure 1. Fluorescence microscopy images of HELA cells on laser induced asymmetric arrow heads on TiN thin films (image base is 1 mm).

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Session S05: Thin films and surfaces in biological applications [o05-02]

New promising self-nanostructured thin films surfaces for antibacterial applications

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Competitive self-separation of crystalline and amorphous phases during thin film growth has been reported for Zr-based binary alloys[1,2]. This allows controlling the surface topography and thus the surface related properties. This study focuses on the possibility to use these surfaces in antibacterial applications, both from a bactericidal and an antiadhesion standpoints. To do so, Zr-V thin films were synthesized by magnetron co-sputtering of Zr and V targets, and these films have then been coated with a thin Cu layer to give them bactericidal properties. The cross-section of such thin films is shown in **Figure 1 (a)**. As shown, these films contain both phases: a columnar amorphous phase and a conical dome-shaped crystalline phase. It is shown that these thin films exhibit promising bactericidal properties against E. Coli (see **Figure 1 (b)**), as well as a reduced bacterial adhesion, preventing biofilm formation.

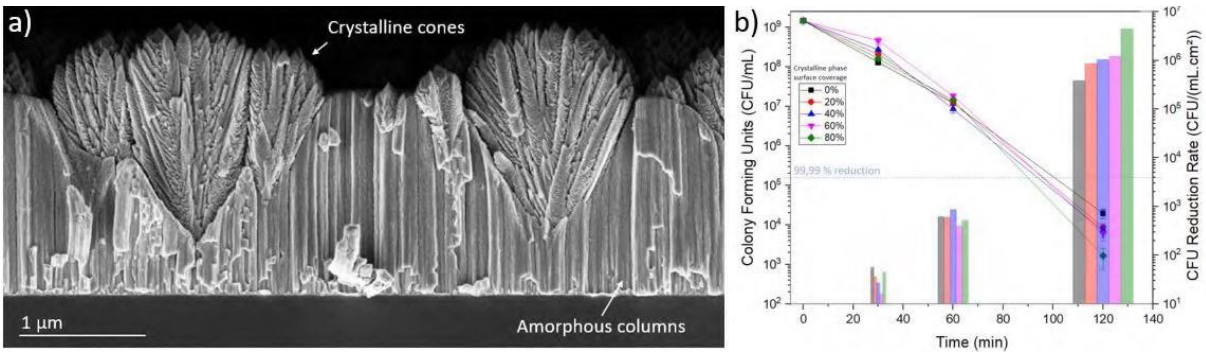

Figure 1. Cross-section SEM micrograph showing a Zr-V thin film with amorphous columns and crystalline cones (a), results of a bacterial viability test on the surface on the thin films (b).

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Session S05: Thin Films and Surfaces in Biological Applications [o05-03]

Ultrathin TiO2 ALD coatings strongly enhance biological response of biomedical materials

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TiO_2 surfaces are in general recognized as excellent biocompatible materials owing to their low cytotoxicity, high stability, antibacterial properties, and wetting ability. Among various TiO_2 nanostructured surfaces that show very good cell interactions (various cell types) and osseointegration, anodized TiO_2 nanotube (TNT) layers have emerged as extremely suitable substrates. A pioneering work demonstrated that TNTs with diameter of 15 nm are the most suitable for the growth of various cells [1]. But numerous papers also showed that anodization is a very viable tool for nanostructuring of various biomedical alloys, including frequently used TiAlV.

Recently, we demonstrated that an ultrathin coating on TNT by suitable oxides (e.g. TiO_2) using Atomic Layer Deposition (ALD) can enhance cell growth and adhesion [2]. These properties make them excellent as final surfaces for medical and dental implants based on Ti alloys.

The presentation deals with the comparison of the influence of ultrathin ALD TiO_2 coatings (achieved by few cycles of TiO_2 ALD process) on TNT layers, reference Ti foils and Ti biomedical alloys for the proliferation of fibroblast, osteoblast and neuroblasts cells. For that Ti sheets and anodized TNT layers with a distinct inner diameter of 12 nm, 15 nm, and 100 nm were used as substrates, as they appear to be the most suitable for cell growth in general [2,3,4]. We investigated the shaping, adhesion, proliferation, and cell density on these substrates.

Moreover, the single-cell adhesion of the cells to the TNTs was studied by the Bio-atomic force microscopy (bio-AMF) technique [3]. Last, but not least, black form of TiO_2 nanotubes was investigated for cell proliferation in comparison to classical TNTs [4].

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Session S06: Thin films in energy harvesting and storage [o06-01]

Environmental stability of perovskite solar cells with water-repellent fluorinated thin films coatings by plasma assisted technology

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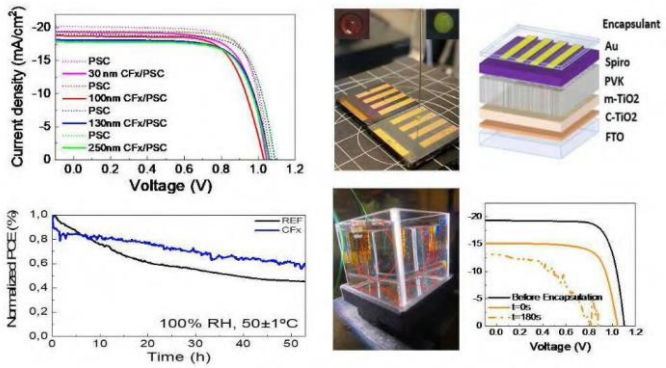
Stability and reproducibility of perovskite solar cells (PSC) technology is compromised due to their high sensitivity to temperature, moisture and/or oxygen species coming from real application environments.[1] The main degradation mechanism has a chemical nature consisting of the interaction between organic cations present in organometal-halide perovskites with water molecules. To solve it, strong efforts are being contemplated to preserve the performance and stability of the PSCs with different encapsulation strategies, most of them based on polymeric-like coatings.[2][3] Here, we present a promising coating alternative by surface functionalization with hydrophobic, water-repellent agents through the employment of vacuum and plasma assisted techniques. Thin fluorinated carbon layers with variable stoichiometry (CFx) deposited by radiofrequency Plasma Enhanced Chemical Vapor Deposition (PECVD) at room temperature [4] have been explored for the development of waterproof and protecting surfaces compatible with the PSCs performance. [5] A complete physicochemical characterization of the fluorinated surfaces has been carried out by X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) whereas optical properties have been followed by Variable Angle Ellipsometry and UV-Vis Spectrophotometry. Special attention has been paid to the wetting behavior of the fluorinated surfaces incorporated onto the PSCs. Fluorinated surfaces are characterized by a compact pinhole-free microstructure characterized by a very high transmittance (above 90%) and high hydrophobicity (Water Contact Angle, WCA>110º). The photovoltaic performance is preserved after the fluorinated surface encapsulation in the plasma reactor, ensuring the compatibility with PSCs and other technologies such as organic solar cells. Finally, a significantly improved stability of the water-repellent PSCs is observed, with a reduced degradation under illumination at environmental conditions, in presence of high relative humidity and temperature cycling or even being immersed in liquid water.



s06) Thin films in energy harvesting and storage [o6-02]

EBSD analysis of III-V layers on Ge:Si virtual substrates for multijunction solar cells

Elisa García-Tabarés[1], Víctor Orejuela[2], Monalisa Ghosh[3], Lise Watrin[3], Beatriz Galiana[1], Pere Roca[3], Ignacio Rey-Stolle[2], Iván García[2]

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The integration of III-V structures on cost-effective substrates is highly pursued in the solar energy field to overcome one of the main limitations of multijunction solar cell (MJSC) technology (i.e., high costs associated to the substrate). In this sense, replacing the usual Ge substrate by Si offers a high potential for cost reduction while preserving high efficiencies. However, the integration of III-V on Si (by epitaxial growth) includes a graded buffer layer which dramatically affects the epitaxial growth cost. In this context, Ge|Si virtual substrates are excellent candidates to integrate the III-V and Si platforms for achieving low-cost MJSCs.

Among the different approaches for manufacturing virtual substrates, the one here analyzed is based on the use of ultra-thin Ge layers (20-120 nm) grown by standard Radio-Frequency Plasma-Enhanced Chemical Vapour Deposition (RF-PECVD) at temperatures below 200ºC. The use of low temperatures reports/ brings ? several benefits such as absence of thermal strain, cost reduction or less reactive surfaces. Moreover, the thin Ge layer bridges the lattice constant difference between Si and GaAs and enable the deposition of III-V materials on top without surpassing the critical thickness for crack formation [1].

The first experimental results on GaInAs/Ge|Si dual-junction solar cell shows functional devices demonstrating the stability of these virtual substrates [2]. However, the low structural quality of the layers prevents the exploitation of the higher photovoltaic efficiency potential of III-V structures. In this sense, this work aims at understanding the origin of these structural properties by using substrates formed using different Ge thickness or PECVD conditions. To this end, plastic deformation induced on GaInAs layers grown on Ge|Si virtual substrates have been measured by Electron Backscattered Diffraction (EBSD). The results shown in Figure 1 corresponds to Kernel Average Misorientation (KAM) measured on GaInAs layer grown on a) Ge(120nm)|Si and b) Ge(20nm)|Si virtual substrates, evidencing the effect of the Ge thickness on the III-V quality. In order to understand the origin of this phenomena, Transmission Electron Microscopy (TEM) will be carried out to evaluate the quality of the Ge thin film and the role it plays on the final structure.

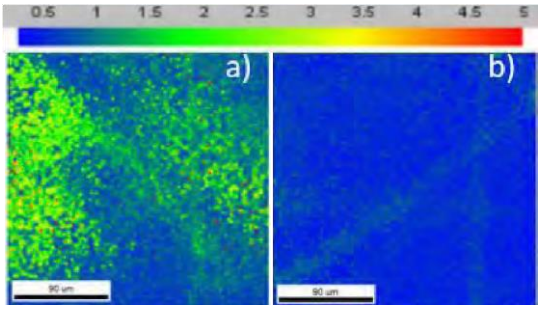

Figure 1. KAM maps (0-5) of GaInAs on a) Ge(120 nm)|Si and b) Ge(20 nm)|Si virtual substrates.

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Session S06: Thin films in energy harvesting and storage [o06-03]

Molecular inks route for high efficiency kesterite based solar cells

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After several years unbeaten, recent progress on molecular inks methodology for the synthesis of kesterite, has allowed to increase the solar cell conversion efficiency of this technology up to 13.8%.[1] Main improvements are related to the precise control of the molecular inks formulation, and the fine tuning of the selenization process, which directly impact in the phase purity and crystalline quality of the material.[1,2] In this work, we present a complete analysis of the selenization and sulfurization processes of molecular inks based Cu_2ZnSnS_4 precursors, to better understand the relationship between precursor/absorber in both type of chalcogenization. We demonstrate that the chalcogen vapor pressure and annealing temperature are key for the reproducibility of the processes. We tune these parameters in a wide range of values, performing a complete characterization of the morphology, composition, phase purity and optic properties of the absorbers. By adapting our chalcogenization process in a semi-closed system, we report more than 12% efficiency for $Cu_2ZnSn(S,Se)_4$ based solar cells, and almost 11% efficiency for Cu_2ZnSnS_4 ones. Future strategies for further improve the conversion efficiency will be also presented.

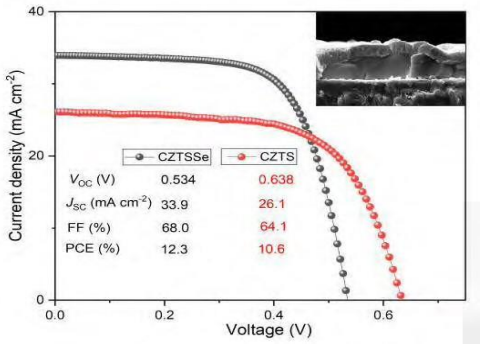

Figure 1. JV AM1.5 illuminated curves and corresponding optoelectronic parameters of best CZTSSe and CZTS solar cells. Inset shows the large grains with high crystalline quality of CZTSSe absorbers.

Acknowledgement

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Session S06: Thin films in energy harvesting and storage [o06-04]

Novel (Sb,Bi)(S,Se)(Br,I) van der Waals materials for thin film photovoltaic applications

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In the last years, the steady rise of emerging thin film photovoltaic absorbers with exotic properties leads to the discovery of a plethora of new materials.[1,2] Among them, pnictogen chalco-halides with van der Waals structure and low dimensional morphology are attracting a lot of attention due to the unusual combination of bandgaps suited for different photovoltaic applications, excellent stability and possible high tolerance to defects. Nevertheless, the inclusion of chalcogens and halogens in the same structure, complicate the synthesis and stoichiometry control of these compounds. In this work, we present an innovative synthesis route for (Sb,Bi)(S,Se)(Br,I) compounds based on a sequential process that combines co-evaporation of the chalcogenide compounds, followed by a high pressure reactive annealing under halogen atmosphere. We demonstrate the potential of this technique, by presenting a complete analysis of the synthesis of the 8 compounds in the P-T space, showing that by fixing these parameters, the morphology and phase of these compounds can be controlled and tuned. We demonstrate high purity phase compounds, by performing a complete characterization of their morphology, composition, structure and optical properties. In all cases, quasi one-dimensional columnar structures are reported, which thickness and height can be tuned by changing the synthesis T and P. First solar cell prototypes will be presented, demonstrating very encouraging open circuit voltages around 600 mV, and conversion efficiencies in the 1-5% level in a very short period of time.

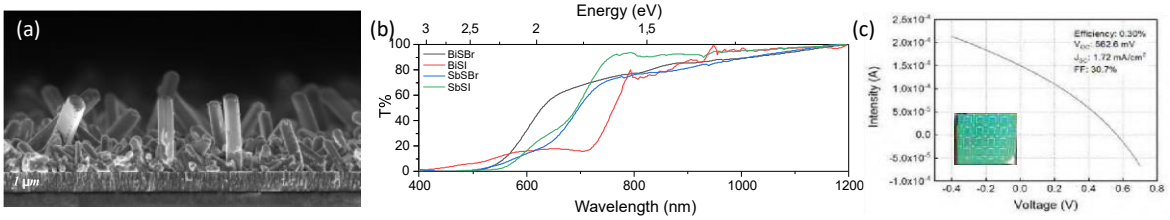

Figure 1. Example of quasi one-dimensional structure for BiSeBr (a), transmission spectra of (Sb,Bi)S(Br,I) series of compounds showing different bandgaps (b), and example of a working prototype based on SbSeI on substrate configuration (c).

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Session S06: Thin films in energy harvesting and storage [o06-05]

Ultrathin plasma polymer for improved stability and reproducibility of perovskite solar cells

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In the context of a global climate crisis caused by human action, green energy such as solar energy has positioned itself as a clean alternative to traditional energy sources such as coal. On the other hand, global energy demand is expected to continue to enhance in the coming years due in part to the increased use of wireless devices. Given these forecasts, the use of highly polluting energies, and the use of batteries to charge the wireless devices will become unfeasible in the coming years. Thus, the need arises to develop a clean technology that self-charges the devices by surroundings energies. Solar and indoor light energies are one of the most promising sources for developing that wireless technology that captures environmental energy. About this, organometallic halide perovskite (OMHP) materials have attracted the attention of the solar energy research field due to their excellent optoelectronic and photovoltaic (PV) properties. However, the stability of the OMHP material to environmental conditions still needs to be optimized before integrating such devices into single/multisource harvesters in one device.

With this background, during the last years, we have focused on developing organic plasma polymers that mainly improve the stability of OMHP solar cells. Herein, an ultrathin plasma polymer has been used as an encapsulation material for OMHP solar cells.[1] The encapsulation method, that does not affect the PV performance, is carried out at room temperature by the remote plasma-assisted vacuum technique. The encapsulated devices show a significant increase in stability in humid air (RH>85%) and even keep their PV performance intact within the first 60 seconds immersed in liquid water. In addition, this plasma polymer is also positioned as a promising interlayer passivation material for OMHP solar cells. A higher fill factor and PV parameter reproducibility are obtained for solar devices incorporating the polymer at the electron transport material/OMHP interface. More impressively, these solar cells retain more than 80% of initial efficiency after being stored at environmental conditions for more than 1000h, without any encapsulation.[2]

Acknowledgement

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Session S06: Thin films in energy harvesting and storage [o6-06]

NEW ANODES BEYOND GRAPHITE FOR INCREASING THE ENERGY DENSITY OF LITHIUM-ION BATTERIES

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Lithium-ion-batteries (LIBs) are currently the most used power source in portable electronic devices. Their main advantages are the high gravimetric and volumetric capacities, with theoretical values of 250 $Whkg^{-1}$ and 2060 WhL^{-1}, respectively [1]. Also, lithium has the most negative electrochemical potential, which ensures a high operating voltage. Nevertheless, the use of lithium metal is related to security issues, so nowadays, most of the commercial rechargeable LIBs use graphite, which reduces in an order of magnitude the capacity. This is acceptable for small devices, but it is insufficient for applications in which increasing the energy density is crucial such as electric vehicles.

Here, we present different types of anodes for increasing the energy density of LIBs. First, amorphous Si grown on Ta particles provide great capacity without suffering from the typical cracks due to extreme volume change during lithiation and delithiation processes (Figure 1) [2]. Second, a study of different metal-organic framework materials will be presented. Their main advantage is the possibility of tuning their functional groups and structure to optimize their performance. Finally, we will propose a potential application of the Langmuir technique to obtain ultrathin layers of MOFs to perform preliminary electrochemical studies to evaluate the behavior of materials using extremely low quantity of reagents and as potential tool for fabricating protective layers for the incipient technology of anode-less batteries [3].

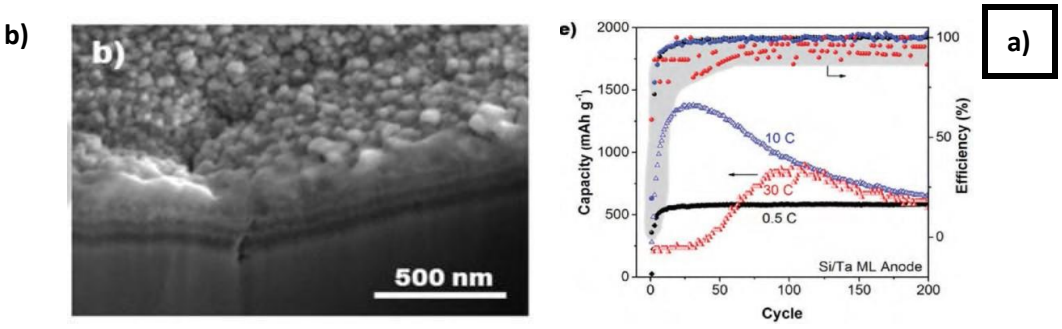

Figure 1. **a)** FIB-SEM image, and **b)** capacity and Coulombic efficiency of Si-Ta electrodes

Acknowledgement

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Session S06: Thin films in energy harvesting and storage [o06-07]

UNDERSTANDING AND DEVELOPING PHOTORECHARGEABLE LITHIUM-ION BATTERIES

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Renewable energy sources are vital for achieving the seventh Sustainable Development Goal about affordable and clean energy. Among these sources, solar light outstands because Earth crust receives in just one hour enough energy to fulfill humanity needs for one year. Solar cells can efficiently convert solar light into electricity, but the intermittent nature of Sun requires energy storage systems such as lithium-ion batteries that can release energy upon needed. These batteries take advantage of Li^+ small size and weight and high negative redox potential to storage a relatively high gravimetric and volumetric energy density, so they are widely use in portable electronic devices.

