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## Abstract Book

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## *Quo Vadis Session Talk*

# Surface Engineering - The Key to a Sustainable Future

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Sustainability, net zero, and reducing carbon footprints are some of the key areas being addressed by many Governments around the world, but how do we go about achieving these goals and what are the key areas that we should be concentrating on?

Virtually every manufactured product, from aero engines to razor blades, printed circuits to smart phones, utilises a treated surface in some form or other to achieve functional properties that are not present in the bulk material, such as corrosion resistance or wear resistance, or to protect against heat and/or oxidation. Surface engineering provides one of the most important means of engineering product differentiation in terms of quality, performance and life-cycle cost. Its importance to the UK's industrial and financial well-being is beyond question.

This presentation, the first of the Quo Vardis Surface Engineering Panel Sessions, will seek to highlight the vital role of surface engineering in the manufacturing supply chain and show how surface engineering really is the key to a sustainable future. It will feature examples of where surface engineering has been employed to help towards the journey to net zero and it will ask if it is possible for  HiPIMS to be at the forefront of this journey.

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# Gold Nanoparticles' Decorated Plasmonic Thin Films

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Gold nanoparticle (AuNP) decorated thin films are used in many applications such as photocatalysis, biosensing, solar cells etc. The morphology and structure of AuNPs are important factors determining the functionality of the sample. Usually, to alter the AuNPs decorated devices' performance one has to change either the AuNPs' fabrication process or the thin film's material.

In this paper, we report the results of a study where we have explored an alternative method. Using the strain engineering approach, we deposited on thin films of the same material AuNPs with a dramatic variation in their size, morphology, and degree of crystallisation.

On a tensile strained film, the Au aggregates to form large NPs with an average size of up to 3500 $nm^2$. These AuNPs are highly crystallised with sharp edges and corners. In contrast, the average size of the AuNPs deposited on compressively strained films, is reduced dramatically to 250 $nm^2$. This shrinking in the average size is compensated with a rise in the NPs' number density. The resulted AuNPs are of round shape which indicates a decrease in the extent of crystallisation.

We present the results of the samples' crystal structure (X-ray diffraction), morphology (SEM and AFM), and correlate the material properties of these films with their optical properties measured using spectroscopic ellipsometry in the Visible-Near Infrared (Vis-NIR) region. Finally, we contrast the epsilon-near-zero behaviour of both types of samples and the effect of the AuNPs on their optical properties. Our analysis showed that only tensile strained samples display tunable (e.g. AuNP dependent) epsilon-near-zero behaviour.

The results of this study can be used for the design and development of strain-engineered gold nanoparticle decorated devices for surface-enhanced Raman spectroscopy (SERS) and photocatalysis.

### Keywords
AuNP decorated thin films, strain-controlled optical properties, plasmonic materials

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# Room Temperature Deposition of Plasmonic Titanium Nitride via HIPIMS

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Transition metal nitrides (TMNs) such as titanium nitride (TiN) display increased mechanical stability, thermal stability, and spectral tunability when compared to the noble metals gold and silver and as such have emerged as promising alternative materials for plasmonic and optoelectronic applications.[1,2] However, the high temperatures (> 800 °C) typically required for the deposition of TMNs with optical properties suitable for plasmonic applications has proven a significant barrier to the integration of plasmonic TMN components in CMOS fabrication processes. Additionally, device fabrication methods are also restricted to those compatible with such high deposition temperatures, often at the expense of scalability or added process complexity. To successfully develop TMN-based optoelectronic devices it is therefore necessary to deposit high quality thin films at CMOS compatible temperatures (< 400 °C).[3]

In this work, we use High-Power Impulse Magnetron Sputtering (HIPIMS) to deposit plasmonic TiN thin films onto Si and glass at room temperature. The optical, structural, and morphological properties of the thin films are fully characterised via spectroscopic ellipsometry, XRD, and AFM. Furthermore, we present the fabrication of plasmonic TiN nano-features and investigate their optical properties and plasmonic performance.

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# How Surface Togography, Microstructure and Applied Potential Effect Wear and the Formation of Low Friction Tribofilms on Titanium Alloys

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Friction and wear play a central role in so many engineering applications, such as transport, manufacturing, medical devices and many more, with the impact of tribology on the economies of developed nations estimated at a substantial 5-8% of GDP. The tribological performance of a component is a strong function of the interaction between the component surfaces and the operating environment, and how the surface changes in response to the contact stresses. In many cases, the tribo environment can activate chemical or electrochemical reactions that generate distinct and unique surface structures by the sliding contact, including surface deformation and the formation of tribofilms. It is these dynamic changes that determine the success or failure of the component.

Ti-6Al-4V has been used as a surgical implant material for a long time because of its combination of strength, corrosion resistance and biocompatibility. To evaluate the complicated nature of the dynamic surface microstructural changes on the wear track, high resolution transmission electron microscopy (TEM), scanning transmission electron microscope (STEM) and electron energy loss spectroscopy (EELS) have been used to characterise the structure and chemical composition of the worn surface, including the tribofilm. A detailed, quantitative, analysis of surface deformation was undertaken, in particular, the geometrically necessary dislocation (GND) density was quantified using a new approach of precession electron diffraction (PET). A clear correlation between applied potential, tribofilm formation and the surface strain was established. In addition, a novel surface texturing method using selective laser melting technology was applied to Ti-6Al-4V. This provided a remarkable reduction of up to three orders of magnitude in specific wear rate. The laser modified surface exhibits superior strain accommodation with 70 % higher strength compared to untreated sample based on *in-situ* micropillar compression tests. The reasons for this dramatic improvement in wear resistance is discussed.

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# Solid Lubricants - From Atomistic Design to Applications

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Sliding processes are inevitably related to energy loss due to friction. In fact, friction losses represent about 5% of all produced energy and represent one obstacle in reaching zero-carbon economy. A traditional way to minimize friction is using liquid lubricants, such as oils and greases. However, they are often produced from non-renewable resources and are related to high environmental load/risk. Solid lubricants, namely 2D materials, such as graphene or transition metal dichalcogenides, promise extremely low coefficient friction (often called superlubricity state). Unlike liquid lubricants, their frictional properties are almost independent of temperature and contact pressure. And they possess one crucial advantage – 2D materials are almost inert in normal sliding conditions, and the tribological contact is thus relatively simple being limited to a few atomic layers. Using 2D materials thus allows, perhaps for the first time, the prediction of friction at a nanoscopic contact scale by atomistic simulations (ab initio, molecular dynamics) and simulation-driven design of a new generation of solid lubricants.

We have shown that a combination of 2D materials with a large lattice mismatch, such as graphene and MoS2, leads to one of the lowest coefficients of friction ever obtained, $10^{-6}$ [1]. Using a combination of ab initio [2] and molecular dynamics simulations [3], we can predict the interaction of these 2D materials with atmosphere and/or contaminants and their effect on friction and select an optimum contact pair to reach ultra-low friction in a wide range of contact conditions. However, direct use of 2D materials is limited; they have to be fabricated elsewhere, transferred into contact, and cannot be easily replenished. Our strategy is thus to prepare tailored solid lubricant coatings with the ability to produce 2D solid lubricants during the sliding.