Considering both systems, we have based our research on the pioneering study that was done by Hodes et al had in 1976, which consisted of a three-electrode cell that could directly convert light into chemical energy [1]. In contrast to this, our system is a two-electrode system consisting of an adapted coin cell with holed upper spacer and case to allow the illumination of a photoelectrode (Figure 1) [2]. This electrode is composed by a Cu_2O film obtained by electrodeposition, which is the photovoltaic component that transforms light into electrical current, and a TiO_2 layer deposited on top of the semiconductor by doctor-blade technique, which is the capacitive element. This device was photocharged in ~9 hours in open circuit conditions and it provided an energy density of ~150 $mAhg^{-1}$ when discharged at 0.1C in dark for 3 charge-discharge cycles.

Figure 1. Photo of the photobattery consisting of an adapted coin cell.

Acknowledgement

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Session S06: Thin films in energy harvesting and storage [o06-08]

Synthesis and characterization of 2D-GeSe for photovoltaic applications

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GeSe has recently emerged as a promising absorber material for photovoltaic applications. This is due to its bandgap energy of 1.15 eV, high absorption coefficient > 10^5 cm^{-1}, high carrier mobility, p-type conductivity, high stability, and low toxicity [1]. This is a 2D material, being crucial the control of the growth orientation to enhance the device performance. Currently, GeSe-based solar cells have achieved an efficiency of 5.2% with a superstrate structure [2]. Considering the theoretical efficiency limit of nearly 30% for GeSe single junction solar cells, there is still room to enhance its performance.

In this work, GeSe thin films were deposited onto Mo/soda-lime glass (SLG) substrates. GeSe was fabricated by the selenization of previously evaporated amorphous Ge films. The influence of different factors on the selenization process and on the final structural and optoelectronic properties has been investigated. They include the thickness of the initial Ge layer, the effect of maximum temperature (320°C to 400°C) upon annealing, and the amount of elemental Se added in the process. The results show that the films present orthorhombic GeSe phase with the (100) preferred crystal orientation. It will be shown how we can control the presence of the $GeSe_2$ phase switching the selenization factors during the annealing. Cross-sectional SEM images of GeSe/Mo configuration showed 2D nanosheets structure for the absorber layer. The surface of the thin films was also investigated by Raman spectroscopy and XPS measurements, revealing the presence of germanium oxide together with germanium selenides. Further optical and electrical characterization of the GeSe grown on different substrates is in progress, in order to identify the best configuration for the fabrication of efficient solar cell devices.

Acknowledgement

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Session S06: thin films in energy harvesting and storage [o06-09]

Hydrogen Absorption and Desorption in Thin Mg Films Driven by Heat and Light

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Magnesium has emerged as a promising candidate for hydrogen storage due to its high hydrogen capacity of 7.6 wt% as well as its abundance, cost and safety [1]. Moreover, its reversible changes in optical properties, switching between reflective and transparent states (fig.1) upon hydrogenation and dehydrogenation [2], make it an appealing choice for hydrogen sensing. However, magnesium's thermodynamic and kinetic properties need improvement, as it requires high temperatures (>300ºC) for uptake and release [3].

To overcome these difficulties, two approaches were explored in this study. Firstly, the H_2 absorption/desorption process of thin magnesium films (d □ 100 nm) was investigated near ambient temperatures (< 80□C). Secondly, plasmonic heating was utilized to promote the H_2 uptake/release process by covering the films with gold nanoparticles (□ 5nm) and illuminating them with an appropriate light frequency. The films were structurally and morphologically characterized using X-ray diffraction and field emission gun scanning electron microscopy, respectively. Optical transmission and reflection curves during H_2 absorption/desorption process were analyzed to determine the rate limiting mechanism and the activation energies of the absorption and desorption processes. The obtained results were compared with previously available studies [3], and based on their evaluation, the following steps to be taken will be presented.

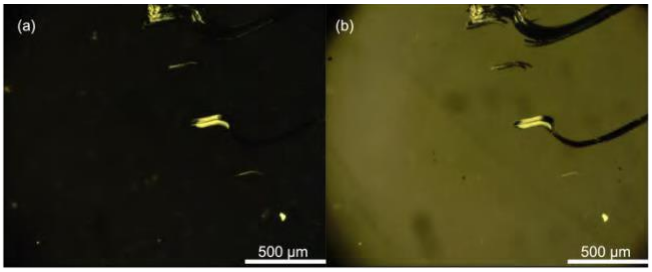

Figure 1. Optical image of the Mg thin films before hydrogenation (a) and after hydrogenation process (b) in transmission mode.

Acknowledgement

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Session S06: Thin films in energy harvesting and storage [o06-10]

Study of Oxide Equilibrium in Pulsed Laser Deposited $LiCoO_2$ for Li-Ion Batteries

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We focus on the study of the phase equilibrium between $LiCoO_2$ (LCO, widely used material as LIB cathode) and spinel Co_3O_4, in the form of a thin film deposited by Pulsed Laser Deposition (PLD). Recently, LCO has regained prominence in the design of "zero-strain" composite CATs since this is the only commercial CAT with a negative chemical expansion coefficient [1]. On the other hand, PLD is a physical vapor deposition technique extensively exploited for the stoichiometric preparation of multicationic oxides, and conformal interfaces with improved wetting and mechanical clamping between components [2]. Combining both solutions by using prepared "zero-strain" CATs forming a conformal interface with solid-state electrolyte is expected to improve the mechanical stability of solid-state LIBs, which is one of the crucial issues hindering the marketing of these devices. LCO is sensitive to Li stoichiometry, which is hard to achieve by PLD due to the interaction of the light species with the deposition atmosphere, the low sticking of Li metal and the lower enthalpy of formation of non-stoichiometry LCO. Losses of Li beyond 50 % irreversibly give rise to the segregation of Co-oxide phases. Here, we study the dependence of the phase equilibrium of LCO-Co oxides on the PLD deposition parameters (temperature, oxygen pressure and film thickness). Four phases (hexagonal LCO [HT-LCO], spinel LCO [LT-LCO], spinel Co_3O_4 and CoO) were identified, whose evolutions with the PLD parameters are investigated by µRaman spectroscopy, grazing incidence X-Ray diffraction (GIXRD), Rutherford Backscattering Spectrometry and Nuclear Reaction Analysis (RBS-NRA) and Atomic Force Microscope (AFM). Raman and GIXRD reveal that the two HT-LCO and Co_3O_4 phases coexist in the films for the entire explored range of PLD parameters, while LT-LCO and CoO appear under low temperature conditions. The HT-LCO/Co_3O_4 ratio presents a maximum at 500 ºC and 0.1 mbar of oxygen pressure, and an increasing behavior with the thickness. Combined NRA-RBS reveals that Li is depleted on the surface and at the interface with the substrate, suggesting that the sources of Li loss are the diffusion towards the substrate and Li reevaporation from the surface. AFM shows two grain-sizes distributions at low temperature, which can be related to the coexistence and competition between the phases observed in confocal µRaman. Finally, electrochemical tests show that the films with higher HT-LCO proportion exhibit higher specific charge capacities and coulomb efficiencies.

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Session S06: Thin films in energy harvesting and storage [o6-11]

Doping impact on thermal and electrical properties of transparent ZnO and TiO_2 thin films for thermoelectric applications

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Transparent thermoelectric materials are a promising technology for touchscreen displays and solar cell applications, rendering a sustainable powering of the device. In order to enhance the thermoelectric performance, the material must have a high Seebeck coefficient and high electrical but low thermal conductivity. This work focuses on the effect of doping on ZnO and TiO_2-based thin films (200-300 nm) deposited by magnetron sputtering. The properties of the films depend strongly on the dopant type and concentration. On the one hand, it has been documented that Al and Ga doping can improve the electrical properties in ZnO, as can Nb doping in TiO_2. On the other hand, introducing heavier elements (such as Bi, Sb or Nb) into the metal-oxide matrix hinders phonon mediated heat conduction, consequently reducing the thermal conductivity, which is a promising approach. Atom Probe Tomography analyses enabled the determination of the composition and inherent homogeneity, as well as to investigate the cation and anion segregations to interfaces and grain boundaries. For the ZnO-based films, all elements are homogeneously distributed within the crystals, with the exception of Bi, which is not incorporated in the ZnO wurtzite cell and segregates at the grain boundaries, especially at the triple junctions. Thus, Bi contributes to grain boundary scattering of phonons and has no significant effect on thermal conductivity, unlike Ga, Al and Sb (Figure 1).

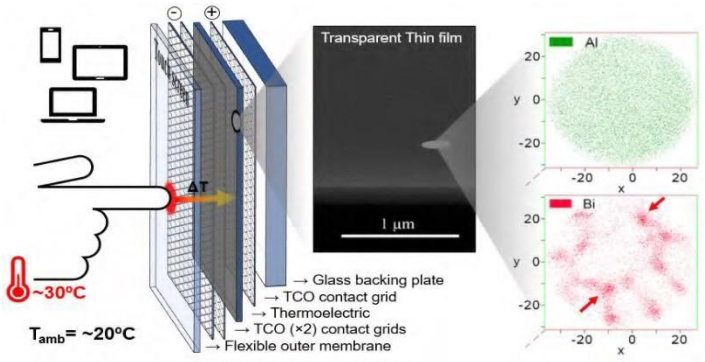

Figure 1. A transparent touch screen prototype featuring a thermoelectric thin film layer. APT reconstruction of ZnO:Al:Bi shows Al homogeneity and Bi segregating to the grain boundaries.

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Session S06: Thin Films in Energy Harvesting and Storage [o06-12]

Thermoelectric and structural properties of transparent Sb-doped ZnO thin films

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This study focuses on understanding the influence of low Sb-doping in the ZnO electrical, optical and thermoelectrical properties, with the addition of also studying its structural and morphological parameters. For this, several ZnO films with varying Sb-target current density, in the range of 0 – 0.27 mA/cm2, were produced by DC magnetron sputtering in a confocal geometry. As a result, thin ZnO:Sb films with an average transparency in the visible region greater than 80% were produced, revealing for optimized conditions an absolute Seebeck coefficient of 100 $\mu V \cdot K^{-1}$ and respective power factor of 1.1 $mW \cdot m^{-1} \cdot K^{-2}$ at 300K effectively modifying the electrical, optical and thermoelectrical properties of the material and ensuring its suitability for heat harvesting applications. From atom probe tomography (APT) experiments, a larger Zn content is registered at triple junctions of the grain boundary, which matches the approximate 25 nm crystallite grain size derived from the X-ray diffraction analysis.

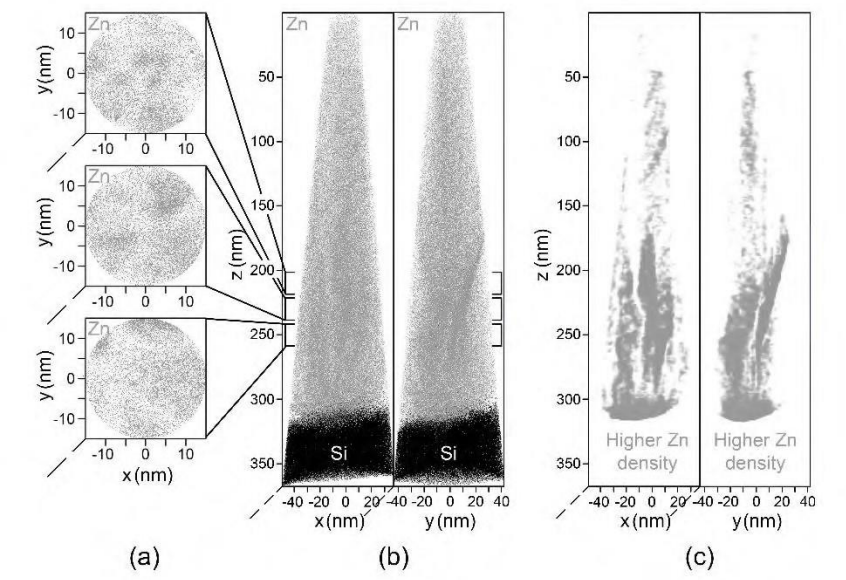

Figure 1. Top and side views of a 3D reconstruction obtained by APT of a tip of the ZnO:Sb07 sample; (a) top view sliced section of 30 nm x 30 nm x 20 nm sections; (b) side view displaying Zn and Si ions; (c) side view of higher density of Zn ions located inside the sample.

Acknowledgement

This research is funded by FCT / PIDDAC through the Strategic Funds project reference UIDB/04650/2020-2023. Joana M. Ribeiro is grateful to the Fundação para a Ciência e Tecnologia (FCT, Portugal) for the Ph.D grant SFRH/BD/147221/2019. This work (proposal ID 2021-025-030112) was carried out with the support of the Karlsruhe Nano Micro Facility (KNMFi, www.knmf.kit.edu), a Helmholtz Research Infrastructure at Karlsruhe Institute of Technology (KIT, www.kit.edu).

Session S06: Thin films in energy harvesting and storage [o06-13]

Comparative study of QDSSC solar cells using TiO_2/QDs SnS solar paint and SnS thin films solar cells

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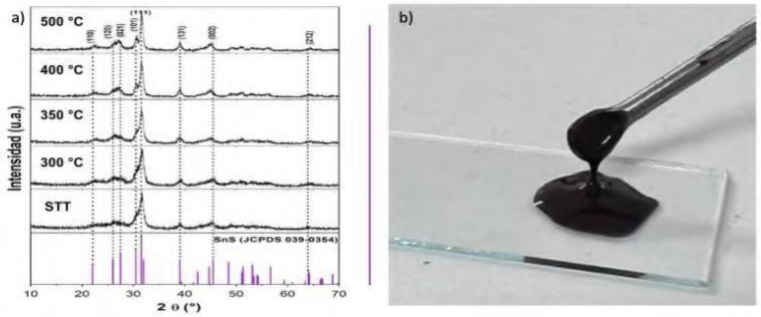
Tin sulfide (SnS) has been a promising material as absorber material for the development of solar cells, since they can be manufactured by solution techniques at low cost [1]. That is why in the present work different routes of incorporation of SnS are used for the manufacture of solar cells with different structures. Firstly, SnS QDs were used and incorporated into TiO_2 to form a solar paint that was later deposited by screen printing onto FTO substrates. For this type of solar cell, Pt was used as a counter electrode and I^-/I_3^- as an electrolyte [2], also evaluating its photovoltaic properties.

In a complementary study, SnS thin films were deposited through non-toxic precursors by the chemical bath deposition (CBD) technique. The films were characterized by XRD, Raman, and SEM and were incorporated into cell structures with substrate and superstrate configuration where photovoltaic properties such as Voc, Jsc, FF, and were evaluated. The films were also deposited on TiO_2, and the photovoltaic properties were also evaluated. From this study it is possible to see the versatility of solar cells from SnS and the potential to continue studying this material.



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Session S06: Thin films in energy harvesting and storage [o06-14]

Effect of magnetic nanoparticles on the performance of triboelectric nanogenerator

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Triboelectric nanogenerators (TENGs) are systems that can convert mechanical energy into electrical energy from various mechanical energy sources such as walking, running, and jumping due to the triboelectric effect in daily life. The TENG is a system with a new type of energy harvesting strategy and there are various ways to increase the output performance of TENGs such as by changing the surface morphology of triboelectric films[1], increasing the external force and its frequency, and enhancing the surface charge density[2]. Among ways to improve the performance of TENGs, the introduction of magnetic nanoparticles into the triboelectric film can affect the electric field and the output performance of TENGs in several ways[3]. In this study, the effect of magnetic nanoparticles on the output performance of TENGs was investigated. It was clear that the Nylon/Fe_3O_4 nanocompositebased TENG performed better than the conventional Nylon film-based TENG because of the dielectric and magnetic properties of Fe_3O_4 nanoparticles. The value of open-circuit voltage and short-circuit current of TENG made with conventional Nylon was measured as U_{OC}=30 V and I_{SC}=2 μA, respectively. The output voltage and current of the nanocomposite-based triboelectric nanogenerator increased and showed values of U_{OC}=45 V and I_{SC}=2.8 μA, respectively. In order to investigate the effect of Fe_3O_4 magnetic nanoparticles on the performance of TENG, a nanocomposite material is obtained using Nylon (nylon socks, nylon 100%) as a polymer matrix. Magnetite nanoparticles were obtained via the co-precipitation method. Firstly, a 0.5wt% solution of Fe_3O_4 magnetic nanoparticles was prepared in ethanol. Then the obtained solution is dispersed by the sonochemical method within 2 minutes. The dispersed solution is sprayed on the surface of the Nylon material, which was previously attached to the aluminum foil by double-sided adhesive, through the spray coating method. The samples were dried at room temperature for one day, and the next day a 5x6 cm section was cut, and a TENG was fabricated using polysiloxane film as another triboelectric material.

Acknowledgment

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Session S06: Thin films in energy harvesting and storage [o06-15]

Tailored nanolaminates for innovative photovoltaics

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Considering the energy and climatic crisis, the photovoltaic portfolio needs to be augmented, through the improvement of existing established technologies toward more innovative and efficient solutions. For 2nd generation Cu(In, Ga)Se_2 (CIGS) solar cells, recent absorber improvements have allowed for efficiency values above 23%[1], without extensive architecture changes. One major aspect to tackle is the interfaces, through the incorporation of passivated selective contacts (SC), enhancing carrier collection.[2] When devising devices, the choice of materials is limited and often, there must be a compromise. So, what if we could revert materials engineering, developing materials for a specific application? In this work, the use of nanolaminates to develop key sections of a CIGS solar cell is proposed. Nanolaminates are a nanometric multilayer concept of alternating materials, whose properties are highly tuneable, dependent on each sublayer composition and thickness, and exceed the ones from the individual materials used as sublayers.[3] For now, the possibility of developing custom electron SCs for CIGS, based on nanolaminates, was explored. Nanolaminates of dielectric materials (SiO_x, SiN_x, TiO_x, ZnO_x, and HfO_x) were developed through PECVD and PVD, and underwent an in-depth fundamental study of structural, elemental composition, electronic, optical, and electrical properties, as well as their single layer counterparts. The obtained results clearly indicate the possibility of tailoring properties to match technological requirements, when varying the nanolaminates' architecture. Furthermore, a TiO_x-ZnO_x nanolaminate showed promising optical properties and electronic potential to be tailored, to achieve an electron SC in CIGS solar cells.