We will summarize the most promising solutions, typically co-sputtering transition metal dichalcogenide with an additional element, and discuss new techniques to analyze solid lubrication formation using simulations and experiments. In particular, we will shed light on the role of oxygen, which is traditionally considered detrimental for sliding, and use atomic force microscopy (AFM) and Raman spectroscopy mapping [4] of the worn surface to provide complete information about the sliding mechanism and 2D lubricant formation. Finally, we will discuss how HIPIMS can be explored to develop a new generation of solid lubricant coatings.

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# Detection and Prevention of Early Surface Degradation

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Wear in highly stressed contacts can generate work function differences and charge distributions on worn surfaces through phase transformations, material transfer and tribofilm evolution. This paper presents the use of Electrostatic and Acoustic Emission (AE) sensing to study early wear in lubricated bearing steel contacts. Calibration tests of Electrostatic sensors were using a reciprocating facility with steel plates and a twin rolling disc facility with different metals inserted. The calibration results showed the sensors could distinguish metals with different work functions. AE sensors calibrated by pencil lead break tests were used to detect elastic wave generation caused by asperity interactions and crack propagation. A twin-disc tribometer was then used to perform rolling contact fatigue experiments on bearing steel discs under rolling-sliding contacts in mixed lubrication regime. Optical and electron microscopes were used to identify wear patterns and measure wear development after initiation of tribofilms and pitting respectively. Features of early wear were extracted using time domain and frequency domain analyses of Electrostatic and AE data. Time synchronous average analyses of Electrostatic signals identified surface features which changed surface work functions i.e. tribofims and pits. Time domain features of AE appeared to be sensitive to asperity contact conditions and frequency domain features were sensitive to crack propagation and pitting propagation. It is therefore concluded that Electrostatic and AE provide considerable insight into early surface degradation.

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# Unravelling the Ion-Energy-Dependant Structure Evolution and its Implications for the Elastic Properties of (V, Al)N and (Ti, Al)N Thin Films

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Ion irradiation-induced changes in the structure and, mechanical properties of metastable cubic (V,Al)N [1] and (Ti,Al)N deposited by reactive high power pulsed magnetron sputtering (HPPMS) and cathodic arc evaporation (CAE) are systematically investigated by correlating experiments and theory. Although, (Ti,Al)N and (V,Al)N thin films deposited by HPPMS show a close to random orientation at ion kinetic energies ($E_k$) above 104 eV with no apparent ion energy-dependent elasticity change, an evolution towards (111) preferred orientation is observed in CAE synthesized (Ti,Al)N thin films at $E_k$ > 144 eV which is accompanied by an up to 18% reduction in elastic modulus. All here considered ion irradiation-induced changes in elasticity can be rationalized by considering the population of generated point defects and stress state evolution based on density functional theory simulations. It is shown that the evolution of the film stresses and mechanical properties can be understood based on the complex interplay of ion irradiation-induced defect generation and annihilation in transition metal aluminum nitrides.

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*Quo Vadis Session Talk*

# The Role of Vacuum Deposited Coatings Towards a Carbon Neutral Future, the Ionbond Perspective

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IHI Ionbond, and the vacuum coating industry in general, are active contributors towards lowering the carbon footprint and a net zero economy. The current situation is 2-fold, i.e. on the coating production side as well as the use of the applied coatings.

PVD, CVD, and PACVD coatings are already applied in many applications that support net zero impact. Most buildings have heat reflecting glass and DLC coatings have been the enabler of high-pressure fuel injection systems for combustion engines, leading to much lower fuel consumption and lower emissions. More recently, such coatings are crucial in solar cells, fuel cells, and electrolyzers. The wear resistant nature of hard coatings leads to less wear of parts, longer lifetime of components (increased warranties), and stripping and re-coating minimize the use of raw materials. In cutting and forming operations, the coatings have a proven track record to minimize cutting fluids, run at lower forces, and higher productivity levels.

In general, the vacuum deposited coatings are seen as environmentally friendly in the way they are produced. Also here, there are steps to be made to further reduce the impact on our climate. Electrical consumption is the driver, as it is used to heat the loads, to evaporate target materials, and heat the wet chemical cleaning line tanks. It is too easy to focus on only buying green electrical power. The more classic building improvements do have a positive impact on coating factories as well. Roof, wall, and window insulation, combined with LED lighting are good starting points. Next are the peripheral equipment, like chillers, compressors, and air conditioning units. In general, we see a need for heat generation (heating) and cooling (chillers). One can be smarter about this, by using for example the excessive heat from PVD chambers to warm up the cleaning line tanks, rather than running it through the chiller. Local nitrogen generating machines are also more efficient than buying it from suppliers in bulk deliveries. Several of Ionbond's coating centers have their own water evaporating systems to re-use cleaning line water, rather than running it in to the sewer system.

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# Digitalising High Power Impulse Magnetron Sputtering for Thin Film Microstructure and Texture Design

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Plasma synthesis of thin films by physical vapour deposition (PVD) enables the synthesis of materials that drive significant innovations in modern life. High value manufacturing demand for tighter quality control and better resource utilisation can be met by a digital twin capable of modelling the deposition process in real time.

Optical emission spectroscopy (OES) was combined with process parameters to monitor all stages of both High Power Impulse Magnetron Sputtering (HIPIMS) and conventional magnetron sputtering processes to provide a robust method of determining process repeatability and a reliable means of process control for quality assurance purposes. Strategies for the in-situ real-time monitoring of coating thickness, composition, crystallographic and morphological development for a CrAlYN/CrN nanoscale multilayer film were developed. Equivalents to the ion-to-neutral ratio and metal-to-nitrogen ratios at the substrates were derived from readily available parameters including the optical emission intensities of Cr I, $N_2$ (C B) and Ar I lines in combination with the plasma diffusivity coefficient obtained from the ratio of substrate and cathode current densities. The optically-derived equivalent parameters identified the deposition flux conditions which trigger the switch of dominant crystallographic texture from (111) to (220) observed in XRD pole figures and the development of coating morphology from faceted to dense for a range of magnetron magnetic field configurations. OES-based strategies were developed to monitor the progress of chamber evacuation, substrate cleaning and preventative chamber wall cleaning to support process optimisation and equipment utilisation.

The work paves the way to implementation of machine learning protocols for monitoring and control of these and other processing activities, including coatings development and the use of alternative deposition techniques. The work provides essential elements for the creation of a digital twin of the PVD process to both monitor and predict process outcomes such as film thickness, texture and morphology in real time.