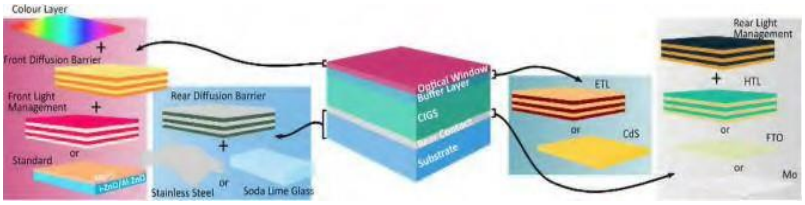

Figure 1. *Graphical representation of the possible applications of nanolaminates on a CIGS solar cell.*

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Session S07: Plasmonic and photonic sensors based on thin films [o07-01]

Growth of Metal-Organic Framework films on nanostructured-SERS substrates

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Metal-Organic Frameworks (MOFs) thin films have been in the focus of the scientific community over the last decades given their high (micro)porosity, structural and chemical versatility. This makes them suitable for consolidating functional devices [1,2] capitalizing on their large surface area, with the presence of different metals and well-controlled interfacial properties.[3] Of particular interest is their use in gas sensors, where their porosity allows pre-concentrating target analytes on their surface for further analysis.[4]

Among different analytical tools, Surface-Enhanced Raman Spectroscopy (SERS) has positioned itself as a powerful and versatile tool providing the means for direct fingerprinting of target molecules with fast detection times, *in-situ* sampling, and the possibility of implementations to miniature portable devices.[5,6] This approach requires the docking of target analyte in the close proximity of the SERS active surface and, indeed, MOFs represent a type of attractive materials that can be combined with the SERS substrate and provide an efficient scaffold for collecting target analytes on its surface.[7,8] MOF films can be grown on different surfaces properly modified.[9] Surface modification typically involve Self-Assembled Monolayers,[10, 11] but film growth can be also achieved by polymer brushes as nucleation points.[12, 13] However, it needs to be noticed that each surface chemical modification will have an impact on the growth and final structural properties of the MOF films, by the generation of the so-called *Constructional Porosity*, with wider dimensions and distinct adsorption characteristics.[14]

Here, we analyze the impact of plasmonic surfaces on the overall properties of MOF thin films towards SERS applications. We aim to address how growth and film constructional porosity are influenced by the nanostructured SERS substrate and the effect on their final SERS performance.

Acknowledgement

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Session S07: Plasmonic and photonic sensors based on thin films [o07-02]

Vacuum soft-template methodology for perovskite-based core@shell nanotubes with enhanced optoelectronic properties.

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Halide perovskites, particularly organometal-halide perovskites, have been extensively investigated during the last decade due to their exceptional optical properties, low production costs, and facile fabrication by means of a wide variety of methods. Halide perovskites are a versatile class of materials with a high absorption coefficient, direct bandgap, that find applications in diverse fields ranging from solar cells, light-emitting diodes, and image sensors. However, the most significant unresolved challenge of halide perovskites is their low stability when exposed to ambient conditions, radiation, and temperature. Nanoscale engineering carried out by vacuum processes holds tremendous potential for improving the performance of halide perovskite optoelectronic devices [1-3].

In this study, we present a full vacuum methodology for the synthesis of methylammonium lead iodide ($CH_3NH_3PbI_3$) perovskite core@shell nanostructures using supported TiO_2 nanotubes as a template [4,5]. We analyzed the optoelectronic properties and stability of these nanostructures in comparison to their thin film counterparts. The nanostructures presented improved photoluminescence properties and long-term stability even after 4 sequential tests of 40 hours of irradiation under highly stressing atmosphere conditions. In addition, the stability of the nanostructures was tested in dark storage under room conditions and showed no changes in the photoemission intensity for months.

Acknowledgement

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Session S07: Plasmonic and photonic sensors based on thin films [o07-03]

Thin films manifesting localized surface plasmon resonances for applications in sensing and photosynthetic mechanisms

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When noble metal nanoparticles have sizes much lower than the light wavelength, collective oscillations of conduction band electrons occur, enabling strong scattering bands, and electromagnetic-field enhancements near the nanoparticles. The physical phenomenon is known as Localized Surface Plasmon Resonance (LSPR). For Au and Ag nanoparticles, the resonance condition is met in the visible range, giving important colour effects since ancient times (e.g., the Lycurgus Cup and stained-glass windows of medieval cathedrals). Plasmonic nanoparticles have received considerable attention over the past decade in many scientific fields. For each application, there are critical issues to be considered once LSPR properties are dependent on the size, shape, interparticle distance, and surrounding dielectric material. Manipulating each one of these morphological characteristics and properties, opens a wide range of possible applications, taking advantage of far-field and near-field phenomena.
In the past few years, different LSPR thin film systems were developed, namely those composed by Au and Ag nanoparticles, dispersed in dielectric hosts as TiO_2, CuO, ZnO, Al_2O_3, etc. The thin films were prepared with variable composition, by reactive magnetron sputtering followed by heat-treatment at different temperatures to promote the growth of the nanoparticles in different size distributions. The LSPR band was monitored in transmittance mode using a high-resolution LSPR spectroscopy system, to evaluate the performance of the thin films as chemo-, bio- and physical (deformation) sensors [14]. More recently, far-field and near-field effects are being applied in photosynthetic mechanisms with promising results.

Acknowledgement

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Session S08: Protective, hard and tribological coatings [o08-01]

Fabrication, characterisation and fretting wear testing of Cr and CrN coated Zr alloy cladding using magnetron sputtering for enhanced accident tolerance in light water reactors.

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Research on accident-tolerant fuels (ATFs) for light water reactors (LWRs) has focused on improving the safety of zirconium alloy fuel rods since the Fukushima accident in 2011[1]. Additionally, normal operation causes fretting wear on the fuel rod surface, which requires tribological improvements[2,3]. Chromium-based coatings on zirconium alloys are one of the most advanced concepts for developing a fuel that can withstand accidents[4,5]. Under operating conditions and when subjected to hightemperature steam, Zr alloys with Cr coatings demonstrated improvements[6]. Cr coatings have been deposited using magnetron sputtering a well-stablish technique that produces high quality and dense films[7]. The aim of this work is to produce Cr and CrN coatings for Zr alloy nuclear fuel rod cladding material to enhance oxidation and mechanical resistance using the magnetron sputtering technique. Zr alloy substrates were Cr/CrN coated with varied coating parameters. This research is examining how the integrity and microstructure of the coating is affected by deposition conditions and coating thickness. The coatings were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), atomic force microscopy (AFM), optical profilometry and contact angle goniometry. A linear reciprocating wear tester was used to mimic fretting. Our results demonstrated that fretting resistance can be related to the different densities and thickness of coating produced.

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Session S08: Protective, hard and tribological coatings [o08-02]

Development of High Durability and Low Cost Ta Coated Polymer Electrolyte Membrane Water Electrolysis (PEMWE) Bipolar Plate by DC Magnetron Sputtering

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The Proton Exchange Membrane Water Electrolysis (PEMWE) technology is an efficient and environmentally-friendly process for producing hydrogen fuel. However, the anode of the PEMWE system is subjected to harsh operating conditions, such as high voltage, low pH, high temperature, and oxygen saturation, which requires the use of materials with good corrosion resistance, electrical conductivity, heat distribution, and mechanical support for the stack [1]. Although Titanium (Ti) meets these requirements, its high cost of production and machining results in up to 50% of the stack price being attributed to bipolar plate processing costs [2]. To address this challenge, we developed a tantalum-coated stainless steel bipolar plate using DC magnetron sputtering at 500°C. The coated bipolar plate was compared with commercial Ti bipolar plates through corrosion experiments, contact resistance measurements, and cell tests. The results showed that the tantalum-coated stainless steel bipolar plate had similar durability to the Ti bipolar plate while being significantly less expensive. Microstructural analysis using Scanning Electron Microscopy (SEM) and Focused Ion Beam (FIB) crosssectional SEM confirmed the effectiveness of the Ta coating in improving durability. The development of this tantalum-coated stainless steel bipolar plate offers a promising alternative to expensive Ti bipolar plates, contributing to the development of more efficient and cost-effective PEMWE systems.

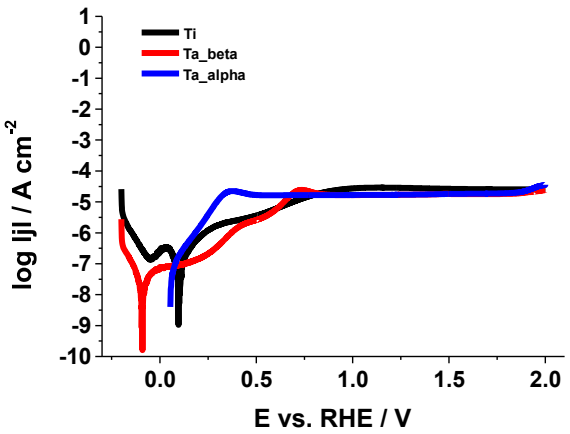

Figure 1. Comparison of Ti and Ta corrosion currents under PEMWE operating conditions.

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Session S08: Protective, hard and tribological coatings [o08-03]

Wear of the arc deposited TiAlN coating at elevated temperatures

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Hard coatings are frequently used in high-temperature and high-pressure applications such as cutting. TiAlN was the first coating to successfully withstand the increasing temperatures generated between the cutting edge of a tool and a workpiece. The addition of Al to the TiN matrix results in a significant improvement in hardness and coating oxidation resistance compared to its predecessor, TiN. During high thermal load operation, such as cutting, the spinodal decomposition of cubic-TiAlN into coherent cubic-TiN and cubic-AlN domains activates additional self-hardening effects. Moreover, the high thermal stability of TiAlN coating is attributed to the formation of a dense, protective Al_2O_3 layer.
Cathodic arc evaporation is the most commonly used method for depositing coatings on cutting tools, but it can result in a relatively rough surface due to the emission of micro-droplets. This roughness can have a significant impact on the wear and friction properties of the coating. Our goal was to monitor the wear and friction properties of the TiAlN coating during both the running-in and steady-state periods under different temperature conditions. To evaluate the performance of the TiAlN hard coating, we conducted tribological tests using a hightemperature pin-on-disc tribometer. The tests were carried out at different temperatures, including room temperature, 250, 500 and 700 °C. At specific temperatures we varied the test duration, which ranged from 50 up to 140,000 cycles. Coating experienced the highest wear at room temperature test, while at 250 °C the wear during the running-in phase as well during steady state friction was the lowest. After the temperature increased, the wear rate rose, which can be attributed to the increased tribo-oxidation and fatigue experienced during high test lengths. This ultimately resulted in the delamination of the coating from the WC-C substrate at the highest temperature. Detailed 3D profilometry, SEM and FIB analysis was carried out on numerous samples to determine the wear mechanisms in different stages of high temperature wear. Beside tribological evaluation, a high temperature mechanical tests were also performed at the same temperatures as the tribological tests.

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Session S08: Protective, hard and tribological coatings [o08-04]

Advanced Coating Techniques using Sputtering and PEALD for Enhanced Corrosion Resistance and Interfacial Contact Resistance of PEMFC Bipolar Plate

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Proton exchange membrane fuel cells (PEMFC)s are regarded as essential tools for energy conversion in the context of future clean energy.[1] PEMFC consists of several essential components, including the bipolar plate, which plays a vital role in the efficient operation of the fuel cell. The bipolar plate serves as the backbone of the PEMFC, facilitating the flow of reactant gases and conducting electrons produced during the electrochemical reaction between the cell's anode and cathode. A significant portion of the total stack cost is accounted for by bipolar plate.[2] Thus, the manufacturing techniques of bipolar plate significantly impact cost-effectiveness of PEMFC. Graphite and titanium-based materials are the most commonly used bipolar plate materials due to their excellent electrical conductivity, corrosion resistance, and mechanical properties. However, there are ongoing efforts to develop new and innovative materials to improve the performance and reduce the cost of bipolar plate. The use of stainless steel-based material in bipolar plates has demonstrated promising results in enhancing the durability and cost-effectiveness of PEMFC.[3] However, the harsh operating environment of PEMFC severely corrodes SUS, making coatings essential to prevent this corrosion.[4] In this study, multi-layered Ta TiN thin film coating was applied to the SUS 316L to improve the corrosion resistance on the surface. A polarization test simulating the operating environment of the PEMFC was conducted, and the corrosion current was reduced by more than two orders of magnitude. Additionally, through the coating, the contact resistance with carbon paper before and after coating was improved by more than 10 times. This can greatly reduce ohmic losses due to contact resistance during the operation of the PEMFC.

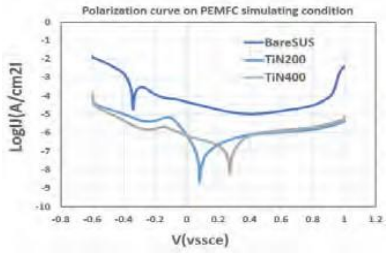

Figure 1. Polarization curve for coated and uncoated stainless steel

Acknowledgement

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Session S08: Protective, hard and tribological coatings [o08-05]

Amorphous and dual-phase nanocomposite coatings within Zr-B-Cu system

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In order to synthesize new materials having exceptional physical and chemical properties, amorphous–nanocrystalline alloys have attracted increasing interest in recent years. The synthesis of these dual-phase materials can eliminate the drawbacks of the individual phases and improve the resulting properties such as thermal stability, strength, or ductility. The non-equilibrium process of magnetron sputtering has been extensively used for the synthesis of amorphous alloys (thin-film metallic glasses). With high cooling rates of more than 10^6 K/s at atomic scale, magnetron sputtering makes it possible to deposit even immiscible elements with a low glass-forming ability into fully amorphous or dual-phase amorphous-nanocrystalline structures.

The present work aims at the preparation of dual-phase Zr-B-Cu coatings composed of a nanocrystalline ZrB_2 phase and an amorphous ZrCu phase with metallic glass behavior by nonreactive magnetron co-sputtering and investigation of their structure and properties. The elemental composition was varied so that the stoichiometry of both phases remained the same, but only the volume fraction was changed gradually. The depositions were carried out in argon (4 mTorr) using four unbalanced magnetrons equipped with two ZrB_2 targets, one Zr target, and one Cu target. The magnetrons with ZrB_2 and Zr targets were connected to dc power supplies, while the magnetron with Cu target to a high-power impulse power supply. All depositions were carried out on a rotating substrate (40 rpm) with rf biasing (50 W) at different substrate temperatures (no heating, 250°C, 350°C, 450°C).

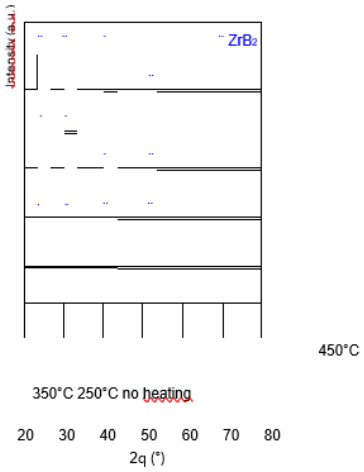

Figure 1. XRD patterns of $Zr_{35}B_{60}Cu_5$ films deposited at different substrate temperatures.

Our first results show that the structure of Zr-B-Cu coatings deposited by magnetron sputtering without external heating is amorphous for all compositions. Increasing the substrate temperature promotes the crystallization of the coatings (Fig. 1), leading to the formation of a dual-phase nanocomposite structure based on a nanocrystalline ZrB_2 phase and an amorphous ZrCu phase. This effect becomes more pronounced as the volume fraction of the ZrCu phase decreases. Mechanical properties such as hardness and stress are affected by the volume fractions of both phases and exhibit a temperature dependence. It is anticipated that the deformation behavior, which is now being studied and will be discussed, will be closely related to the phase composition and microstructure.

Session S08: Protective, hard and tribological coatings [o08-06]

Protective CoCrFeNiMo-based coatings via High Power Impulse Magnetron Sputtering

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Based on a multi-principal-element-design concept, Complex Concentrated Alloys (CCAs) show excellent mechanical strength, enhanced thermal stability, and superior wear and oxidation/corrosion resistance [1]. Moreover, microstructure and properties of CCAs can be fine-tuned changing their composition, boosting their possible applications, including severe environments as the marine one. In particular, CCA-based protective coatings could improve the wear and corrosion resistance of substrate materials under different service conditions [1, 2]. In this work, $(CoCrFeNi)_{100-x}Mo_x$ CCA micrometric films were deposited on Si and AISI 304 stainless steel coupons by high-power impulse magnetron sputtering (HiPIMS) technology using equimolar CoCrFeNi and pure Molybdenum targets. The Mo content influence on microstructure, mechanical properties, corrosion and tribocorrosion (in simulated seawater) behavior of the coatings was studied by modifying the Mo target-to-substrate distance. Higher amounts of Mo favored the formation of a dense microstructure, resulting in increased hardness values. Accordingly, differences were found, in terms of tribocorrosion behavior. Moreover, a series of $(CoCrFeNi)_{100-x}Mo_x$ CCA nitride samples was grown in reactive HiPIMS mode using the same dual-source configuration. The nitrogen percentage in the Ar-N_2 working atmosphere was progressively risen from □15 to □75% in an attempt to affect the film properties and further reduce tribocorrosion.
HiPIMS CCA-based coatings showed a comparable or superior corrosion resistance with respect to AISI 304 and, at the same time, enhanced mechanical and tribological properties, paving the way towards protecting low cost and low quality substrates.

Acknowledgement
The present work was carried out thanks to funding in the framework of the Italian Research Program for the Electric System (RdS).

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Session S09: Photo-, electro-, thermo-, gas-chromic and luminescent coatings [o09-01]

Tuning of photochromic properties of rare-earth oxyhydride thin films

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Materials showing photochromic properties attract increasing attention in the scientific community due to their ability to change optical properties in response to illumination, which makes them enticing for numerous applications, e.g. in smart windows [1]. Photochromic materials eliminate the need for electrodes and/or electrolytes as used in electrochromic devices. This advantage results in a simpler design and reduced fabrication costs. Until recently, photochromic properties were documented only for a rather limited number of materials, e.g. some transition metal oxides [2]. Typically, they feature an additional absorption band in the photodarkened state changing their color unless doping or multilayered structures are used. Photochromic rare-earth metal oxyhydrides (REHO) are a new expanding class of materials showing color-neutral photochromic effect at ambient conditions (see Figure 1) [3]. Thin films of REHO are commonly prepared in two steps: i) YH_2 precursor films are deposited using reactive magnetron sputtering or e^--beam evaporation, ii) formation of oxyhydride by exposing the hydride to air. It was demonstrated that the photochromic properties of the films can be altered in a broad range via changing deposition conditions and thereby changing O to H ratio [4].

In this work, we study alternative methods to modify the photochromic properties of REHO in a controlled way. Photochromic films were produced using magnetron sputtering and characterized regarding their photochromic properties. The thermal stability of the samples was assessed by exposing them to elevated temperatures in ultra-high vacuum and simultaneously monitoring optical transmittance and composition of the residual gas. We find H desorption at temperatures above 90 °C. Since the photochromic effect is closely related to the hydrogen and oxygen content, thermal annealing opens up a possibility for the modification of photochromic properties after deposition. We conducted in-situ experiments where chemical composition and photochromic response were measured while annealing the sample.

Studying REHO in different gases (H_2, O_2, air and UHV) and temperatures showed that the environment does not have a noticeable effect on the photochromic kinetics while bleaching is faster at elevated temperatures [5]. Since the effect might be related to the defect structure of the material, REHO films were irradiated with keV or MeV ions. The results demonstrated that damage above 0.1 DPA reversibly decreases photochromic contrast, the photochromic effect is vanished for the damage around 1 DPA.

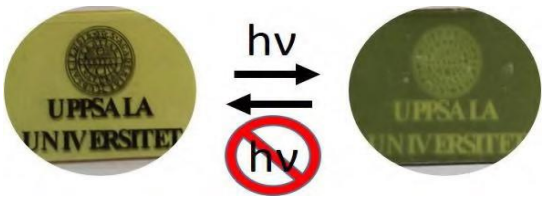

Figure 1. Photochromic effect in YHO thin film.

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Session S09: Photo-, electro-, thermo-, gas-chromic and luminescent coatings [o09-02]

Optimization of electrochromic thin film by reactive magnetron sputtering controlled by plasma emission monitoring

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In recent years, the global shortage of energy storage has received more attention. Since the Industrial Revolution, the increasing amount of CO2 has reached the highest levels in human history. These levels are related to climate change and the increased combustion of fossil fuels brought on by urban heat. An efficient method of minimizing carbon emissions and the energy needed for building thermal control is established by electrochromic devices. Magnetron sputtering is widely employed in the industry to create some of the essential layers of the electrochromic device. By implementing adequate controls in the production process, current difficulties with performance, stability, and costeffectiveness could be resolved. Therefore, issues from large-scale applications are solved using the Optical Emission Spectroscopy (OES) control. In this study, we analyse the electrochromic properties associated with plasma species and provide an example of such a control tool. A quick and effective solution is provided by improving the manufacturing process by controlling the reactive magnetron sputtering on the electrochromic layer. In order to limit the amount of experimental trial-and-error procedures, a novel data application has been developed. The method uses multiple sensors readings to collect data on the dynamic process behaviour for the plasma emissions of selected atomic metal and gases during the deposition.

Session S09: Photo-, electro-, thermo-, gas-chromic and luminescent coatings [o09-03]

Green-solvent deposition of electrochromic thin films of poly(3-hexylthiophene) nanoparticles

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Currently, conventional lab scale deposition of in-solution electrochromic polymers is mainly carried out with toxic solvents. A possible future implementation of electrochromic materials/devices mass production, or other related products where deposition could be carried out by end-user, would be greatly benefitted from the use of non-hazardous green solvents. In this regards several strategies have been applied [1]; among them, the synthesis of electrochromic polymer nanoparticles from aqueous solutions have been recently shown [2].

In this work we have synthesized aqueous and ethanol nanoparticle dispersions of poly(3hexylthiophene) through the reprecipitation method, and the electrochromic performance of the spray and spin-coated resulting thin films has been evaluated. A complete characterization in terms of optical contrast, switching speed and stability has proven the excellent behavior of the resulting films, with nanoparticle films showing similar response to that of conventional films. These results prove the viability of the use of these green solvents, which would reduce safety hazards to a great extent regardless of their final use.

Acknowledgement

This work was funded by Ministerio de Ciencia e Innovación-Agencia Estatal de Investigación (AEIMICINN,Spain) Grant numbers PID2019-104272RB-C55/AEI/10.13039/501100011033 and PID2019-104272RB-C51/AEI/10.13039/501100011033. A.C-S acknowledges financial support from UPCTBanco Santander through a research grant ("Iniciación en investigacion" Program 2021). W.M. acknowledges financial support from Gobierno de Aragon (DGA) under project "Grupos Consolidados" T03_20R. E.C. is grateful for his PhD grant from MINECO (FPI BES2017-080020) and associated European Social Funds (ESF).

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Session S09: Photo-, electro-, thermo-, gas-chromic and luminescent coatings [o09-04]

High-performance thermochromic YSZ/W-doped VO_2/YSZ coatings for energy-saving smart windows

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Vanadium dioxide (VO_2) exhibits a reversible phase transition from a low-temperature monoclinic VO_2 (M1) semiconducting phase to a high-temperature tetragonal VO_2 (R) metallic phase at a transition temperature of approximately 68 °C for the bulk material. The automatic response to temperature and the abrupt decrease of infrared transmittance without attenuation of luminous transmittance in the metallic state make VO_2-based coatings a promising candidate for thermochromic smart windows reducing the energy consumption of buildings.

To meet the requirements for large-scale implementation on building glass, VO_2-based coatings should satisfy the following strict criteria simultaneously: a deposition temperature close to 300 °C, a transition temperature close to 25 °C, an integral luminous transmittance T_{lum} > 60 %, a modulation of the solar energy transmittance ΔT_{sol} > 10 %, long-term environmental stability, and a more appealing color than yellowish or brownish colors in transmission.

The paper deals with a scalable sputter deposition technique for the preparation of strongly thermochromic YSZ/W-doped VO_2/YSZ coatings on standard soda-lime glass at a relatively low substrate surface temperature (350 °C) and without any substrate bias voltage. The W-doped VO_2 layers were deposited using a controlled reactive deep oscillation magnetron sputtering of a V-W target while the antireflection Y-stabilized ZrO_2 (YSZ) layers were deposited using a controlled reactive standard high-power impulse magnetron sputtering of a Zr-Y target. The fundamental principles of this technique, and the structure and optical properties of the thermochromic coatings are presented. The coatings exhibit a transition temperature of 33-35 °C at T_{lum} = 64.5 % and ΔT_{sol} = 7.8 % for a $V_{0.986}W_{0.014}O_2$ thickness of 37 nm, and T_{lum} = 46.1 % and ΔT_{sol} = 13.2 % for a $V_{0.986}W_{0.014}O_2$ thickness of 67 nm (see the figure). Such a combination of properties, together with the relatively low deposition temperature, has not yet been published by other teams for thermochromic VO_2based coatings prepared by a scalable technique.

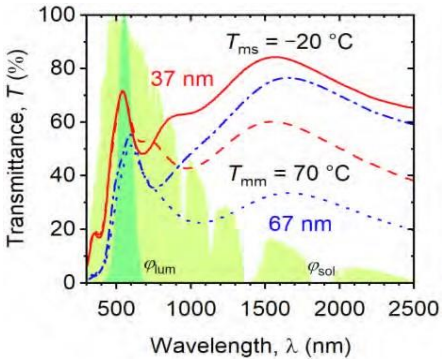

Figure 1. Spectral transmittance of the coatings on 1 mm thick glass.

Session s09. Photo-, electro-, thermo-, gas-chromic and luminescent coatings [o09-05]

Defining standard characterization procedures for electrochromic films and devices

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A proper quantification of the main performance parameters of electrochromic thin films or devices is crucial to achieve successful advances in the development of this technology. Despite the relevance of this topic through the extensive history of electrochromism, there are still few widely spread and standardized tools to properly achieve that quantification. Assessment of any advance towards broader transmittance modulations, faster switching rates or increasing durability, which may be identified as the three main key performance indicators, is severely hindered by the absence of consensus procedures to experimentally obtain these parameters and, more importantly, report them.

Through a combined interlaboratory effort, we have been able to develop a set of analytical tools that properly describe contrast [1,2], switching speed [3] and cycling stability [4], together with simple and generally applicable procedures to obtain them. These procedures have been experimentally validated for some of the most frequently used electrochromic materials (conducting polymers, metal oxides, metallo-supramolecular polymers and viologens) under a variety of test conditions. Through the application of the mentioned procedures, it is possible to get a significant set of parameters that allow meaningful comparisons between different materials/devices under various testing conditions. We believe these tools, if generally accepted and used, may constitute a powerful tool for the electrochromic community.

Acknowledgement

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Session s09) Photo-, electro-, thermo-, gas-chromic and luminescent coatings [o09-06]

From hidden explosive sensors to environmental plastic degradation: opportunities of the locally directed oxidation events on surfaces

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Directed oxidation of surfaces by external agents with a subsequent change in spectroscopic properties constitutes a useful approach for the design of new sensor materials or new ways to measurement of degradation of the surface of polymer materials. By the controlled detection of the oxidation of a fluorescent dye on the surface of silica ananoparticles, we have described the proof of concept of a portable testing setup for the detection of triacetone triperoxide (TATP), a common component in improvised explosive devices. The system allows for field-testing and generation of real-time results to test for TATP vapor traces in air by simply using circulation of the air samples through the sensing mechanism under the air conditioning system of an ordinary room. On a different oxidation event, we have described that wax worm enzymes secreted in the saliva oxidize and degrade polyethylene, on the way to the future solution to the global threat of plastic waste accumulation. In this way, we have described that the saliva of Galleria mellonella larvae (wax worms) is capable of oxidizing and depolymerizing polyethylene (PE), one of the most produced and sturdy polyolefin-derived plastics. This effect is achieved after a few hours' exposure at room temperature and physiological conditions (neutral pH). The wax worm saliva can overcome the bottleneck step in PE biodegradation, that is the initial oxidation step. Within the saliva, we identified two enzymes, belonging to the phenol oxidase family, that can reproduce the same effect. These enzymes are the first animal enzymes with this capability, which opens the way to new ground-breaking solutions for plastic waste management.

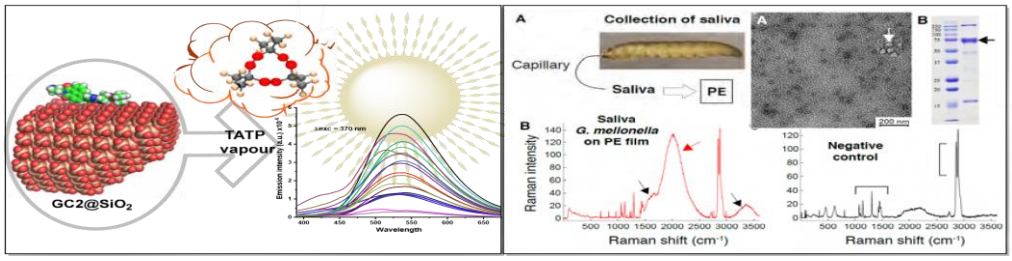

Figure 1. Directed oxidation events giving rise to hidden explosive sensors and PE degradation.

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Session S10: Thin film catalysts for energy transition [o10-01]

BiSeI: New van der Waals semiconductors for energy conversion applications

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Emerging quasi-1D (Q1-D) van der Waals materials such as BiSeI have the potential to become a breakthrough in next-gen photovoltaic (PV), photocatalytic (PC), piezoelectric, and thermoelectric applications. This class of materials fits the urgent necessity for innovative and renewable sources of energy based on earth-abundant, low-toxicity, thermally stable, and defect-tolerant materials. Moreover, the intrinsic combination of covalent and van der Waals bonds creates a highly anisotropic material formed by nano/micro-ribbons with peculiar conductive properties when properly oriented.

The ribbon structure together with the extremely uniform single-crystal phases lead to an increased amount of photons that reach the space charge region and to a reduction in reflection. This type of morphology not only can boost the optoelectronic properties of BiSeI-based solar cells but also enhance the photocatalytic activity of BiSeI-based photocatalysts. The dense coverage of properly oriented ribbons determines an increase in the surface area, allowing the synthesis of an efficient, photoactive, photostable, and nontoxic photocatalyst. The obtained BiSeI band gap is 1.25 eV, making BiSeI active to visible light and determining a big step forward compared to TiO_2, the most studied compound for photocatalytic applications so far, but inherently limited by a ~ 3 eV band gap.

Up to date, no mixed chalco-halide compounds have been synthesized through physical vapor deposition techniques, due to the complexity of the material and the different vapor pressures involved. The present work presents the very first successful attempt to synthesize and explore Q1-D van der Waals BiSeI-based semiconductors, through an innovative methodology implying the coevaporation of chalcogenides followed by high-pressure annealing under halogen atmosphere. XRD, XRF, SEM, EDX, PDS, UV-Vis, and Raman spectroscopy demonstrated the high tunability of the morphology of this family of compounds by modifying the annealing conditions and confirming the possibility to synthesize high-quality single-phase materials. The versatility of the system allows us to obtain optimal nano/micro-ribbons distribution in terms of height, thickness, density, and orientation, according to the final device use, proving how these novel compounds are a sliver of light in terms of advanced PV and PC applications. The first working devices for both technologies will be presented and discussed, together with the preliminary results obtained with SbSBr.

Acknowledgment

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Session S10: Thin film catalyst for the energy transition [o10-02]

Photoelectrochemical water splitting with ITO/WO_3/$BiVO_4$/CoPi multishell nanotubes enabled by a vacuum and plasma soft-template synthesis

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The development of efficient hydrogen production methods from renewable energy sources is one of the most important current scientific and technological challenges. In this context, the design of new catalytical systems for the photoelectrochemical (PEC) splitting of water based on sustainable materials and fabrication methods is a key factor in the development of these new technologies. Reported strategies to increase photocatalysts efficiency are related to the use of highly porous structures providing active electrochemical surfaces in a large electrolyte-electrode interface. In this work[1], we propose a new kind of multishell nanostructured electrode consisting of indium tin oxide nanotubes (NTs) concentrically covered by sequentially deposited films of WO_3 and $BiVO_3$ acting as metal oxide semiconductor, and CoPi as heterogeneous co-catalyst. Single crystalline organic nanowires are applied as inexpensive and vacuum-processable one-dimensional soft templates compatible with the formation of high-density arrays of NTs directly on a wide variety of commercial substrates[2]. Photoelectrode manufacturing follows a multistep procedure easily implemented at a large scale combining thermal evaporation, magnetron sputtering, and solution dripping processes. This work incorporates a complete structural and physicochemical characterization of the fabricated multishell NTs, and an extensive PEC analysis of the photoexcitation process, the photo-hole kinetic transfer at the interface and the optimal semiconductor thickness ratio. The resulting multishell NTs electrodes outperform by more than one order of magnitude the efficiency of planar electrodes consisting of a layered stack of the same materials. The proposed fabrication strategy offers a general methodology for the synthesis of highly electroactive nanostructured materials suitable for the design and development of complex electrodes for photocatalytic systems, electrocatalysts, sensors, or device charge collectors, among others.

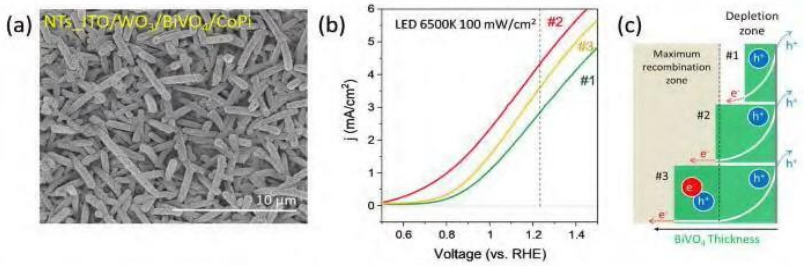

Figure 1. Catalyst SEM microphotograph (a), LSV photocurrent (b), and depletion zone scheme (c).

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Session S10: Thin film catalyst for the energy transition [o10-03]

Phase Selectivity in Sputtered Titanium Dioxide Films Upon Flash-Lamp Annealing

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Titanium dioxide (TiO_2) is a relevant material in many technological applications [1], mostly arising from its photoactivity [2]. The performance of TiO_2materials depend ultimately on the obtained (single or mixed) structural phase and the crystalline quality. Typically, anatase and rutile phases are obtained depending on the processing method and conditions, where the former case seems to provide a higher photoactivity [3]. In this work, we report the impact of millisecond-range flash-lamp-annealing (FLA) on the structural evolution of amorphous TiO_2 films produced by reactive magnetron sputtering. The samples were grown at room-temperature under different oxygen partial pressure (P_{O2}) to study the impact of *as-grown* defects on the phase formation and crystal structure during FLA. The structural evolution has been evaluated by the combination of X-ray diffraction (XRD) and X-ray absorption nearedge structure (XANES). The results reveal that the transition from anatase to rutile appears by increasing the flash input energy (temperature). Interestingly, the anatase to rutile transformation is achieved at lower energies for higher P_{O2}. Detailed analysis of the pristine amorphous structure carried out by XANES reveals the relevance of oxygen defects on the observed phase selectivity. Further, the promotion of the anatase phase results in a marked improvement of the photocatalytic (PC) response of the films, as derived from the degradation of methyl blue and methyl orange organic compounds. The observed PC yield seems to correlate with the size of the anatase grains attained after FLA, providing room for further improvement. In conclusion, this study highlights the potential of FLA to tailor the structure of highly-efficient photoactive TiO_2 films in combination with defect engineering.

Acknowledgement
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Session S10: Thin film catalysts for the energy transition [o10-04]

Effect of Anode Nanostructure on Thin-Film Solid Oxide Fuel Cell Performance

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Thin-film solid oxide fuel cells (TF-SOFCs) are gaining considerable attention for their potential to provide high efficiency, low emissions, and the use of a wider range of materials.[1] Recent research has indicated that the structure of the electrode plays a vital role in determining TF-SOFCs performance. Specifically, the columnar nanostructure of the anode has been identified as a significant parameter affecting efficiency and overall performance of TF-SOFCs.[2] This study aimed to investigate the impact of the anode's nanostructure on TF-SOFCs performance by creating four different types of TF-SOFCs on a nanoporous substrate, anodic aluminum oxide (AAO), using a combination of deposition techniques. The fabrication process involved using glancing angle deposition (GLAD) and co-sputtering techniques to create four types of columnar anode nanostructure such as vertical, slant, zigzag, spiral by changing the azimuth angle of the substrate. The anode was deposited by co-sputtering yttriadoped ceria (YDC) ceramic target and nickel (Ni) metal target. Then, yttria-doped ceria (YSZ) electrolyte was deposited using an yttrium zirconium (YZr) metal target by reactive sputtering. Lanthanum strontium cobalt ferrite (LSCF) ceramic target and gadolinium cerium (GdCe) metal target were cosputtered as a cathode. Finally, a platinum (Pt) target was deposited as a current collect layer. To determine how the nanostructure of the anode impacted performance, four distinct cells were analyzed using several electrochemical methods such as i-V and EIS in pure hydrogen 500℃ condition. Further analysis using FE-SEM, XPS, and XRD revealed that the columnar structure affected the surface triple phase boundary (TPB) of the anode, which in turn influenced the electrochemical performance of the cells. These findings highlight the significance of optimizing the nanostructure of the anode in TF-SOFCs to achieve the highest efficiency and performance. Overall, the study provides valuable insights into the design and optimization of TF-SOFCs for practical applications in energy conversion and storage.