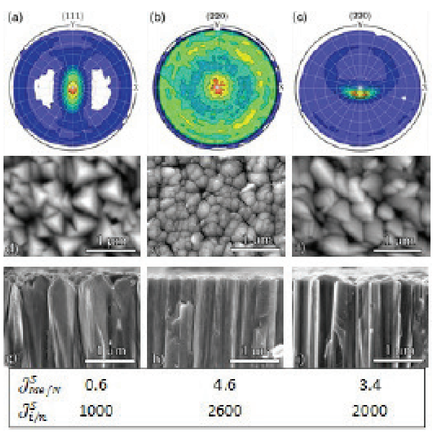


**Figure 1**: CrAlYN/CrN coatings deposited at a range of dissociated nitrogen-to-metal and ion-to-neutral ratios: Pole figures illustrating preferred out of plane texture (a, b, c), SEM images showing the surface morphology (d, e, f) and cross-sectional SEM views of the films (g,h,i)

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# Digitalization and Data Management for Vacuum processes

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Process simulation is becoming increasingly relevant for a systematic process understanding, control, and optimization. This simulation can be based on physical/chemicals equations or data-driven models; where experimental data are essential for their calibration and validation. During the production of thin-film components, a lot of (digital) information is generated along the process chain. This information is generated on different devices at different times and the assignment to one produced component might be difficult. The process parameters have to be mapped to the tracking and tracing properties of the substrates to generate meaningful correlation with findings from quality assurance.

Some of the components generate data on a scale that cannot easily be handled in real time. Data preparation and evaluation steps must thus take place on offline data to derive and train (AI) models for real-time control of processes based on the extracted knowledge.

This presentation will show an approach, how to automatically collect and store data. For this purpose, an inline sputtering system with four compartments equipped with different power supplies like RF, MF, DC, and HIPIMS and target lengths of about 500 mm was upgraded with an OPC-UA server. A python-based software tool is collecting and storing the data into a database. This database can be accessed by different tools such as visualization dashboards or data science modules. Furthermore, tools for storing additional process information and handling the measurements results will be presented. The stored data are a prerequisite for calibration and training of semi-empirical or artificial intelligence-based process models. This enables digital twins for model-based process control and optimization.

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## *Quo Vadis Session Talk*

# The DSM NetworkPlus leads the way to 'Net-Zero' in Surface Engineering

Allan Matthews, University of Manchester

The EPSRC NetworkPlus in Digitalised Surface Manufacturing seeks to encourage research which will create a transformational change in the Surface Engineering sector. This involves fostering a Digital Manufacturing culture, which brings many benefits, including improvements in productivity and reductions in wastes in manufacturing processes. This involves closing the "digital gap" with the provision of improved information about manufacturing processes, better utilisation of assets, reduced time and cost linked to product verification and improved visibility for business performance metrics. All of that is in addition to the known sustainability benefits obtained from coatings (for example in energy generation, conversion, conservation and storage). The DSM Network has grown from its early days (with 27 members ad 16 partner organisation) to now having more than 1000 members and over 100 partner organisations. The Network hosts focussed Workshops and Webinars (recordings of which are freely available to members on the Network website). The funded feasibility awards and demonstrator projects place special emphasis on training and development, especially for early career researchers (ECRs). The Network has a strong presence in social media and hosts events with a topical theme. For example. In 2021 two special COP26-themed webinar sessions were held, one with established leaders presenting and the other with presentations led by early career researchers. Examples are given of the webinars presented and also of funded Feasibility Awards, many of which have a Sustainability theme.

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# Tuning the Elastic Properties of Epitaxial $V_{1-y}Al_yN_x$ Thin Films by Controlling the Occupancy of Metal and Non-Metal Sublattices

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Vivid morphological differences which are typically not considered in ab initio treated superstructures make correlative experimental and theoretical studies challenging from the mechanical properties' point of view. To this end, we have grown epitaxially, close to single-crystal $V_{1-y}Al_yN_x$ thin films on single crystal MgO(001) substrates by direct current and high power pulsed magnetron sputtering to meticulously evaluate the point defect structures and their implications for elasticity of $V_{1-y}Al_yN_x$. By combining experiments and ab initio calculations, it is demonstrated that elasticity of epitaxially grown cubic $V_{1-y}Al_yN_x$/MgO(001) thin films can be enhanced through engineering of the metal and non-metal sublattices. Reduction of N content in $VN_x$/MgO(001) from x = 1.01 ± 0.05 to 0.75 ± 0.04 leads to a decrease in the relaxed lattice parameter $a_0$ from 4.119 Å to 4.096 Å, respectively. This reduction in lattice parameter is accompanied by an anomalous 19% increase in elasticity due to vacancy-induced bond strengthening. Addition of minute amounts of Al to the binary understoichiometric $VN_x$/MgO(001) would stabilize the stoichiometric ternary compound as predicted by density functional theory and observed experimentally. Additionally, by increasing the Al content from $VN_{0.85}$ (y = 0) to $V_{0.7}Al_{0.3}N_1$ (y = 0.3), a concurrent 11% increase in elastic modulus of $V_{1-y}Al_yN_x$/MgO(001) has been observed which can be rationalized by strong $sp^3d^2$ hybridization between Al and N. Our work offers a route for controlling the stability and elasticity of hard coatings through point defect engineering.

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# Hot Carrier Optoelectronics with Titanium Nitride

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Plasmonic devices provide control of light on the nanoscale [1] and highly-sensitive molecular detection [2] through the enhanced interaction between a conductor's free carriers and light via surface plasmon resonances. Although plasmonic modes decay on the order of tens of femtoseconds [3], much of the energy remains in excited carriers that relax ultimately through lattice interactions over picosecond timescales. Exploiting the energy that remains in these carriers has evolved into so-called 'hot-carrier' applications. Due to the low absorption of gold in the red and infrared, nanoparticles are needed to enhance absorption but this comes at the cost of more expensive fabrication. Transition metal nitrides provide an advantage in such situations due to their strong broadband absorption [4] as well as the ability to tune their electronic and optical properties by deposition conditions [5].

Titanium nitride (TiN) is a ceramic with tunable stoichiometry and is known to have a high free carrier density such that it exhibits optical properties similar to gold in the visible and near-infrared regimes [6]. Additionally, TiN has been shown to achieve enhanced hot electron harvesting relative to gold, [7,8] and indeed is reported to have long-lived hot carriers [9], although the physical origin of this phenomenon is poorly understood. TiN is also expected to be resilient to high operating temperatures [10]. The physical properties of TiN are extremely sensitive to the substitution of oxygen within its lattice, enabling also the tuning of its optical response [11].

In this talk, we discuss the hot electron extraction efficiency across Au/$TiO_2$ and titanium oxynitride/$TiO_2$-x interfaces, where in the latter case the spontaneously forming oxide layer ($TiO_2$-x) creates a metal-semiconductor contact. Time-resolved pump-probe spectroscopy is used to study the electron recombination rates in both cases. Unlike the nanosecond recombination lifetimes in Au/$TiO_2$, we find a bottleneck in the electron relaxation in the TiON system, which we explain using a trapmediated recombination model. We thus investigate the tunability of the relaxation dynamics with oxygen content in the parent film. An optimized film ($TiO_{0.5}N_{0.5}$) exhibits the highest carrier extraction efficiency ($N_{FC}$≈2.8 x $10^{19}$ $m^{-3}$), slowest trapping and largest hot electron population reaching the surface oxide ($N_{HE}$≈1.6 x $10^{18}$ $m^{-3}$). Our results demonstrate the productive role oxygen can play in enhancing electron harvesting and elongating electron lifetimes of titanium oxynitride.

We also discusse the application of hot carriers in titanium nitride (TiN) thin film coatings on silicon for CMOS-compatible sub-bandgap photo-detection [14]. Here the titanium nitride serves as an adjustable broadband light absorber for photon energies lower than the silicon bandgap with high mechanical robustness and strong chemical resistivity. Backside illuminated TiN on p-type Si (pSi) constitutes an alternative for photodetection providing a photo responsivity of about ~1 mA/W at 1250 nm and zero bias while outperforming conventional metal coatings such as gold (Au).

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## *Quo Vadis Session Talk*

# Erosion Weather Maps for Surface Coatings; Some Future Strategies

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In studies of wear of materials in environmental conditions, weathering plays a major role in the degradation. In particular, erosion by raindrop, hail, and thrust forces from high wind speeds can result in a change of surface finishing leading to crack initiation and propagation. In such cases, the wear may be accelerated by the presence of chlorides or other matter arising from bird strike.

Increasing interest in sustainable energy has resulted in development of offshore wind farm structures. The replacement of such turbine blades may involve a significant effort. Additionally, reliability of energy efficiency is dependent on smooth surface finishes.

In this talk, the role of surface coatings to improve surface finish and reduce erosion and wear is addressed. In the light of weather maps which can be used to predict erosion rates from raindrop and hail erosion, some suggestions are proposed on how such a technique may be applied to surface coatings. In addition, strategies to identify complex coating structurs which can be applied to such blades is also addressed in this talk.

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# High Volume Production Bipolar Plate Coating for High End Applications

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PEM-type fuel cell technology is explored on global scale and is meanwhile moving to pilot production in several industries. The current market trend towards commercial transportation puts more challenges on fuel cell life time demands, and as a consequence more challenges to device and individual component quality level. For bipolar plates the main challenge is to provide a highly conductive anti-corrosion coating on the stainless steel base material, at very high output and very low costs. Based on a 30-year experience in carbon-based PVD coatings for the automotive industry, IHI Hauzer has successfully demonstrated excellent coating performance and attractive production solutions that will support the ramping of fuel cell production in the next years.

The work that has been conducted to achieve durable fuel cell stack performance will be explained in more detail, and an overview of high volume production solutions will be presented.

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# Using the ee-HIPIMS to Improve the Crystallinity of Cr and Ti Thin Films

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Last year we showed the first results obtained with our new HiPIMS power supply: ee-HiPIMS. At the time, we compared three different configurations : classic HiPIMS (30 µs, 1 kHz), classic HiPIMS and an additional pulse at the end of the on time and at the start of the off time (25-40 µs) and HiPIMS classic and two additional pulses, one between 5 and 15 µs and the other between 25 and 40 µs. We had also shown measurements by Langmuir probe showing the increase in the electron density and the variations in the electronic temperature, thus showing the interest of this new supply in terms of controlling the evolution of the ionic population and the properties structures of the deposited films. The ee-HiPIMS power supply is composed of 3 stages, each stage can be turned on or off, and can output voltage between 150 and 300 V with 50 V steps. This means that we can superimpose a pulse at different times while the plasma is on. Thus, by using two stages to perform a conventional HiPIMS discharge with a pulse duration of 30 µs, the third one can be used to superimpose a pulse of variable voltage and duration. The purpose of this feed is to use the hot electrons at the start of the pulse to amplify the ionization of specific species.

Thus, we have proceeded to the characterization of titanium and chromium layers deposited from the 3 pulse configurations. SEM analyzes revealed that the layers of each metal obtained from configuration 3 have larger grains. XRD measurements showed that the additional voltage pulses have an influence on the crystallinity. An improvement in the properties of thin films is well observed by adding additional voltage pulses. This ee-HiPIMS power supply, clearly offers promising perspectives which have not been exploited until now. Thus, the use of a multi-level pulse power supply contributes to the increase in the amount of metallic ions. The first deposits show an improvement in the crystallinity of the thin layers. The classic HiPIMS has two degrees of freedom: pulse width and frequency. The ee-HiPIMS power supply adds the possibility of one or more additional pulses of adjustable duration, of which we show the benefit.

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# Active Feedback Control of HIPIMS Processes using Spectroscopic and Electrical Parameters

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Reproducibility and long-term stability are key demands for industrial production. In the case of HIPIMS, due to the nature of the process, even in pure metallic processes a long-term drift, resulting in dramatic change of the process conditions and therefore the resulting coating properties can occur within millimeters of target erosion. For reactive processes the situation becomes even more complex due to target poisoning and the interaction of enhanced ionization in HIPIMS and addition of reactive gas and changes in e.g. the plasma impedance.

Concerning these issues monitoring of the process and tracking of changes is minimum requirement for better understanding and management of the coating process. Active control adds even more flexibility to the process e.g. by adjusting the ion-to-neutral ratio or the working point in reactive processes in the transition regime and thus supports the reliability and long-term operation of coating systems in HIPIMS mode essentially. Starting with pure metallic processes we will show how to actively control or modify the ion-to-neutral ratio of the film forming species. Furthermore, in the case of reactive processes the independent control of reactive gas flow and ionization will be demonstrated.

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# In-situ Investigation of Growth Behavior of Metals Deposited by HiPIMS with Synchrotron-based X-ray Scattering

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High-power impulse magnetron sputtering (HiPIMS) received great interest in the scientific community and is getting deployed in industry because of the improved coating properties, e.g., enhanced adhesion, hardness and density [1, 2], compared to regular DC magnetron sputtering (DCMS). These changes in film properties are the result of a high degree of ionization and increased kinetic energy of target material.

In order to gain a better understanding on the role of these key features on film formation and interface characteristics, X-ray scattering experiments were performed to investigate the morphology evolution during film growth. The use of grazing-incidence small-angle X-ray scattering and grazing-incidence wide-angle X-ray scattering (GISAXS and GIWAXS) allows for the in-situ monitoring of even sub-monolayer nanostructures with high temporal resolution. The size, shape and density of clusters on the substrate surface can be followed during deposition until a closed layer is formed. Since comparable experiments with metals on different polymers with DCMS were already performed in the past [3–5], we use these systems as a well-established basis.

The in-situ measurements were performed for different HiPIMS parameters and DCMS as comparison on four polymer templates, namely polystyrene (PS), polyvinylalcohol (PVA), polystyrene sulfonicacid (PSS) and poly-4-vinylpyridin (P4VP). The distinct functional groups of these polymers influence the growth in different ways. Au, Ag and Cu are chosen as target materials because they are used in organic electronics and photovoltaics. The higher energy of ions during HiPIMS leads to an enhanced mobility on the substrate surface influencing the nucleation process directly. Furthermore, the creation of defects on the polymer surface due to ion bombardments provides additional starting points for nucleation and a local heat release due to recombination of electrons and positive ions promotes higher crystallinity below thermal equilibrium. These changes on the nanoscale in the interface could be very important to gain a better understanding of macroscopic effects like better adhesion. Lastly, by utilizing a very high acquisition rate for GISAXS and synchronising the X-ray detectors with the HiPIMS power supply, we are trying to investigate the temporal sequence of HiPIMS pulses as we expect different surface dynamics during the plasma on-time compared to the much longer off-time.