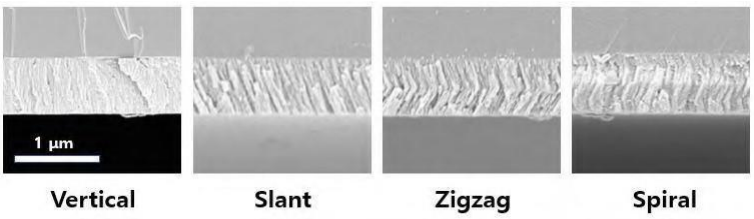

Figure 1. Four different types of anode nanostructures

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Session S10: Thin film catalysts for the energy transition [o10-05]

Low Pt loading electrode for hydrogen production in PEMECs by magnetron sputtering

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The decarbonization of the actual fuel-based energy system has become urgent, so developing and improving feasible alternatives, like H2 production through Polymer Electrolyte Membrane (PEM) electrolysis, has become a priority to move on to a more sustainable system. In PEM electrolyzers, problems related to the catalysts, such as the reduction of their loading, since metals like Pt or Ir are needed to catalyze the reactions that occur inside the electrolyzer, or finding an industrial technique that able the upscaling of electrodes' fabrication for time and cost reduction, need to be solved. The fabrication of PEM electrodes through magnetron sputtering (MS) could fix both problems, given that is a well-established industrial technique for thin film development and also, allows precise control of the morphology and properties of the coatings. In this work, a low Pt loading electrode was developed, through magnetron sputtering, for hydrogen evolution reaction (HER). Through thermogravimetric analysis (TGA), the Pt loading of the developed electrode was obtained, showing a 56% reduction in Pt loading when compared with a commercial Pt black electrode with a Pt loading of 0,3 mg/cm2. Also, electrochemical characterization was done through linear sweep voltammetry (LSV) and cyclic voltammetry (CV). The obtained results are promising, with overpotentials at 10 mA/cm^2 of 66 mV for the commercial electrode and 84 mV for our electrode.

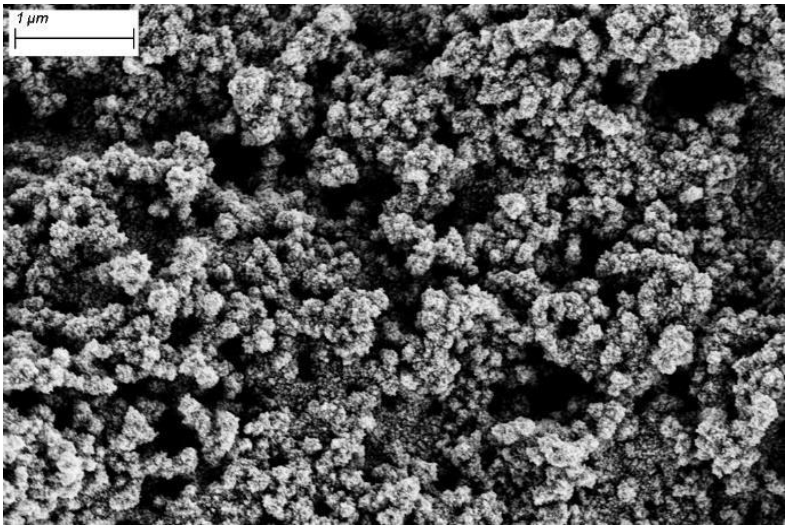

Figure 1. SEM image of a sputtered Pt electrode for HER.

Session S10: Thin film catalysts for the energy transition [o10-06]

Effects of Ni/YSZ Composition on Performance and Carbon Deposition in Syngas-Fueled Thin Film SOFC

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Solid oxide fuel cells (SOFCs) have emerged as a promising technology for clean and efficient energy conversion. The Ni/YSZ anode is widely employed in SOFCs fueled with syngas due to its high activity for electrochemical oxidation of hydrogen and carbon monoxide. However, carbon deposition on the anode surface can cause performance degradation and long-term stability issues.[1] To overcome these challenges, it is crucial to investigate the relationship between the Ni/YSZ composition and the performance and stability of the anode under syngas fuel conditions.[2] In this study, we investigated the effects of Ni/YSZ composition on the performance and carbon deposition of SOFCs operating at 650°C and 750°C using syngas fuel. Ni/YSZ coatings were deposited on YSZ electrolyte substrates using co-sputtering with varying Ni content, and characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and electrochemical impedance spectroscopy (EIS).

Our results indicate that increasing the YSZ content in the anode enhances the electrochemical activity of the anode and improves the cell performance up to a certain ratio. However, beyond an optimal Ni/YSZ ratio, the performance deteriorates, and carbon deposition becomes more severe, which can be attributed to the loss of the Ni skeleton structure.

Overall, our study provides valuable insights into the design and optimization of Ni/YSZ anodes for syngas-fueled SOFCs. The results suggest that the Ni/YSZ composition plays a critical role in determining the performance and stability of the anode. We also observed that increasing the YSZ content in the Ni/YSZ coating can help prevent carbon deposition by reducing the surface energy, but it also leads to decreased electronic conductivity and lower cell performance. Our findings contribute to the development of sustainable and efficient energy technologies by providing a better understanding of the complex processes involved in SOFC operation under syngas fuel conditions.

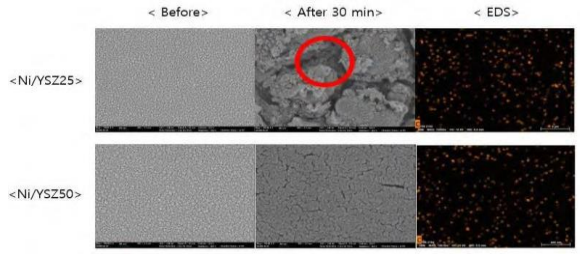

Figure 1. SEM, EDS Analysis for the anode after cell test.

Acknowledgement

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Session S10: Thin film catalysts for the energy transition [o10-07]

Tuning Photoelectrocatalytic Performance of Titania with Atomic Hydrogen Reduction

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One of the main challenges to expand the use of titanium dioxide (titania) as photocatalyst is related to its large bandgap energy and the lack of an atomic scale description of the reduction mechanisms that may tailor the photocatalytic properties. In this contribution, we will show how the photoelectrocatalytic performance of rutile TiO_2 single crystals can be improved upon enhanced light absorption (from the ultraviolet to the near-infrared spectral range) thanks to a controlled reduction and structural rearrangement induced when annealed in the presence of atomic hydrogen. We will demonstrate that both magnitudes behave oppositely: heavy/mild plasma reduction treatments lead to large/negligible spectral absorption and poor/enhanced (x 10) photoelectrocatalytic performance, as judged from the hydrogen evolution reaction (HER) photocurrent. We will also correlate the photoelectrochemical performance with the atomic and chemical structure of the hydrogen-reduced materials by modelling the process with in-situ scanning tunneling microscopy (STM) measurements, which allow us to determine the initial stages of oxygen desorption and the desorption/diffusion of Ti atoms from the surface.

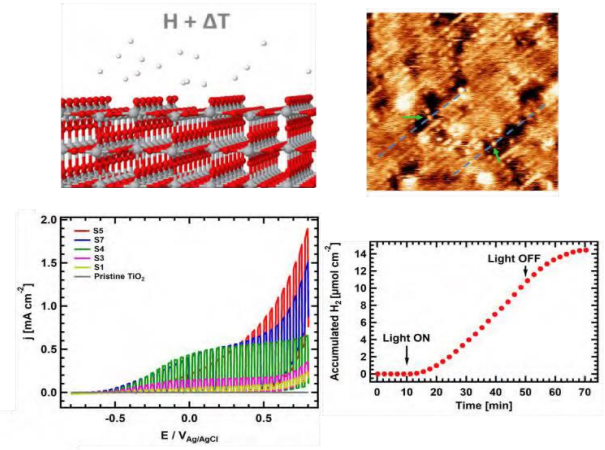

Figure 1. Atomic hydrogen reduction modifies TiO_2 structure and photoelectrocatalytic performance.

Acknowledgement

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Session S10: Thin film catalysts for the energy transition [o10-08]

High-performance Nanocomposite Nickel Cermet Anode on Non-conductive Substrate for Thin Film Solid Oxide Fuel Cells

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Solid oxide fuel cells (SOFCs) have been widely studied owing to their advantages, such as high efficiency and fuel flexibility. However, the high operating temperature of conventional SOFCs leads to several problems, including thermal instability, limited material selection, and long start-up time. To address these issues, it is imperative to lower the operating temperature of SOFCs without deterioration of electrochemical performance. To achieve this, it is required to improve the low ionic conductivity and sluggish reaction kinetics of low-temperature SOFCs.

In this study, thin film solid oxide fuel cells using Ni−GDC, a mixed ionic-electronic conductor (MIEC), were fabricated through magnetron sputtering systems. To precisely control the composition, crystallinity, and surface morphology of the anodes, we deposited NiO−GDC via a reactive cosputtering process. The *ex situ* analyses, including X-ray diffraction (XRD), field emission−/focused ion beam−scanning electron microscope (FE-/FIB-SEM), energy dispersive spectroscopy (EDS), and highresolution transmission electron microscopy (HR-TEM) were conducted to investigate their characteristics. To compare electrochemical performance using the current density−voltage−power density curve (J−V−P curve), we employed the potentiostat. Electrochemical impedance spectroscopy (EIS) was also conducted to identify the performance deterioration source in detail.

Consequently, we successfully optimized the electrochemical performance of Ni-GDC anodebased TF-SOFCs. Our results reveal that the optimized NiO composition in the cermet anode of TFSOFC is higher than that of conventional SOFCs, which showed the most stable structure and highest performance.

Figure 1. Schematic illustration of the reactive co-sputtering process.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. NRF-2022R1A2C3012381)

Session S10: Thin film catalysts for the energy transition [o10-09]

Au – loaded Se – doped porous Ta_2O_5 thin films for enhanced visible-light photocatalytic activity

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In recent years, interest in processing materials with visible light photocatalytic activity has grown due to the need to develop new methods of energy production, pollutant degradation, or water splitting or purification, among others [1,2]. In the present work, porous, thin films of oxygen-deficient Se-doped Ta_2O_5 have been synthesized by the sol-gel method and characterized. Their photocatalytic activity in the degradation of methyl orange has been studied both under solar and UV light and compared with that of compact thin films of Ta_2O_5. The UV photocatalytic efficiency of porous samples is a factor of 10 higher than that of compact samples, which is attributed to their much larger specific surface area. Also, it has been observed that photodegradation under solar illumination occurs exclusively for Se-containing samples. This is attributed to a synergistic contribution of the narrowing of the band gap caused by Se-doping and a suppressed electron-hole recombination due to Se^{4+} associated energy levels, that act as electronic traps.

The effect of Au nanoparticle loading on the structure has also been studied. A synergistic effect has been observed between Se-doping and loading with Au nanoparticles. Our study points to a plausible reduction in radiative recombination at Se^{4+} mid-band levels of the electrons promoted to the conduction band because of the excitation of the Au nanoparticles by the local surface plasmon resonance.

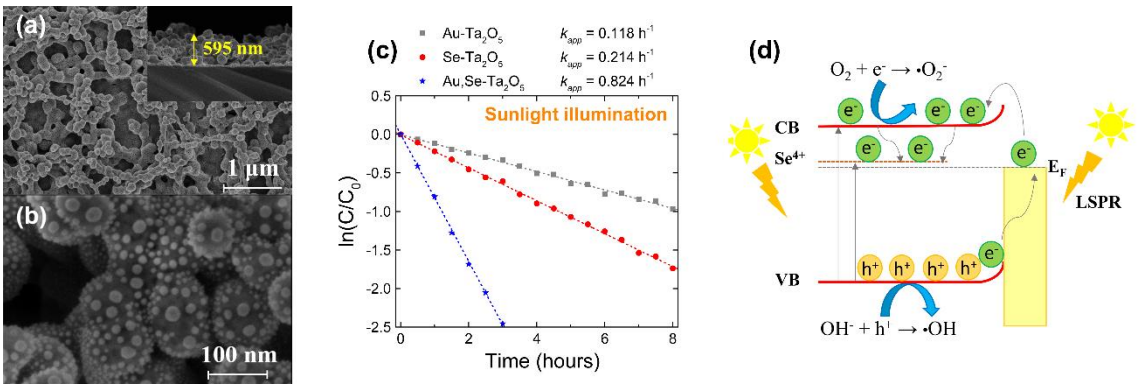

Figure 1. SEM images of the porous Se-doped Ta_2O_5 films (a) before and (b) after Au nanoparticle loading. (c) Temporal evolution of the concentration of methyl orange under solar illumination. Note that $k_{app}(Au,Se\text{-}Ta_2O_5) > k_{app}(Se\text{-}Ta_2O_5) + k_{app}(Au\text{-}Ta_2O_5)$. (d) Proposed mechanism for enhanced visible-light photocatalytic activity.

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Session S11: Thin films for optoelectronics, nanoelectronics, and spintronics [o11-01]

Highly surface and interface sensitive studies of oxidation mechanisms of thin amorphous Si films at room temperature

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Interesting routes to low-temperature formation of ultrathin oxides on a Si surface under UHV conditions were discovered. Due to the electronic and atomic structure of such films several nanometer thick films can be fully oxidized at low temperatures, in contrast to crystalline films where only a couple of layers are oxidized at low temperatures. At room temperature the amorphous film is almost completely inert to oxidation, contrary to films with crystalline surfaces. Highly surface and interface sensitive studies of oxidation mechanisms of Si films is investigated under UHV conditions and with highly controlled and reproducible Si deposition and oxygen exposure conditions. The process involves oxidation of amorphous Si grown at room temperature using distinct architectures, in thicker amorphous Si films (ca.8-20ML) followed by oxidation and intercalating layers of silicon oxide (up to 30 cycles of ca. 1ML SiO_2). The role of the substrate conditions, native oxide, or oxidized Si (111) (7x7) single crystalline surfaces are also investigated. Following the low temperature studies all systems are annealed at different higher temperatures. For the amorphous silicon deposition an electron beam evaporation source was used. All steps of the processes, Si growth and oxidation, were followed insitu by synchrotron photoemission spectroscopy carried out using the SGM-beamline with a SCIENTA analyzer at ASTRID (Denmark). Si 2p core-level- with photon energy of 130 eV and 200 eV and valence band studies with 38 eV and 130 eV are of importance for the understanding of the atomic mechanisms involved and relevant for the oxidation of such ultrathin oxides. Following all steps in-situ the role of the intermediate oxidation states is also revealed. The results obtained for these systems are compared with other architectures of Si-oxides, with a silicon continuous wedge followed by several cycles of oxidation, carried out in the same experimental conditions regarding the UHV chamber, ebeam source and synchrotron beamline [1,2].

Acknowledgement

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Session S11: Thin films for optoelectronics, nanoelectronics, and spintronics [o11-02]

Defect-induced abnormalities in the bulk and surface electronic properties in semiconductor thin films

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Selecting a semiconductor material for a particular electronic application requires careful understanding of its electronic structure, microstructure and thereby induced optoelectronic properties. Moreover, the poor performance of several electronic devices could be attributed to the uncertainty in their electrical properties, attributed to the presence of a large number of native point defects in the bulk. Besides, the surface electrical properties of a thin film play an equally important role as this layer is usually present in a stack, thus affecting the electrical properties of the entire heterostructure and thereby the device efficiency. This is because surfaces could have completely different electronic structures than their bulk owing to the relaxation of the surface atoms. Additionally, appearance of native point defects on a semiconductor surface could completely alter the band structure, further altering the transport properties. Furthermore, surface defects can be harmful as these could act as recombination centres, thereby degrading the device performance. This necessitates the fundamental understanding of these band structures and thereby associated electrical properties for preparing efficient electronic devices.

In this regard, we will discuss the defect-induced modifications in the electronic properties of bulk thin films as well as the anomalies in the bulk and the surface electrical properties of semiconductor thin films, based on a combinatorial approach of experiment and theory. More specifically, here $Cu_{2-x}S$ and SnS are discussed as these are promising low-cost, non-toxic *p*-type semiconductor with suitable band gap for solar absorber applications. Experimentally, both the vacuum as well as non-vacuum-based deposition techniques are used to deposit these thin films, following which a range of characterization techniques are used to do a detailed investigation. First principles DFT calculations are used to understand the fundamentals behind the experimentally-observed anomalies in the surface and bulk electronic structure and their electrical properties. Physicochemical insights developed through this work could help in understanding the transport properties in a heterostructure and then play a significant role in designing high performance devices.

Acknowledgement

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Session S11: Thin films for optoelectronics, nanoelectronics and spintronics [o11-04]

Intensified luminescence performance of Methylammonium Lead Bromide Perovskite films by the introduction of Bathocuproine Organic Additive

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Solution–processed hybrid metal halide perovskites (PVKs) have emerged recently as astounding semiconductors for optoelectronic applications and lightning [1,2]. In particular, they are excellent for emissive applications because they present an efficient luminescence band, reaching quantum efficiencies > 20%. Additionally, they are fabricated by cost – effective and low temperature processes and are therefore presented as economic and green alternativematerials. Nevertheless, several challenges, such as low operational stability, need to be unravel.

In this work, the organic molecule bathocuproine (BCP) has been introduced during the preparation of the perovskite methylammonium lead tribromide ($CH_3NH_3PbBr_3$) ($MAPbBr_3$) by spin coating, with the target of optimizing the luminescent performance of this material [3]. By introducing BCP in the antisolvent step of the perovskite growth, the objective was also to obtain a smoother film with improved morphology, and hence, passivate defects between grain boundaries and obtain pinhole – free perovskite films due to the increment in the density of nucleation seeds [3, 4]. Our results focus on the effect of the polar/antipolar character of the antisolvents (chloroform/toluene), and the mixture with BCP on final morphological, structural and optical properties. The introduction of BCP does not alter the crystalline structure but it induces more oriented films (XRD) and significantly alters film morphology. AFM images shows denser films with reduced grain sizes, both aspects reduce non–radiative recombination due to improved inter-grain interfaces and pin-hole density reduction. In fact, this is confirmed by the observed increase of the photoluminescence (PL) intensity upon BCP addition. Moreover, the short component of the PL decay curves, which is related to the presence of traps at grain boundaries, is reduced with BCP demonstrating that traps associated to defect states, are effectively reduced. BCP also increases the stability of the films maintaining almost unchanged the decay curves after 130 days while decay times are significantly decreased without the additive. These results encouraged us to implement test solution-processed LED devices and higher efficiency is observed in the case of using a polar solvent in the processing of PVK, demonstrating the great impact of the final morphology of the active layer and trap reduction on the performance of the final device.