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# Is 10 A/cm$^2$ the Upper Current Limit in HiPIMS?

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High Power Impulse Magnetron Sputtering (HiPIMS) becames nowadays a very versatile way to taylor the film properties and better control the growth of the thin fims. However, after two dec-ades of research, the focus was limited to an operation range within the abnormal discharge. The transition to arc is, in this case, simply avoided by the pulse duration control, typically 100 µs. The average power is comparable with the direct current magnetron sputtering (dcMS) operation, adjusting the duty cycle as the inverse of the current density ratio in HiPIMS over dcMS mode, which is typically between 100 to 1000. However, the peak current densities reported stay below 10 A/cm$^2$ averaged over all the target surface.

This contribution explores the operation of the discharge beyond the limit of 10 A/cm$^2$. Indeed, recently we succeded to stabilize a new glow discharge mode using commercial magnetron cathode. This pulsed mode corresponds to the typical arc current density, in terms of current density far beyond the HiPIMS limit [1]. This mode is undoubtedly a gow discharge since the voltage stays larger than in dcMS, which is not the case in arc regime, characterized by an operation volt-age below 100V.

Moreover, the pulse duration is very long (~1 ms) corresponding to a quasi-steady state. This new pulsed glow at very high current, approaching 1 kA for a 2 inch target diameter – and it was called Hyper Power Impulse Magnetron (HyPIM) glow discharge.

HyPIM is clearly different from both, HiPIMS and arc discharge, since the operation voltage stays well between the two typical ranges, 500 V for HiPIMS and a few 10 V for arcs.

The specificies of this discharge are presented and discussed, as they come out from the spectro-scopic diagnostic of the plasma density and metastable densities. A image of the glow discharge in HyPIM regime is shown in Fig. 1, taken with a high speed camera. The transition to arc is also discussed [2], as a limitation of the operatio in HyPIM mode.

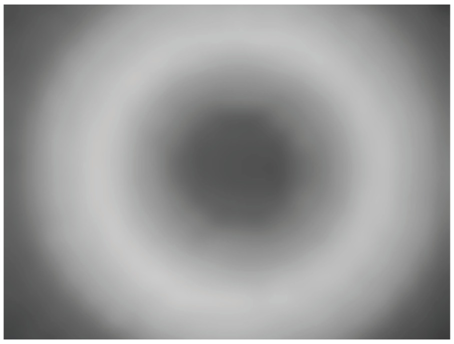

**Figure 1**: Typical HyPIM glow discharge.

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# HIPIMS - The Modern Coating Technology for Advanced Tools and Components

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Modern manufacturing technologies for cutting tools or components are focused on easy maintenance, low production costs per part, reliable processes and high efficiency. Surface engineering is determined as one of the key disciplines for reducing CO2 footprint e.g. extending the life time of cutting tools or components and helping to create more sustainable products.

HIPIMS is such an enabler for surface enhancement by adding or extending properties, like higher hot hardness, better corrosion resistance and many more.

Since HIPIMS enter the coating scene a lot of investigations and publications on this topic had been carried out. Discovering new properties, different material behavior compared to conventional sputter or arc coatings and having better performance in cutting, forming and tribology applications. Most of the investigations were done on small scale deposition units. Additional requirements for modern production technologies are the high scale ability to react fast on growing customer needs and demands. To full fill these requests different, especially, larger machine sizes are needed and also an easy process transfer between the machine platforms are mandatory.

In this regard we present resent results from different applications on different Hauzer platforms, where HIPIMS show benefit compared to other used and state of the art deposition technologies. The obtained results shown, that the HIPIMS technology is ready on different platform sizes for serial production in a modern production environment.

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# HiPIMS Makes Machining Sustainable

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Almost all objects around us in daily life require metal machining for their production. This includes cars, trains, and aircrafts. Almost any product used in engineering, medical implants such as hip joints and even the housings of our cell phones are milled to shape. Despite all additive manufacturing activities, classical machining centres using cutting tools made of cemented carbide stand for >95% of the market. As a rule of thumb, a milling centre utilizes 30% of its maximum power consumption just when switching the unit on. This considerably high energy share is required for running the drives systems and their cooling, for the pumps and filtration units of the coolant.

Clear message is to increase the number of parts machined per time to reduce the energy footprint per part. This is where coating technology comes into the picture: HSC (high speed cutting with highest cutting speed) and HPC (high performance cutting with maximum feed and chip thickness) both depend on the next generation coating technology for carbide cutting tools.

The trend to dry machining without oil in the coolant liquid makes the already extreme temperature in HSC processes due to the extraordinarily high cutting speed even more problematic. Doping an AlTiN chemical composition with Si is known to improve the resistance against wear and oxidation. HiPIMS overcomes the brittleness of traditional TiSiN coating by a fine-grained morphology for a fully new level of toughness of super hard TiAlSiN coatings. With HiPIMS, the energy per pulse can be finely tuned to influence the physical properties of the film independently from its chemical composition. Increasing the cutting speed directly increases the metal removal rate and thus the number of parts machined per time. The avoidance of oil makes high speed cutting even more sustainable compared to conventional cutting. A case study of machining medical implants from CrCo will be presented. SteelCon® – a HiPIMS TiAlSiN – allows milling of this highly abrasive material with so far unachieved cutting speeds. Anther HiPIMS plus: medical implants always require a perfect surface. HiPIMS is based on sputtering and the 100% droplet-free nature of the technology gives smooth coatings.

The other strategy for sustainable machining is high performance cutting. Such heavy-duty machining for railway tracks and pipeline tubes is characterised by extremely high cutting forces and mechanical loads on the cutting edge. To cope with this, the coating should be as thick as possible. Traditional CVD technology can make thick coatings, however with high tensile stresses, which makes it unsuitable for high performance milling. Important in today's discussion about sustainability: HiPIMS is a clean process using solid target materials and inert gases only. Very different from CVD systems which rely on toxic precursors.

The HiPIMS innovation is stress management by synchronising the HiPIMS pulses on the cathodes with the substrate bias. A case study of FerroCon®Quadro as a 12 µm PVD coating illustrates how HiPIMS moves the frontiers of the possible in tool coatings. Applications such as the milling of crank shafts, railway tracks and heavy duty turning show the enormous performance benefit of very thick PVD coatings for cutting tools. 12 µm PVD work, in HiPIMS.

HiPIMS coatings are a contribution to sustainable machining by improving the energy efficiency of the metal cutting process and by the clean sputtering technology itself.

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# Using Positivity to your Advantage - Bipolar HiPIMS Discharges and their Application for Plasma Treatment, Cleaning and Etching

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The last decades have seen an ever-growing need for technologies that ensure extremely clean substrates and reproducible surface activation methods in the field of vacuum coating, mostly due to the stringent demand for cleanliness and process reliability in markets such as the semiconductor and display production industries.

Any process of surface preparation might involve the removal of contaminants, the breaking of surface atom terminations to increase surface reactivity, as well as some degree of material etching in specific cases. Sources for surface preparation rely typically on anodic plasmas, which provide a flux of high energy, positive ions. The management of positively charged particles needs to be accompanied by control over the electrons that are produced in the discharge since these have a key role in the process stability. Important aspects include the neutralisation of the ion flux as well as the current load that samples can sustain.

Using a dual-target magnetron system, we demonstrate a high etch rate plasma-surface technology suitable for application on metal, plastic, and glass. Our innovative method incorporates positive voltage pulses at the end of the conventional HiPIMS discharge on one target, producing a highly ionised flux of positive ions, complimented by a DC discharge on the other target to produce the necessary electron flux for neutralisation. The characterisation of our system will probe the optical emission from the plasma to observe highly ionised species, as well as the effect of etching on a range of substrate types. Finally, we will compare our results with similar high etch rate plasma processes based on AC and RF/microwave plasma excitation.

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# Effect of the Pulse Power in HiPIMS Discharges on Groundstate Populations of Ti Atoms and Ions Measured Near the Target by Cavity Ring-Down Spectroscopy

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Cavity Ring-Down Spectroscopy (CRDS) is a laser absorption technique for the measurement of the absolute densities of atomic, ionic, and molecular levels. A big advantage of CRDS is that no special calibration routine is needed, CRDS is an autocalibrating technique. The laser light pulse is coupled into a stable optical cavity formed between two spherical mirrors with high reflectivity (> 99,9%) and the decay of laser light intensity in the cavity is recorded. From the difference between the decay times with and without an absorbing medium in the cavity, the total absorption along the laser path in the absorbing medium is deduced. Finally, from the integral absorption measured over the absorption line profile, the absolute density of a given atom/ion/molecule level averaged along the laser path in the absorbing medium is calculated.

We have applied the CRDS technique close to a Ti target (in the distance of 10mm from its surface) sputtered by a HiPIMS discharge in argon gas at a pressure of 1 Pa. A circular planar magnetron (a diameter of 100mm, a type-2 unbalanced magnetic field configuration) was driven by a custom-built HiPIMS pulsing unit providing voltage pulses with a duration of 100µs and repetition frequencies of $f_r$ = 50, 100, 200, and 500Hz. The average power density was fixed for all $f_r$ values and it was 3.8Wcm$^{-2}$. It means that the average power density in a voltage pulse increased with decreasing $f_r$. The CRDS system consisted of an Nd:YAG pumping laser (532nm wavelength, 10 Hz repetition frequency) and a tunable dye laser (a Pyridin 1 dye and a KDP frequency doubling were used). The laser pulses were coupled into the optical cavity by prisms via the first mirror and the light intensity decay in the cavity was monitored behind the second mirror by a photomultiplier tube equipped with a band-pass filter (345nm, FWHM of 10nm). The densities of levels belonging to the ground-state multiplets (GSM) of Ti atom and $Ti^+$ ion were measured in the wavelength range of 335–339nm. The density distributions along the laser path were constructed from laser-induced fluorescence (LIF) images for $f_r$ = 100 and 500Hz.

Here, we will present the result of the CRDS measurements at t ≈ 60µs from the pulse beginning when the power density is close to its peak value, specifically $S_d$ = 114, 267, 491, and 976Wcm$^{-2}$ for $f_r$ = 500, 200, 100, and 50Hz, respectively. A common result is that the GSM levels with higher energy have a higher density leading in the case of ions to a significant inversion in the population (density divided by degeneracy) and to negative excitation temperatures. The total (sum of GSM level densities) averaged (along the laser path) density of Ti atoms decreases from $2.0\times10^{11}$ to $9.4\times10^{10}$cm$^{-3}$, but it rises for $Ti^+$ ions from $1.2\times10^{11}$ to $4.3\times10^{11}$cm$^{-3}$ with the increasing power density. The peak $Ti^+$ ion density is detected above the target racetrack and it is $8.3\times10^{11}$cm$^{-3}$ for $f_r$ = 100Hz.

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# HiPIMS Pulse Shape Influence on the Deposition of Diamond-like Carbon Films

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Two high-power impulse magnetron sputtering (HiPIMS) systems were used to prepare DLC films using two types of pulse shape, one normal HiPIMS pulse and the second with short multi-pulse HiPIMS. Similar DLC film performance was achieved, however, recurring to different substrate bias values showing that the pulse characteristics are one determinant factor to the film properties.

The results show that the short multi-pulse HiPIMS increases the amount of charged species reaching the substrate location. It is also confirmed that the deposited DLC films using those conditions demand lower energy (lower bias values) to achieve the same mechanical properties.

The effect was related to the decrease of back attracted carbon ions occurring during the off-time between the oscillations. A second effect is the easier plasma ignition of the consecutive oscillations that significantly increase the carbon ionisation and, as a result, decrease the need of high substrate bias level allowing to obtain DLC films with increased amount of $sp^3$ bond hybridisation.

**Keywords**

HiPIMS, burst-HiPIMS, pulse shape, hard DLC, ionization level

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# Electron Heating during the Positive Pulse of a Bipolar HiPIMS Discharge Measured by Laser Thomson Scattering

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Using a Laser Thomson Scattering (LTS) system, developed at the University of Liverpool, time-resolved electron density and temperature measurements can be made throughout the bipolar HiPIMS waveform, both in the active-glow, positive pulse delivery and afterglow [1,2]. LTS is often referred to as the "gold standard" for electron temperature and density acquisition and is a non-perturbing diagnostic tool, unaffected by magnetic fields, meaning that electron properties can be measured with precision with unambiguous data analysis. The LTS system has an excellent temporal resolution of ~ 5 µs with a spatial resolution of 3 mm.

In this study, +300 V, 300 µs duration positive pulses have been delivered to an unbalanced magnetron with tungsten target immediately after the high density creating negative pulse of length 50 µs. Scattered light was collected on the centre-line of the magnetron axis and at several positions above the racetrack, by altering the relative height of the magnetron with respect to the focused laser beam. Data for the unipolar case, where no positive pulse was delivered to the target, has also been collected to allow comparison. With the inclusion of the positive pulse, a significant steep increase in electron temperature was measured in the positive afterglow, for both centre-line and racetrack measurements. The elevated electron temperature was found to be greater at further distances above the racetrack, but little significant difference was found between two centre-line positional measurements. The electron density also decayed faster than with the negative pulse only. The electron temperature was found to reach values of above ~ 2 eV in the positive afterglow, where the electron density dropped to ~ 20 % of the comparable unipolar afterglow. Shown also is time-resolved optical emission of neutral argon and tungsten lines and plasma potential profiles measured by an emissive probe. The results are discussed in terms of the creation of reverse discharge during the positive pulse period.

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# Metal Oxide Nanocoatings by HIPIMS for Resistive Random-Access Memory Application

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The paper is devoted to the technology and characterization of thin films fabricated by reactive magnetron sputtering using HIPIMS discharge. The metal oxides and nitrides, such as zirconium oxide (ZrOx), titanium oxide (TiOx) or titanium nitride (TiN) play important functions in various structures for novel electronic and photonic devices. The aim of this work is to determine dependences between the input parameters of the fabrication process and the properties of the obtained materials in order to obtain ultrathin layers for the application of the MIM (Metal-Insulator-Metal) structures. Those structures are the basis of resistive random-access memory (RRAM) devices.