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Session S11: Thin films for nanoelectronics [o11-05]

Quantitative analysis of hydrogen during metal-insulator transition of rare-earth nickelate thin films

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The rare-earth-element nickelates ($RNiO_3$, R=rare earth element) with a perovskite structure reveal a thermally-induced metal-to-insulator transition (MIT) [1], which has been a topic of intensive studies to date. Recently, it is reported that hydrogen doping to $RNiO_3$ induces MIT [2] and various applications such as sensors and energy conversion devices are proposed. However, the detailed relation between the conductivity and hydrogen concentration is yet to be clarified. In the present study, we have insitu measured the resistance and hydrogen depth profile in $RNiO_3$ thin films.

The samples used in this study are thin films of $RNiO_3$ (R=Sm, Nd, and La) with a thickness of about 80 nm fabricated on either $LaAlO_3$(001) or $SrTiO_3$(001) substrates by pulsed-laser deposition. A meshpatterned Pt layer (10x10 μm^2) with a separation distance of 5 µm was deposited on the $RNiO_3$ films, which act as catalysts to dissociate molecular hydrogen and promote hydrogenation of the films. The experiments were performed at the 2C beam line (base pressure: $2x10^{-5}$ Pa) of Micro Analysis Laboratory in the University of Tokyo. While the samples were exposed to H_2 gas, the sample resistance was continuously monitored. At various hydrogenation stages, as shown in Fig. 1, the hydrogen depth profile was in-situ measured by nuclear reaction analysis via the $^1H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction [3]. Figure 2 shows the depth profile of H measured for $SmNiO_3H_x$ after various hydrogen exposures, where the dip at ~10 nm is due to the Pt mesh and the depth of 15 – 90 nm corresponds to the $SmNiO_3H_x$ film [4]. With increasing H exposure, it is found that the hydrogen concentration x increases up to ~1. When the films of R=Nd and La are exposed to H_2 gas, the depth profiles reveal hydrogenation of the films as $SmNiO_3$. It is noted however that the depth profile for $LaNiO_3$ shows an enhanced intensity at the near-interface region indicating that the near-interface region is preferentially hydrogenated. When the sample resistance is plotted as a function of the hydrogen concentration, the resistance sharply increases at x~0.2 followed by a saturating feature at x~0.5 suggesting that an MIT is induced at x~0.5. Furthermore, the sample resistance is found to decrease at x~1. These results suggest that an insulating state exists at x~0.5 and another insulating state is formed at x~1.0. Based on these results, the electronic mechanism for MIT's is discussed, in which we attribute the insulating states to Mott insulators.

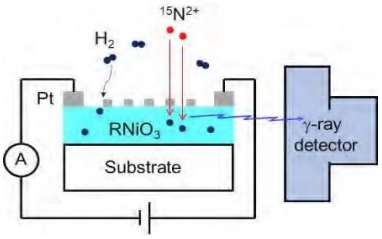

Fig. 1 Experimental setup.

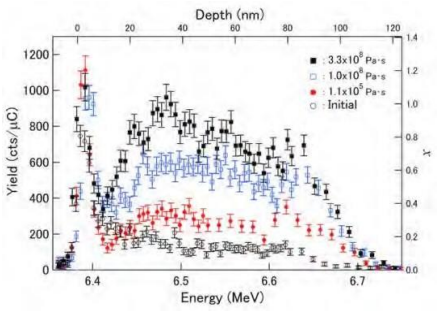

Fig. 2 H depth profile for SmNiO3.

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Session S11: Thin films for optolectronics, nanoelectronics, and spintronics [o11-06]

Thin films of p-block elements for the building of enhanced nanophotonic metasurfaces

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Recently, there has been an increasing interest in the use thin semimetals films from the p-block (Bi, Sb) and their compounds towards the realization of integrated solid state optolectronic, photovoltaic and photonic devices [1, 2]. This is primary due to their outstanding electronic, optical and thermal properties, combined with their low toxicity and their earth crust abundancy. Particularly in terms of their optical properties, the potential range of applications extends from the UV to the mid-IR (MIR), since both Bi and Sb show giant interband transitions in the MIR that endows them with the possibility to exhibit both plasmonic-like resonances (UV-VIS), and Mie-resonances (NIR-MIR). Furthermore, these elements show relatively low melting points, which are accompanied by extreme changes in the permittivity function, fact that can be exploited for the development of low energy consumption, active reconfigurable electronic and photonic elements based on phase-change. Therefore, the development of advanced methods for high quality thin film growth of p-block elements is highly desirable.
In this work, we report our recent developments in the preparation of thin film metasurfaces formed by bismuth (Bi) and dielectric (Al_2O_3) thin films for a wide range of applications. These achievements have been made possible thanks to the successful fabrication of ultrathin Bi films with high optical quality, which are key elements to achieve the desired functionality. The metastructures are fabricated employing pulsed laser-based deposition, a technique that enables excellent efficiency and quality for the deposition of both Bi and dielectric ultrathin films. Atomic force microscopy measurements revealed that our Bi films are continuous, and extremely smooth (0.5nm RMS roughness), even for a few nanometers thickness. On the other hand, transmission electron microscopy analyses reveal that the films are polycrystalline and oriented in the (001) direction. By using spectroscopic ellipsometry, we determined the film permittivity functions [1, 3]. It will be shown how fine tuning of the deposition conditions allows us to tailor the optical properties of Bi by changing topological variables like grain size or filling fraction. In particular ultrathin films can show a very similar bulk-like behavior, which has been attributed to the appearance of highly metallic surface states [3]. Finally, we will show the successful design and fabrication of Bi-based metasurfaces for several photonic application such as perfect absorption in the VIS and mid-IR, generation of structural colors, and for induced optical laser switching of temporal amplitude (reflectance) modulation of light [4-6]. These results show the potential of metasurfaces including Bi thin films for nanophotonic and optoelectronic applications.

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Session S12: Polymeric thin films for organic electronics [o12-01]

Highly Stable Perovskite Quantum Dots (PQDs) for Light Emitting Diodes Applications

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Halide perovskite quantum dots (PQDs) have been applied to various applications such as solar cell, light emitting diodes, and photo detectors due to their excellent opto-electronic properties. However, poor structural stabilities of PQDs is an issue to be overcome. PQDs are mainly degraded by defects through ion migration (intrinsic defects) and detachment of weekly bound ligands from the surface (extrinsic defects). In order to increase both intrinsic or extrinsic stabilities of PQDs, various strategies were suggested. Through post ligand adding or exchange process, both of photoluminescence quantum yield (PLQY) of PQDs and device performance were improved by surface defect passivation. Core-shell structure PQDs were fabricated by using 3-Aminopropyl-triethoxysilane (APTES) as precursor and ligand at the same time to form ultrathin SiO_2 shell of ~2 nm. Structural stabilities were significantly improved, which is higher than that of pristine under polar solvents such as isopropyl alcohol, ethanol, and water. After replacing surface ligand of PQDs with a polymerizable organic ligand through post-processing, structural stabilities of PQDs were also enhanced. And, synergistic effect of core-shell structure and alkali metal doping to structure stabilities was confirmed.

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Session S12: Polymeric thin films for organic electronics [o12-02]

Spontaneous dipole orientation of fluoroalkyl-based molecules in vacuum-deposited films leading to thin film polarization formation

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Molecular orientations in organic thin films strongly influence optoelectronic device performances. Spontaneous polarizations are formed by a spontaneous vertical orientation of permanent dipole moments of vacuum-deposited polar molecules used for organic light-emitting diodes (OLEDs), such as Alq_3 [1]. A deposited dipolar film exhibits a relatively high surface potential called a giant surface potential (GSP) that is proportional to the film thickness, *e.g.*, 28 V at 560-nm-thick for an Alq_3 film, meaning that the surface potential growth rate (GSP slope) is about 50 mV/nm [1]. Recent studies revealed that most of amorphous-type OLED-related molecules form the spontaneous orientation polarization (SOP) [2]. Further, SOP films were applied to vibration power generators as an electret without any additional charging processes [3]. Since the output power of the devices depends on a surface charge density of the electrets, the development of SOP film with high charge density (surface potential) is essential for the efficient energy harvesting. However, the dipole orientation mechanism is unclear and no molecular design has been established to control the SOP film properties such as dipole orientation degrees and GSP slopes.

Here, I propose a molecular design based on fluoroalkyl units to build up a high GSP of deposited films. This study revealed that the fluoroalkyl units preferentially orient to the vacuum-side on the film surface due to the small surface free energy of the fluoroalkyl units, leading molecular dipole alignments to the substrate normal during vacuum depositions [3]. The spontaneous orientations of the fluoroalkyl-based molecules enhanced the dipole orientation degree, and the GSP slope values reached over 200 mV/nm. These results and the simple molecular design will contribute to improvement of power generation efficiency of the vibration-based energy harvesters.

Acknowledgement

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Session S12: Polymeric thin films for organic eletronics [o12-03]

Novel Development for SLIPS of Lubricating Film on PTFE Fibers for Icephobic Applications

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The development of slippery surfaces has been widely investigated due to its excellent icephobic properties. Recently, a different type of ice-repellent structure based on slippery liquid-infused porous surface (SLIPS) has attracted increasing attention for being a simple and effective passive ice protection. These surfaces are well known for exhibiting very low ice adhesion values (τice <20kPa) [1].

In this work, the electrospinning technique has been used for the fabrication of Polytetrafluoroethylene (PTFE) fibers in order to obtain superhydrophobic (SHS) porous coatings on samples of the aeronautical alloy AA7071. Due to the high fluorine-carbon bond strength, PTFE shows high resistance and chemical inertness to almost all corrosive reagents as well as extreme hydrophobicity and high thermal stability. However, these unique properties make PTFE difficult to process. For this reason, to develop PTFE fibers, the electrospinning technique has been used by an PTFE nanoparticles (nP PTFE) emulsion with addition of very small amount of polyethylene oxide (PEO) followed with sintering process (380°C for 10 min) to melt the nP PTFE together and form uniform fibers. Once the porous matrix of PTFE fibers is place, a SLIPS is obtained by filling the micro/ nanoscale structure with lubricating oil instead of air in the SHS. On one hand, the experimental results show a high-water contact angle (WCA) ≈150° and low roll-off angle ($\alpha_{roll\text{-}off}$) ≈ 22° for SHS porous coating and a decrease of the WCA ≈ 100° and very low $\alpha_{roll\text{-}off}$ ≈ 15° for SLIPS coating. On the other hand, the ice adhesion results show 65 kPa in the case of SHS and 4.2 kPa for SLIPS. These results imply a significant improvement of this type of coatings [2] due to the combined effect of fibers PTFE and silicon oil lubricant.

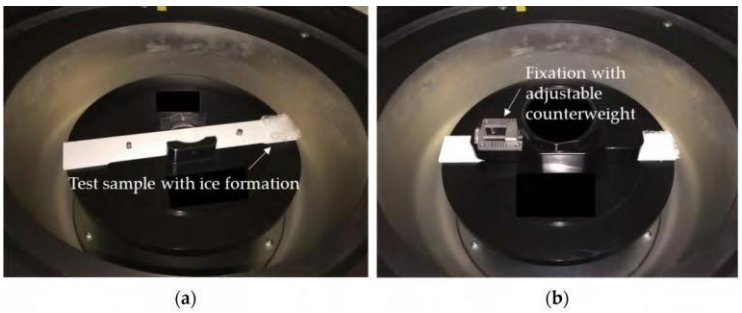

Figure 1. (a) test sample with ice formation placed in the centrifuge; (b) test sample after fixation [3].

Acknowledgement

This work was supported by the Project RTI2018-096262-B-C41–MAITAI, funded by MCIN/AEI/10.13039/501100011033 and by ERDF "A way of making Europe". Grant PRE2019-090656: funded by MCIN/AEI/10.13039/501100011033 and by ESF "Investing in your future". Project

Session S13: Magnetic, piezoelectric thin films [o13-01]

Oxygen orbital magnetic moment in spinels studied by oyxgen K-edge dichroism

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We have been growing highly perfect micrometer wide and tens of nanometer thick spinel transition metal oxides on Ru(0001) by means of high-temperature oxygen-assisted molecular beam epitaxy. In particular we have grown iron (i.e. magnetite) [1], iron rich cobalt [2] and nickel ferrite spinels [3]. Such microcrystals show magnetic domains which are orders of magnitude larger than those observed in high quality thin films. In this work we discuss the information that can be obtained from the anion K edge instead of the cation $L_{2,3}$ edges which we have used in the past. The anion edge shows significant circular dichoism in x-ray absorption. However only information about the orbital moment can be obtained from it. We have succesfully measured the dichroism in the oxygen edge for iron-rich cobalt and niquel ferrites, while we have not observed it in magnetite. The magnetic domains are observed at selected energies at the oxygen edge, and show a ferromagnetic coupling to the octahedral cation magnetic domains. We have performed ab-initio calculations to estimate the magnetic moment induced by the cations on the oxygen anions, which suggest smaller values for the orbital moments than those measured experimentally.

Figure 1. Image of the dichroic O K-edge on a cobalt ferrite island. The field of view is 10 µm.

Acknowledgement
This work is supported by the Grants PID2021-124585NB-C31 and TED2021-130957B-C54 funded by MCIN/AEI/10.13039/501100011033, by "ERDF A way of making Europe" and by the "European Union NextGenerationEU/PRTR".

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Session S13: Magnetic/piezoelectric thin films [o13-02]

Iron semi-shells in vortex state for biomedical applications

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Hybrid nanoparticles have raised great interest for different biomedical applications since they combine properties of different materials in the same structure. Those that have magnetic and plasmonic components are especially interesting, due to the possibility of achieving both magnetic and optical properties, which are potentially useful for multimodal bioimaging, hyperthermal therapies and magnetically driven selective delivery [1]. Moreover, the use of these nanoparticles in cancer treatments, such as hyperthermia or magneto-mechanically induced damage, can be a great advance since they allow a more localized treatment and, therefore, less damage to healthy tissues [2].

In this work, magneto-plasmonic nanoparticles consisting of a 20-nm-thick semi-shell of iron were grown on a polystyrene nanosphere (acting as idle core) and covered by 3-nm-thick Pt shell to avoid oxidation. Then a gold layer was grown over the previous layers. Iron provided the magnetic properties and Au the plasmonic ones. By performing micromagnetic simulations with MuMax3, vortex state was observed in these systems, which made them useful for Magneto-mechanically induced damage as well as hyperthermia treatments. Langmuir-Blodgett technique allowed to form monolayers of polystyrene nanoparticles with diameters of 1 micron and 400 nm [3]. Iron and Pt were deposited by rf magnetron Sputtering. These nanoparticles were characterized with scanning electron microscopy (SEM), X-ray diffraction (XRD); and their magnetic properties were accessed by magnetometry techniques and compared to the micromagnetic simulations. The nanoparticles were released from the substrate by chemical etching to study their biocompatibility with a glioblastoma multiform cancer cell line.

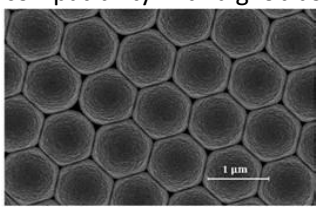
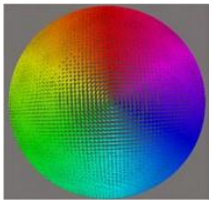
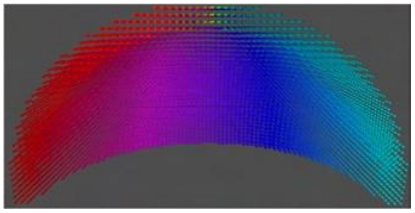
a)  b)  c) 

Figure 1. a) Example of a SEM image of a Langmuir-Blodgett monolayer of 1 µm nanoparticles. b) Example of micromagnetic simulations of a shell of Fe with 400nm of diameter and 20nm of thickness; orientation of magnetics moments, top view, c) side view.

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Session S13: Magnetic/piezoelectric thin films [o13-03]

Magnetic Domain Structure of Ferrimagnetic FeGd Thin Films

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The development of techniques for magnetization switching under the action of currents instead of magnetic fields is necessary for the design of faster and power-efficient magnetic memories. Ferrimagnetic materials have a small net magnetization and show ultra-fast magnetization dynamics near the compensation temperature, at which the net magnetization vanishes [1, 2, 3]. These properties offer multiple advantages over commonly used ferromagnetic materials. To integrate ferrimagnets into future spintronic devices, it is essential to have a deep understanding of the magnetic domain structure and its temperature evolution near the compensation temperature.

For this purpose, we have investigated the temperature evolution of the magnetic domains of several ferrimagnetic ultrathin films such as Fe/Gd and Gd/Fe bilayers and FeGd alloy grown on a W(110) substrate. Samples were characterized by means of synchrotron-based PEEM measurements including XAS spectra and XMCD images at the Gd $M_{4,5}$-edge and Fe $L_{2,3}$-edge, as well as XPS measurements of the Gd 4f, Fe 3p and W 4f core levels. These measurements allowed us to determine the chemical composition and the evolution of the magnetic domain structure as a function of temperature up to the Curie temperature for both Fe and Gd sublattices (see Figure 1).

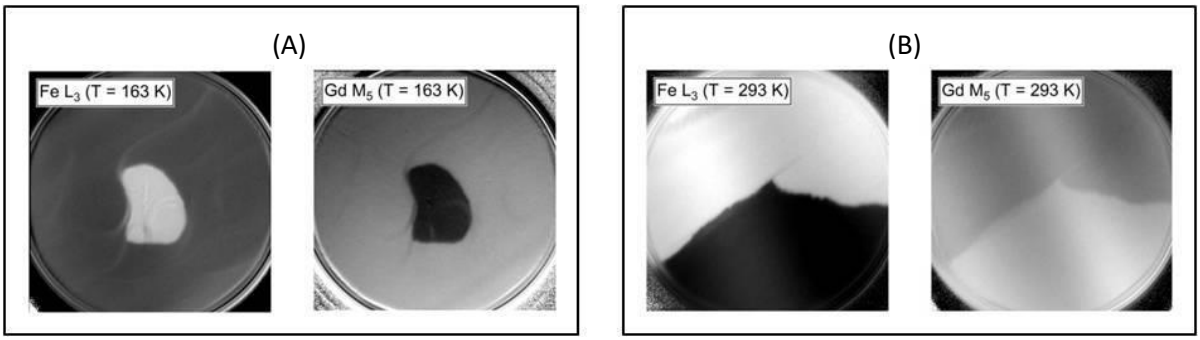

Figure 1. XMCD images (FOV = 10 µm) of a FeGd alloy (A) and a Gd/Fe bilayer (B) taken at different temperatures at the Fe L_3-edge and at the Gd M_5-edge.

Acknowledgement

We thank the Ministerio de Ciencia e Innovación PID2020-117024GB-C43 project and ELETTRA User Travel program for financial support.

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Session S14: Thin films for vacuum and space applications [o14-01]

The realization of the coating plant for the segments of the primary mirror of the Extremely Large Telescope (ELT) in Chile.

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The primary mirror of the Extremely Large Telescope (ELT) currently under construction in Chile by the European Southern Observatory (ESO) has a diameter of 39 meter and is composed of 798 individual coated mirror segments. The segments are quasi-hexagonal, about 1.44 meter in size and 50 mm thick. Each segment is permanently mounted to a support structure containing also electrical components like motors, sensors etc

The magnetron sputtering technology used to deposit the protected silver based reflective layer on each mirror segment is inspired by coating equipment traditionally used within the glass industry. The equipment will be used to coat the mirror segments and will also refresh the mirror surface periodically during the lifetime of the telescope to maintain an acceptable level of reflectivity and low level of diffusion.

The design of a protective skirt to be installed prior to the coating process is required to protect the mirror assemblies from back sputtering. The requirement of a base pressure of 3.10-7 mbar, despite the high outgassing rate, in order to allow for the application of coatings with optimal reflection in the visible and infra-red spectra is another particularity to be taken into account for the design of the suitable coating equipment.

Session S14: Thin film for vacuum and space applications [o14-02]

Electron Emission Yield of Ordered vs Disordered Structured Surfaces

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Secondary electron emission under electron bombardment is a relevant phenomenon in different technologies such as high power RF devices for space or large particle colliders. In this work, we present the study of the secondary electron emission yield (SEY) and the influence of the angle of incidence of electrons for Ag, Cu, Ni, Fe, Fe_2O_3 and Ti micro-nanostructured surfaces (Fig.1a-e). In particular,
porous metallic Ag, Cu, Ni disordered coatings were grown by electroless on AA2024-6061 Al alloys, whereas Ag, Fe, Fe_2O_3 coatings showing ordered column growth were obtained by ebeam evaporation. Micro-textured Ti surfaces were also produced by ion bombardment. We have characterized the samples by scanning electron microscopy (SEM), x-ray photoemission spectroscopy (XPS) and thermal emissivity measurements. SEY measurements were performed as a function of the primary energy from 0 to 1keV and the incidence angle, □, from 0 to 65°. SEY increases as a function of □ and depends on surface composition and roughness. For a constant primary energy, SEY(□) shows a minimum at normal electron incidence for smooth surfaces. In the columnar structured coating, the value of this critical point shifts towards higher □ values depending on the columns orientation and tilt angle, Fig.1e. The particular formation of aligned features in the surface reduces the SEY when the irradiation is in the direction parallel of their long axis and also depends on the aspect ratio. In the case of amorphous rough coatings, SEY does not depend on the incidence angle of the primaries. Disordered and flat surfaces show the minimum (0%) and maximum SEY (40%) variation with the incidence angle, respectively. A model based on the morphology of the samples using the Lambert cosine angular distribution of the secondary electrons and the Bruining formula for the SEY as a function of the angle of incidence have demonstrated a good fit to the experimental data, Fig.1e.

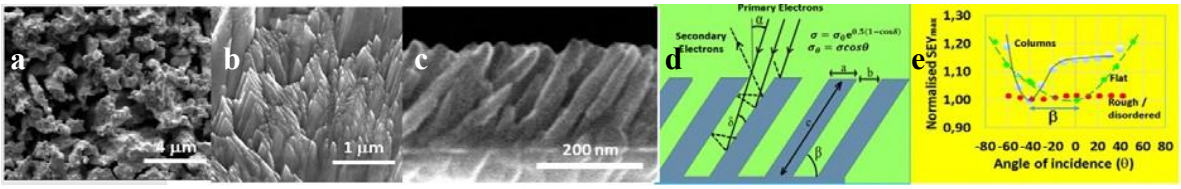

Figure 1. FE-SEM images of a disordered silver coating (a) and two different structured surfaces for Ti and Fe (b-c). Interaction of electrons with the coating pillars (d), SEY as a function of □ at 300 eV (e).

Acknowledgement

This work is part of the Spanish Project PID2021-122761OB-I00 funded by MCIN/AEI/10.13039/501100011033 and EU H2020 program under grant agreement 899352 (FETOPEN-01-2018-2019-2020 - SOUNDofICE), PID2020-112620GBI00.

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Session S14: Thin film for vacuum and space applications [o14-03]

GaAs Based Flexible Solar Cells Grown by Molecular Beam Epitaxy

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There is an increasing demand for high-efficient GaAs-based group III-V solar cells in satellite-space, aviation and similar strategic apllications. Although the GaAs-based single and multiple junction group III-V solar cell technologies have record efficiencies, they are mainly used in special applications where the Watt/weight value is a priority rather than the production costs. The largest input, accounting for 80-85% of these high costs, is expensive substrates. Recently, flexible thin film cell technology based on the epitaxial lift-off method has attracted attention in order to minimize costs. In this approach, based on the separation of the epilayer from the substrate and transferring it to another platform, the production cost can be reduced at several orders as the substrates can be used multiple times. In addition, the cells produced by this method are much more functional in applications due to the advantages brought by their flexibility, having higher temperature and radiation tolerances and record Watt/weight compared to substrate-based solar cells. It is important to use much cheaper Si substrates instead of GaAs substrates to further reduce the cost.

In this study, high-efficient GaAs-based group III-V solar cells were grown by molecular beam epitaxy on both GaAs and Si substrates. The grown structures were then transferred to a flexible platform by epitaxial-lift-off method and the solar cells were fabricated by standard photolithography steps (Figure 1). We achieved a cell efficiency (active area) of 20% and 9% for the single-junction GaAs based flexible solar cells grown on GaAs and Si substrates, respectively. We believe that the Si substrate is a promising substrate for fabricating low-cost and high-efficient GaAs-based solar cells for the future applications.

Figure 1. Fabricated GaAs based flexible solar cells.

Acknowledgement:
This study was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK) under the grant number 118M055 and 120F222 and by Eskişehir Technical University under the project number 21DRP123 and 22GAP296.

Session S14: Thin film for vacuum and space applications [o14-04]

NIST on a Chip, Quantum Based Sensors for Vacuum Metrology and Beyond!

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This oral presentation covers a bit of vacuum metrology history of how we got to where we are today and gives a forward-looking vision for the future of measurement science and its important role in thin film technology and how quantum-based measurements and photonics has the potential revolutionize sensor technologies. The NIST on a Chip program (NOAC) is briefly introduced in this context of the world-wide redefinition of units that occurred on May 20th, 2019. The re-definition of units is now aligned with physical constants of nature and fundamental physics which. The re-definition of the SI units enables new realization routes with quantum-based sensors and standards to realize the units for the pascal (pressure and vacuum) and the kelvin (temperature). These quantum-based systems; however exciting, do raise new challenges and several important questions: Can these new realizations enable the size and scale of the realization to be miniaturized to the point where it can be imbedded into everyday products? What will be the role of metrology institutes in the is new ecosystem of metrology and measurement? [1].

The technical core of the lecture will be a deeper dive into new research on measurement methods for pressure, the Fixed Length Optical Cavity (FLOC) and for vacuum, the Cold Atom Vacuum Standard (CAVS) and a photonic method for measuring temperature. What is exciting about many of these new measurement approaches is that they are both primary (relying on fundamental physics), are quantum-based and use photons for the measurement readout which is key for taking advantage of the fast-growing field of photonics. The FLOC will enable the elimination of mercury barometers pressure standards worldwide and the CAVS will be first primary standard for making vacuum measurements below 1.3×10^{-5} Pa. Photonic bases methods for realizing temperature will eventually enable the elimination of fixed points that underlie the current ITS-90 temperature scale.

Figure 1. QUANTUM based System of Units for Pressure- A Fixed Length Optical Cavity (FLOC) prototype is held by Jay Hendricks and NIST. The FLOC is a new way to realize and measure pressure with light-matter interactions (refractive index) of a gas that will enable the world-wide elimination of mercury manometers. Dr. Hendricks is President-Elect for IUVSTA (International Union of Vacuum Science, Technique and Application). Photo Credit: NIST.

Acknowledgement

Authors Acknowledge the numerous NOAC principal investigators (PIs) and their teams that contributed to this large body of work.

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Session S15: Beyond thin films: low dimensional materials [o15-01]

The Band Structure of Two-Dimensional Hexagonal Boron Nitride on Au Coated Rh(111) Surface Studied by Momentum-Microscopy

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The electronic structure of 2D hexagonal boron nitride (h-BN) on Au coated Rh(111) surface was studied by momentum-microscopy. In addition we verified the surface structure by low energy electron diffraction (LEED) and its chemical composition by X-ray photoelectron spectroscopy (XPS). The h-BN monolayer on Rh(111) is characterized by a periodically undulated morphology ("nanomesh"), consisting of weakly and strongly interacting regions ("wires" and "pores", respectively) [1]. We experimentally proved by XPS that the nanomesh can act as a template toward the subsurface: Au atoms are accumulated with strong preference below the wire regions due to the stronger interaction of h-BN with Rh in the pores. The nanomesh morphology on Rh(111) resulted in energetically splitted bands, in accordance with literature [1], and replica states were also observed. With increasing Au content this complex band structure was gradually transformed into a simpler one, typical for planar h-BN. NanoESCA measurements revealed the presence of new states in hBN/Au/Rh(111) samples not typical either for bulk Au(111) or for h-BN (Fig.1.a); these are assigned to the thin Au film in contact with Rh. Constant energy slices demonstrated the shape of h-BN bands with unprecedented details: the strong interaction of h-BN and Rh in the pores led to significant changes in the □ band compared to the weakly interacting wire regions (Fig.1.b).

a)

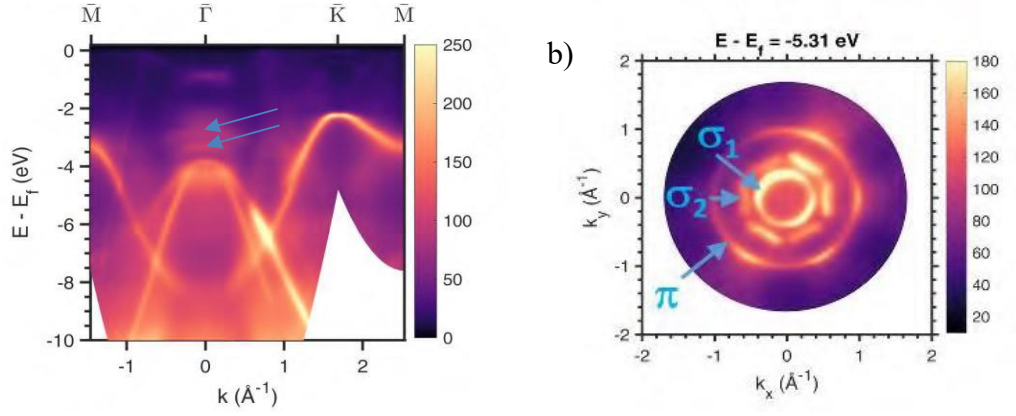

Figure 1. a) Cross section of the whole momentum space of h-BN/1.5MLAu/Rh(111) along the M_{BN}-□-K_{BN}-M_{BN} triangle with new bands at ~3eV; b) Constant energy slice of h-BN/1.5MLAu/Rh(111) at E_b=5.31 eV; FoV: 4.3 1/Å

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Session S15: Beyond thin films: low dimensional materials [o15-02]

Highly porous metal/metal-oxide nanoparticle-based coatings produced using gas aggregation sources of nanoparticles

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Due to their low cost, chemical and thermal stability, and advantageous electronic, optical or bioresponsive properties, metal-oxides (MeO) have become irreplaceable materials in an impressive range of modern technologies, such as (photo)catalysis, sensing, detection or energy harvesting. In many cases, the intrinsic properties of MeO may be enhanced by their nanostructuring that increases the specific surface and facilitates physicochemical phenomena like adsorption and diffusion of chemical species. In addition, further improvement of the functionality of metal oxides is possible if they are doped/combined with other materials. A typical example is the combination of MeO with plasmonic metals that allows for the activation of visible light excitation of MeO and, in this way, improves the photocatalytic performance of MeO-based materials. This study introduces a novel plasma-assisted strategy for producing transparent and nanostructured two component metal/metaloxide nanoparticle-based coatings, which employes magnetron-based gas aggregation sources of nanoparticles. As it will be shown, two principal strategies may be used. In the first and simpler one, the gas aggregation source is used to produce highly porous films composed of MeO nanoparticles. The surface of such produced nanoparticle films is subsequently decorated with metallic nanoislands produced by conventional sputter deposition. In the second investigated approach, the MeO nanoparticles and metal nanoislands are deposited simultaneously that leads to the formation of porous nanoparticle-based structures with metallic nanoislands homogeneously distributed in the entire cross-section of the film (see **Fig.1**). Furthermore, the size/number of metallic nano-islands can be adjusted by changing the ratio of MeO nanoparticles and metallic nano-islands deposition rates, which in turn allows for controlling the functional properties of resulting films. This result thus paves the way for the solvent-free and cost-effective production of nanomaterials with tailor-made properties for future applications that will be discussed.

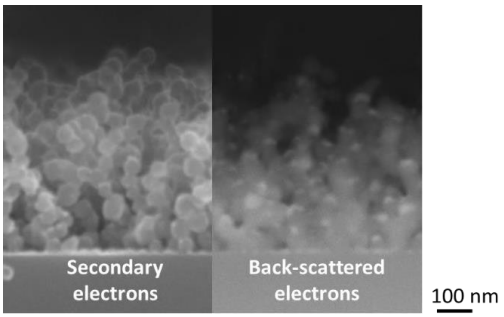

Figure 1. SEM image of cross-section of Ag/TiO_2 nanoparticle-based film composed of TiO_2 nanoparticles (40 nm in size) decorated with Ag nano-islands (bright spots in BSE image).

Acknowledgement

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Session S15: Beyond thin films: low dimensional materials [o15-03]

Epitaxial growth and characterization of SnSe phases on Au(111)

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2D layered IV-VI metal monochalcogenides attract great interest due to their potential applications in nanoelectronics as an alternative to conventional semiconductors [1-3], while their inertness and flatness make them interesting for surface science studies. Among them, Tin Selenide (SnSe) stands out due to its electronic and optical properties derived from its different crystallographic phases. We present a combined experimental and theoretical structural and electronic characterization of epitaxial SnSe grown on metallic Au(111) substrate. We report the formation of almost defect-free 2D layers that exhibit a coverage-dependent transition from a metallic β-SnSe to a semiconducting α-SnSe phase. Thanks to the combination of scanning tunneling microscopy/spectroscopy, non-contact atomic force microscopy, X-ray photoelectron spectroscopy/diffraction and angle-resolved photoemission spectroscopy, complemented with density functional theory calculations, we demonstrate that the strong interaction with the substrate allows the stabilization of the previously experimentally unreported metallic β-SnSe, while the ultra-thin films of orthorhombic α-SnSe are structurally and electronically equivalent to bulk SnSe.

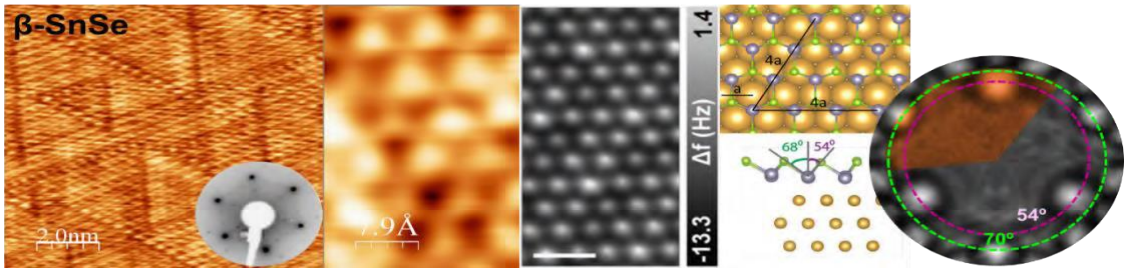

Figure 1. Epitaxial growth and characterization of the β-SnSe phase on Au(111).

Acknowledgement

This work has received funding from the Spanish MCIN/AEI/10.13039/501100011033 and by the "European Union NextGenerationEU/PRTR" (PID2020-113142RB-C21 and TED2021-129999B-C31), and from Comunidad de Madrid (FOTOSURF-CM, Y2020/NMT-6469).

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Session S15: Beyond thin films: low dimensional materials [o15-04]

LiCl photodissociation on graphene: a new route for lithium intercalation

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Lithium-ion chemistry on graphene (Gr) keeps gaining importance due to its potential applicability on the improvement of lithium-ion batteries. The most important contributions, however, have been based on wet chemistry approaches. In the present work, we explore an alternative route, previously developed by our group [1], where lithium intercalates into graphene by photon irradiation. After the growth of LiCl thin films on top of graphene on Ir(111), we expose the system to soft X-ray photons and this leads to a physico-chemical reaction cascade. LiCl photodissociates and we observe a fast chlorine desorption while lithium follows a complex sequence of intercalation processes: it first intercalates and forms an amorphous structure between graphene and iridium. When irradiation time increases, it forms a Li (1x1) surface reconstruction. This ordered structure evolves upon extensive photon irradiation and, for sufficiently long exposure times, lithium promotes within the metal substrate. Finally, we are able to recover the pristine Gr/Ir(111) system by a thermal annealing that allows lithium desorption. We have followed in real time the photochemical processes (schematically shown in figure 1) by a multi-technique characterization with a Photoemission Electron Microscopy/Low-Energy Electron Microscopy PEEM/LEEM. We have studied the structure evolution by means of Low-Energy Electron Diffraction (LEED), the chemical evolution by means of XRay Photoemission Spectroscopy (XPS) and changes in the electronic band structure with a microspot Angle-Resolved Photoemission Spectroscopy (μ-ARPES) [2].

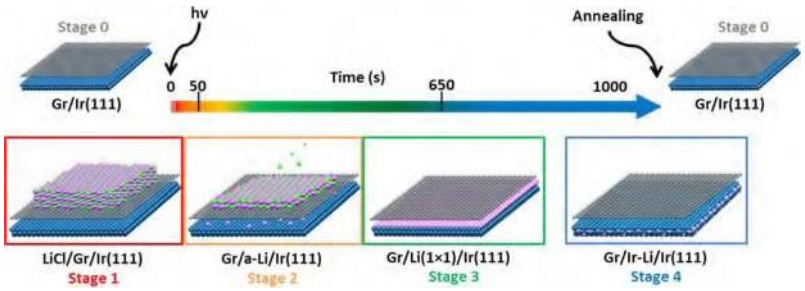

Figure 1. Schematic view of the evolution over time and exposure of the irradiated LiCl/Gr/Ir(111) system. The characteristic irradiation times are given in the upper arrow, being t=0 s the beginning of the irradiation.