In the first part of this work, the optical properties of layers deposited by HIPIMS were examined and compared to the layers deposited using a typical pulsed-DC processes. Several oxide materials were characterized in terms of thickness, refractive indices, transmittance, and reflectance in the UV-VIS range. The resistive switching properties of the MIM structures with the employed oxide materials depend on the presence of oxygen vacancies in the layer bulk. In order to monitor the stoichiometry of the oxide layers, MIS (Metal-Insulator-Semiconductor) structures are fabricated. The analysis of the obtained electrical characteristics was performed. In the last part of this work, selected processes were used to fabricate MIM devices. The results of the electrical characterization of the fabricated test structures will be described indicating concluding remarks on the feasibility of applying the studied structures in RRAM devices.

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# Deposition of Indium Tin Oxide Layers in Roll-to-Roll Hight Power Impulse Magnetron Sputtering onto Ultra-Thin Glass – The Comparison with Pulsed Magnetron Sputtering

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Indium tin oxide (ITO) belongs to transparent conductive oxides (TCO), materials that are optically transparent and electrically conductive. ITO can be used for many applications, such as organic photovoltaic (OPV) technologies.

We present the deposition of indium tin oxide thin films (80-150 nm) on ultra-thin glass (300 mm width and 100 µm thickness) in a roll-to-roll process with High Power Impuls Magnetron Sputtering (HiPIMS) and Pulsed Magnetron Sputtering (PMS). We investigated the film structure (SEM, XRD), surface roughness (AFM) and sheet resistance (4-point probe) at different temperatures for two magnetic fields. Film thickness was obtained by XRF and optical simulation. The outcomes of both sputtering methods are compared.

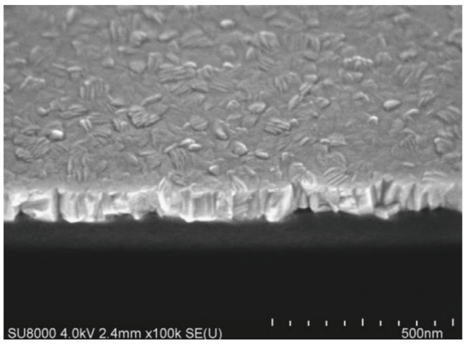


**Figure 1**: SEM image of ITO sample deposited with HiPIMS.

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## *Young Scientist Award Presentation*

# Effect of Controlled Target Poisoning on TiAlCN/VCN Films Deposited in Mixed HIPIMS/DCMS Discharge

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Reactive sputtering in PVD processes can be utilised to fine tune the properties of the coating microstructure. However, the target poisoning effect is an inherent challenge of the reactive sputtering. It can be controlled with a various monitoring tools utilizing PID loop. In this research a controlled target poisoning was used a as tool in the development of the architecture, microstructure and mechanical properties of TiAlCN/VCN films.

Initially, five Single Nanoscale Multilayer Coatings (SNMC) were deposited at various (constant) target poisoning level of mixed Ar, $N_2$, $CH_4$ atmosphere and analyzed in order to determine their composition, microstructure and mechanical properties. Semi-quantitative EDX analysis of the coatings showed a linear increase in nitrogen content with total reactive gas flow. In contrary, no correlation between reactive gas flow and carbon content in the coatings was confirmed. Raman analyses indicated that the intensity ratio of carbon D/G peaks increased continuously with reactive gas flow. Furthermore, higher reactive gas flows increase the hardness of the coating up to 4.8 times.

The structural characteristics shows that for low reactive gas flows the microstructure is dense, with a glossy amorphous morphology with a metal-rich phase. As the reactive gas flow increases, SMNC grow in a NaCl-type cubic crystalline phase with a dense microstructure and randomly oriented grains. A high reactive gas flow leads to large diameter, well defined columns.

Next, to improve the adhesion of TiAlCN/VCN an Advanced Nanoscale Multilayer Coatings (ANMC) with modified coating architecture were deposited at gradient partial pressure of the reactive gases. The TiAlCN/VCN coatings in ANMC architecture exhibit [200] or mixed [111, 200, 222] and [311] orientation, depending the on deposition sequence. The cross-section of the coatings show change in the stoichiometry with the structure. Near the base layer, coatings are more metallic and the contents of N and C increase with thickness. In ANMC coating the individual SMNC layers can be distinguished. The change in stoichiometry influences coatings structure from a dense coating at the bottom to broad, distinct columns on the top.

Improved adhesion and the gradual change of the structure of ANMC architecture deposited at gradient partial pressure of the reactive gases, results in enhanced tribological properties of all TiAlCN/VCN coatings.

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# Materials and Coatings for Future Nuclear Energy Generation

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Nuclear energy generation inevitably leads to the reactor material bombardment with energetic particles. The bombardment initiates various processes which damage materials in a sense that the materials involved either are removed by sputtering and/or change their properties. Many traditional materials are thermodynamically unstable and under irradiation evolve with observable properties modification. Nuclear materials perform in the very demanding environments and any material modification are ranging from highly undesirable to completely unacceptable. The damage is unavoidable and new fundamental solutions are needed to preserve material properties. The solution is thought to be to create materials which can selfheal the damage. The presentation will discuss on High Entropy Alloys (HEAs) and so named MAX phases to identify the basic nature of self-healing mechanisms

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# Optical Emission Spectroscopy of Cu-HIPIMS Discharges (Industrial Scale HIPIMS Copper Deposition - Process and Plasma Parameters)

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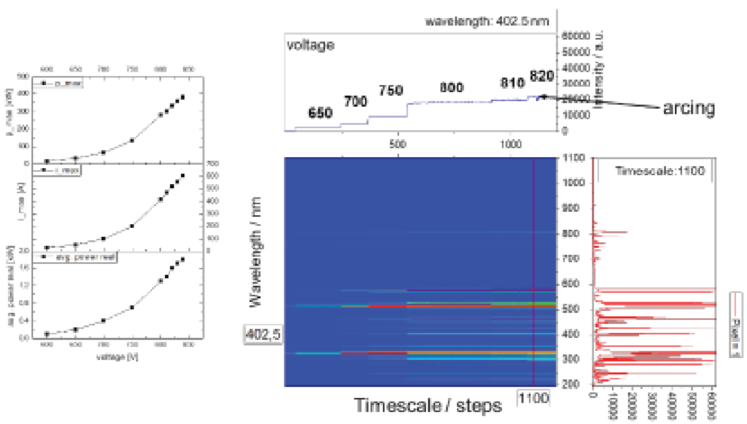
For industrial use of HIPIMS processes, especially in the case of in-line processing instead of batch operation, long term stability and process monitoring and active control is crucial. Even in the case of pure metallic processes the ion to neutral ratio is modified by the applied pulse parameters. Keeping applied voltage or power constant, the ionization degree changes still due to target erosion.