Acknowledgement

This work was supported by the EU Graphene Flagship funding (Grant Graphene Core3 881603), the Spanish MICINN (MAT2017-85089-C2-1R, PID2020-115987RJ-I00 and PID2020-113142RB-C21) and the EU via the ERC-Synergy Program (Grant ERC-2013-SYG-610256 NANOCOSMOS), and the European Structural Funds via the FotoArt-CM project (P2018/NMT-4367).

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Session S15: Beyond thin films: low dimensional materials [o15-05]

Grapevine Varietal DNA Identification on a Portable Graphene Sensor Chip

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It has been shown [1,2] that integrating DNA analysis with 2D materials offers an advantageous pathway toward ultrasensitive DNA detection. In particular, monolayer graphene provides an optimal test bed for nucleic acid detection with single-base resolution [2]. Graphene's ultra-thinness provides a large surface area that, upon functionalization, possesses multiple sites for DNA immobilization and efficient detection. Its highly conjugated electronic structure, high carrier mobility, zero energy bandgap with the associated gating effect, and chemical inertness explain graphene's superior performance. Identifying grape varieties in wine, grape musts, and juices is of great interest in enology and the fight against counterfeiting. However, these matrices' complexity and low DNA content make this analysis particularly challenging. Here, we present a DNA-based analytic tool for grapevine varietal discrimination using an integrated portable biosensor based on a single-layer graphene field-effect transistor array. The system comprises a graphene chip operated under liquid gating and connected to a miniaturized electronic readout. The platform can distinguish closely related grapevine varieties, thanks to specific DNA probes immobilized on the sensor, demonstrating a high specificity even for discriminating single nucleotide polymorphisms, which is hard to achieve with a classical end-point PCR or qPCR. The sensor exhibits a dynamic range of 1 aM to 0.1 nM and a LoD of ~0.19 aM. The reported DNA biosensor provides a promising way toward developing decentralized analytical tools for winegrapes and their derivatives. Moreover, it paves the way for DNA detection in Point-of-Care solutions that, coupled with data acquisition and processing techniques, e.g., AI, can provide reliable data in many applications.

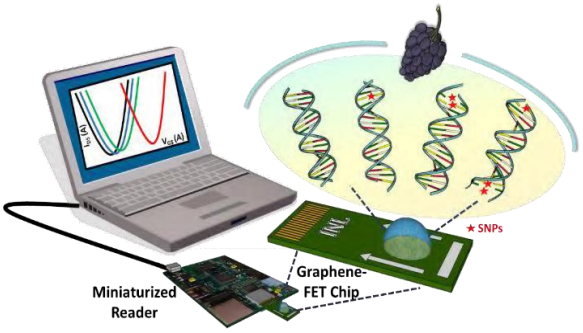

Figure 1. An artist's view of the graphene DNA detection platform.

Acknowledgment

PORTGRAPHE, FCT, Portugal (PTDC/BIA-MOL/31069/2017); SMARTgNOSTICS PRR Plan and NextGenerationEU Fund (C644915155-00000024). M.Martins for the electronic platform construction.

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Session S15: Beyond thin films: low dimensional materials [o15-06]

Black phosphorus analogue – SnS/CdS multidimensional structure for hydrogen evolution visible light photocatalyst

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Recently, the world needs sustainable green energy, and the world is paying attention to hydrogen as an energy source. Although there are still limitations such as low efficiency and stability in green hydrogen production, it will be a technology that needs to be commercialized in the future considering on environmental friendly condition & industry. The CdS, SnS, and SnS_2 materials are similar to black phosphorus (BP) and have a curved honeycomb structure similar to BP as well. The energy bandgaps can be adjusted according to the thickness as well as the electrical and optical properties. Specifically, SnS can absorb a wide range of visible light because its electron affinity is sufficiently low to generate hydrogen from water and its ionization potential is small.

In study, therefore, we synthesized CdS/SnS/SnS_2 and SnS/SnS_2 nanocomposites with 0D/2D multidimensional structures by using hydrothermal and ultra-sonication methods, and demonstrated that when the bandgap of SnS is wider than that of bulk materials, the nanocomposite materials showed good performance in hydrogen production of photocatalytic reactions under the visible light condition. The SnS/SnS_2 acts as an efficient catalyst by developing a *p-n heterojunction*, facilitating the further transfer of photogenerated electrons from the conduction band (CB) of SnS to the CB of SnS_2. When CdS comes into contact with SnS_2, however, electrons from the CB of SnS_2 move to the CB of CdS under the action of the built-in electric field. On the other hand, holes in the valance band (VB) of CdS tend to migrate to the VB of SnS_2, and more tend to migrate to the VB of SnS. As a result, a double charge transfer system is established, which improves the good separation of electron-hole pairs with photocatalytic performance.

Acknowledgement

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Session S16: Industrial applications of thin film technology [o16-01]

Manufacturing and Characterization of Smart Surfaces with Integrated Thin Film Sensors using Femtosecond Laser Scribing

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A novel approach is presented for manufacturing smart surfaces by combining Magnetron Sputtering (MS) and Laser Scribing (LS) techniques. Thin film sensors/actuators can be embedded on the surface of components by depositing a 2-3 µm insulator layer, followed by a 0.5-2.0 µm metallic conductor layer using MS. Alternatively, a 5-10 µm sol-gel coating or a 10-30 µm dielectric lacquer can be used as an insulator layer deposited by spray coating. The metallic conductor is selectively removed by LS, drawing a circuit that is completely isolated from the piece. The femtosecond laser with a wavelength of 517 nm allows for quick and accurate manufacturing of sensors with approximately 30 µm space resolution. The sensors' type can be tailored by modifying the MS and LS parameters and selecting appropriate coating materials. In this work, two types of embedded sensors were tested: resistive temperature detectors made of Al, Ti, W or Cu, and strain gauges made of NiCr. The embedded sensors are highly precise and do not require adhesives or polymer foils, thus minimizing the effects of humidity, organics, or oxygen. Additionally, the sputter sensors can be located in components with complex geometries, making them highly versatile.

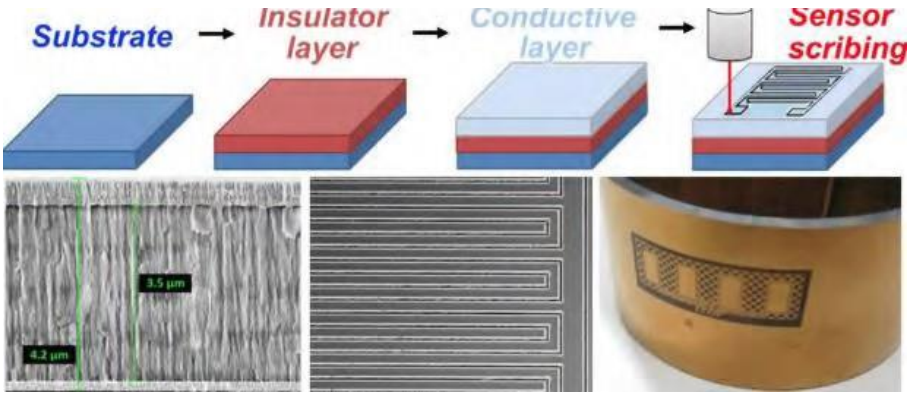

Figure 1. Smart Surfaces fabrication via MS and LS

Session S16: Industrial application of thin film technology [o16-02]

Sol-Gel Coating for Levelling and Easy to Clean Multi-layer Systems.

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Ultrafast-cured sol-gel coating research (by means such as UV light [1] or thermal NIR) without requiring high thermal hardening processes has been the center of attention nowadays. Employing this methodology, it is possible to achieve very interesting properties on the surface of materials. The coatings obtained present high chemical and thermal stability, less harm to the environment, lower processing costs, and higher rates of hardening simply by choosing and combining the correct precursors of the formulation and the suitable application and curing conditions.

We report here a simple methodology for the functionalization of different surfaces, like a leveling layer to smooth the surface of low-cost stainless steel [2] or an "easy to clean" top coat. When this methodology is combined with other coating techniques like PVD, we can obtain multilayer systems to reach interesting features on the selected materials. The formulation is also well defined for scaling up the process, so it is possible to perform a continuous coating in large areas by employing a specific pilot plant installed at our organization. In addition, the sol-gel solution was studied in order to guarantee a long service life before deposition, focusing on industrial applications involved in the automotive, domestic, and machine-tool sectors.

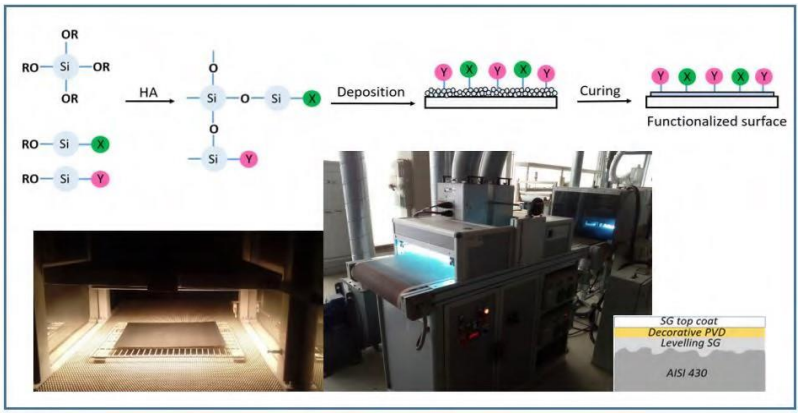

Figure 1. Sol gel coating technology and ultrafast curing equipment at Idonial.

Acknowledgement

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Session S16: Industrial application of thin film technology [o16-03]

Characterization of Tribological Properties of TiB_2 and MoO_x Magnéli-Phase Coatings Deposited by PVD-HIPIMS for Industrial Applications in Aluminum Processing

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Aluminium alloys possess a wide range of advantageous properties such as corrosion resistance, excellent mechanical properties, low density, and high thermal and electrical conductivity. This makes them ideal materials for use in various applications across several industries, including automotive, aeronautical, and energy sectors, among others. However, processing these alloys presents significant challenges. At room temperature, they exhibit poor formability, and high-temperature processing technologies such as warm/hot forging, high pressure die casting or extrusion can result in galling and tribological issues, which lead to severe tool degradation and high energy costs that penalize the performance of these processes [1].

In this study, PVD-deposited thin films are proposed as a promising technology to enhance the performance of these industrial processes, with the goal of reducing wear rates and coefficients of friction at medium-high temperatures while also increasing the chemical inertness of tool surface. Specifically, TiB_2 and Magnéli-phase MoO_x coatings [2] generated by PVD-HIPIMS were compared with commercial coatings and uncoated tool steels to assess their effectiveness. Chemical composition, hardness (measured through nanoindentation), adhesion, and tribological tests were carried on both coated and uncoated samples. Additionally, a specific test involving the immersion of coated and uncoated pins in melted aluminum was conducted to analyze the amount of metal adhered to the surface of the dummies after 48 hours.

Acknowledgement

Research funded by the Ministry of Science and Innovation through the Center for Industrial Technological Development (CDTI), contract number CER-20191003, within the framework of the «Cervera Technology Centers of Excellence» program.

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Session S16: Industrial application of thin film technology [s16-04]

NIR optofluidic device for liquid analysis

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Evaluation methods for the monitoring of industrial fluids such biofuel, milk products, oils, soft drinks, or alcoholic beverages are needed to control evolution of liquid phase reactions and quality of the final products. Among the technique's available, high-pressure liquid chromatography or mass spectrometry provide analysis with great precision, however they are not very attractive for automatic label-free monitoring of industrial processes because they are slow, complex and expensive to operate online. An analytical technique capable of overcoming these drawbacks is Near Infrared Spectroscopy (NIRS) [1], which has been used extensively in the pharmaceutical industry and, in recent years, has spread to other sectors like wine industry. In fact, in recent years many studies report NIRS measurements combined with multivariate analysis to monitor alcoholic fermentation processes. In fact, there are several commercial NIRS based apparatus for label-free analysis of liquid samples available on the market. However, they are often designed for static laboratory applications, difficult to adapt to for automatic evaluation in an industrial environment.

In this presentation we will describe a low cost NIRS based fluid analyzer prototype that allows both static (for traceability analysis and quality control) and dynamic (for control of the time of the transformation processes) liquid monitoring. The fluid-analyzer incorporates specific interferometric variable NIR band-pass filters that replace the use of expensive NIR monochromators based on diffraction gratings or Fourier Transform optics. The variable NIR filters consist of specially designed Fabry-Perot Si/SiO_2 multilayers with a wedged cavity fabricated by a magnetron sputtering. Besides, the optical path of the fluidic cell is selected so the evaluation of the absorptions related to overtones and combination bands of O-H and C-H functional groups of the molecular components of liquid samples in the 1500-2000 nm range are optimized. In this presentation, we will focus on the description of the manufacturing procedure of the interferometric variable band pass filter, as well as the procedure of analysis and performance of the device to monitor an alcoholic fermentation process.

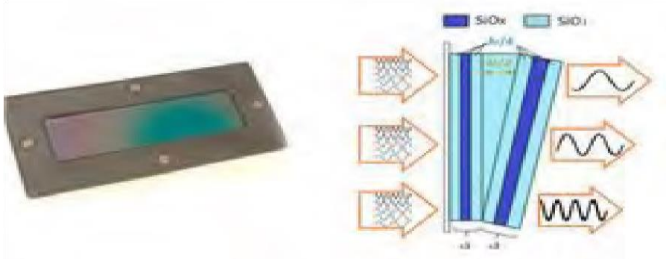

Figure 1.: Manufactured variable NIR band-pass filter (left) and principle of operation (right).

Acknowledgement

Financial support provided by the Spanish Ministry of Science and Innovation (grant PDC2021-121379I00) is acknowledged.

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Session S17: Thin film ices in space [o17-01]

Revisiting the photochemistry of CO_2 molecular ices in dense molecular clouds

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Dense molecular clouds (DMCs) are the densest regions of the interstellar medium (ISM), which are large amounts of gas and cosmic dust grains. On the surface of the dust grains ice mantles are produced when the gas-phase species condense due to the low temperature (10 – 20 K) of DMCs. In addition, in DMCs ultraviolet (UV) radiation triggers an active solid-phase chemistry in molecular ices that might lead to the formation of complex molecules. One of the main species present in the condensed phase of the DMCs is CO_2, which after H_2O is the main component of molecular ices, with an abundance up to 0.2 with respect to H_2O.

In this work, we have revisited the vacuum UV photochemistry (λ = 121.6 nm) of CO_2 thin icy films (≈60 ML) at 15 K in the presence of molecular hydrogen (H_2), the most abundant gaseous species in DMCs, using the INFRA-ICE module [1] of the Stardust experimental station [2-4]. We have used Fourier-transform infrared (FTIR) spectroscopy and Thermal-Programmed Desorption (TPD) to elucidate the chemical pathways leading to the formation of new chemical species. Importantly, from the quantitative analysis of the evolution of IR spectra we have derived the effective formation cross section of the new chemical species and, for the first time, we provide these values for C_2O and C_3O_2. These results are of relevance to model the chemistry of molecular ices in DMCs given its importance in the chemical evolution of the Universe.

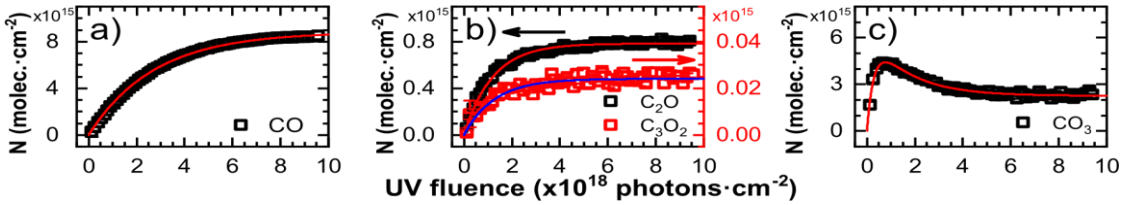

Figure 1. Column density evolution of photoproducts: a) CO, b) C_2O and C_3O_2 and c) CO_3 during UV irradiation.

Acknowledgements

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Session S18: Cultural heritage coatings and surface analysis [o18-01]

Femtosecond laser cleaning of historical stained-glasses

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CaO/K_2O molar ratio is one of the most important parameters associated with the chemical stability of historical stained-glasses. Before the XV[th] century, potash-lime-silica glasses were most common, while after that period Na_2O was added in order to increase the glass´s stability. These differences also define the deterioration processes that take place due to the interaction with the environment. In the case of the oldest glasses, leaching (pH<7-9) or congruent dissolution (pH>9) processes take place. They deteriorate the glass network, generating pits and craters. By contrast, historical soda-potash stainedglasses exhibit different deterioration processes, generating encrustations of inorganic compounds, such as calcium carbonate and/or calcium sulphate.

Laser cleaning protocols have been introduced as an alternative to traditional chemical or mechanical cleaning approaches. The development of ultra-short pulse lasers with different wavelengths offers new possibilities for the application of safe laser cleaning protocols. An adequate selection of laser processing parameters makes possible to limit heat accumulation during the treatment, limiting crack generation on the glass surface. In this study, we extend previous works [1, 2] where UV femtosecond (fs) laser cleaning protocols were applied in both types of historical stained-glasses, with very different surface deterioration effects, glass samples from Maison Lorin collection (Chartres, France) and glasses from Cuenca Cathedral (Spain). In addition, the interaction of these fs lasers with modern stained-glass samples, commonly used in restoration processes, has been analyzed. This comparison shows the strong differences that modern and historical glass samples exhibit when interaction with fs lasers is considered.

Acknowledgement

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Session S18: Cultural heritage coatings and surface analysis [o18-02]

Unveiling Atapuerca. Latest discoveries from the magic mountain

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The Sierra de Atapuerca has witnessed the historical evolution of its territory since the arrival of its first inhabitants almost one and a half million years ago. The presence of this continuous settlement throughout this area is vital for understanding human evolution during the Quaternary period in Western Europe until the arrival of the first scientists who became interested in its archaeology, botany, geology and palaeontology during the first third of the 20th century.

This *magical mountain* is home to a karstic system of almost 4 km in length that coexists with another series of caves and shelters that served for the establishment of our ancestors, being home to up to five different species of hominins, *Homo sp., Homo antecessor, Homo heidelbergensis, Homo neanderthalensis* and *Homo sapiens.*

In the past few decades many advances have helped to unravel the unknowns about our ancestors, but undoubtedly the improvement of DNA analysis and its extraction (mitochondrial and nuclear), palaeoproteomics and the possibility of applying new techniques such as pulsed laser for cleaning archaeological materials have marked a revolution. These advances have been applied to the archaeological record of the Sierra de Atapuerca for a better understanding of the sites of Gran Dolina [1], Galería de las Estatuas [2], Sima de los Huesos [3], but also for the conservation of raw materials [4].

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