To quantify ion to neutral ratio of a metallic process and to develop control strategies we studied the effect of HIPIMS voltage and pulse duration on the ionization in copper discharges using optical emission spectroscopy (OES). The emission spectra show that pulse duration and working pressure influence the amount of neutral and ionized species. This builds the basis for monitoring, tailoring and control of the HIPIMS process.

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# Investigation of HiPIMS Tungsten Films for the Development of Liquid Metal-based Divertor for EU-DEMO

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One of the most critical issues to realize magnetic confinement fusion is the so-called plasma-wall interaction (PWI), since the extreme flux of energetic particles and the intense thermal loads result in the erosion, modification and radiation damage of the plasma facing materials (PFMs) [1]. In ITER (International Thermonuclear Experimental Reactor), due to its favourable properties, tungsten (W) has been selected as a reference for the most critical plasma facing components (PFCs) such as the divertor. However, in view of the EU-DEMO (DEMOnstration Power Plant) development, a viable PFMs alternative can be represented by liquid metals (LMs). Indeed, with respect to ITER, in EU-DEMO the fusion power generated and the neutron flux to the walls will increase by approximately an order of magnitude leading to enhanced damage and deterioration of the W PFCs [2]. In this context, LM-based PFCs could present advantages since they are characterized by regeneration of the plasma facing surface and by lower sensitivity to neutron damage. Among the various designs proposed, the one presented by ENEA [3] is characterized by a porous structure in which liquid tin (Sn) flows. Due to the corrosive behaviour of the Sn, the presence of coatings is mandatory to protect the surfaces in contact with the LM, specifically those constituted by CuCrZr alloy. In this respect, W films deposited by HiPIMS could represent a promising option since the presence of ionized species in the sputtered material flux allows the growth of smooth and dense films which properties can be tuned with a high level of control [4].

This work reports on the investigation of W films grown by HiPIMS with the aim of realizing protective coatings able to avoid the corrosive action of liquid Sn by uniformly covering CuCrZr samples. W films were grown applying HiPIMS pulses 100 μs long (duty cycle=1.75%) with a fixed argon pressure of 0.5 Pa. During the depositions, the effects of two process parameters were analysed: the magnetic field intensity over the racetrack and the application of a substrate bias voltage. The former parameter was varied by using W sputtering targets with two distinct nominal thicknesses. Instead, as the second parameter is concerned, both different values of the bias and time delays with respect to the pulse were considered. The deposited films have been analysed considering mainly the microstructural and morphological properties. Moreover, since the discharge current waveforms characterizing the two values of the magnetic field showed a distinct behaviour, the Ionization Region Model (IRM) [5] was applied to analyze the considered discharges and to obtain preliminary information about how they differ from each other. Relying on the HiPIMS discharges investigated, depositions were performed over rectangular CuCrZr substrates adequately prepared before films growth. Specifically, exploiting the films previously studied, the focus was on the possibility to uniformly cover the total surface of the CuCrZr samples, which is a mandatory condition to avoid liquid Sn corrosion. Lastly, some preliminary results concerning the ability of the films to withstand the typical operation condition of LM-based divertor are presented.

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# Optimising the use of Local Antibiotic Delivery in Orthopaedic Surgery

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Increasing problems with antibiotic-resistant organisms require “smarter” use of antibiotics to maximise their effectiveness and minimise resistance problems. This need is particularly acute in orthopaedic surgery, including hip and knee joint replacements, where infection around the prosthesis can be devastating. It has even been suggested that a situation could arise where the danger of untreatable infections makes elective orthopaedic surgery infeasible, with severe quality-of-life consequences for patients. A key factor in averting this situation is more targeted and prudent use of existing antimicrobial drugs, to maximise their antibiotic effectiveness and minimise the impact of their use on antimicrobial resistance locally within the patient’s microflora and in the wider human population and in the environment.

The unnatural surface of the implant material provides a surface upon which microorganisms can form a biofilm that provides protection from the immune system or antibiotics. The key to preventing orthopaedic infection is to inactivate any microorganisms that gain access to the surgical site before they are able to form a biofilm. Our aim is to enable more effective local delivery from the materials implanted into patients during surgery, thus allowing a wide range of antibiotics to be used when needed and preventing long-term release of antibiotics that may exacerbate resistance problems.

Our multidisciplinary team includes expertise in antimicrobial agents, clinical microbiology, orthopaedic surgery, bone healing and materials science to provide scientifically based and surgically relevant information on existing products and procedures, as well as new products for unmet clinical needs. Our work on antibiotics in bone cement has comprised physical, pharmacokinetic and antimicrobial evaluation of antibiotic-containing materials, both commercially prepared and materials where a range of antibiotics have been added as they would be in the operating theatre. This has provided independent evaluation of the compatibility of a range of antibiotics (including representatives of the amino glycoside, lipopeptide, beta-lactam and glycylglycine classes) with PMMA bone cement. The results have informed surgical practice in the UK and beyond, especially in complex surgical revision cases occasioned by periprosthetic infections.

In order to enable local antibiotic delivery from uncemented prostheses we have developed a controlled antibiotic release sol-gel coating system for application to titanium and other implant materials. The coating releases therapeutic levels of gentamicin sufficient in vitro to inhibit biofilm formation and actually eradicate existing biofilms, as well as permitting normal bone regrowth in an in vivo small animal bone healing model. The coating system is now under investigation for applications on a wider range of materials and with a wider range of antibiotics, in collaboration with a commercial partner.

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# Tailoring of HIPIMS Process Conditions for Improved Photocatalytic Performance of Reactively Synthesised Titanium Dioxide

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The photocatalytic properties of titanium dioxide ($TiO_2$) are widely used to reduce organic matter contamination including fingerprint residues on architectural glazing and displays and bacteria in public spaces. The most efficient photocatalysis is achieved for a phase composition combining anatase (75%) and rutile (25%) as implemented in the bulk chemical P25 Evonik. Utilising PVD technology the application of $TiO_2$ could be expanded on to a range of surfaces. Often thin films cannot meet the simultaneous requirements of durability and photocatalytic performance. For this novel synthesis methods need to be investigated.

In this study we are investigating the influence of oxygen partial pressure, total pressure, substrate temperature and substrate bias voltage on the crystallinity, phase composition and photocatalytic properties of $TiO_2$ prepared by constant current HIPIMS.

Titanium dioxide films were successfully deposited. The phase composition of the films included rutile, anatase and brookite as detected by Raman. Anatase content was highest for the lowest temperatures. Crystallinity was promoted at high pressure, high temperature and low substrate bias voltage. Crystallinity was achieved at pressures above 1 Pa, temperatures of 70 °C and above and bias voltages below 120 V. Photocatalytic activity correlated with crystallinity, which in turn was promoted by temperature and/or bias. Water wetting angles were highest at 0.3 Pa, whilst visible light transmission maxima were above 97% of glass for all conditions.

The constant current mode of operation of the HIPIMS discharge resulted in a stable arc free deposition process with the flexibility to deposit in a wide range of parameters

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# Real-time Monitoring of Thin Film Growth by HiPIMS using Grazing Incidence Fast Atom Diffraction (GIFAD)

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The growth mechanism and the properties of thin materials, which are intimately related, have become a growing field of interest over a few decades. Several techniques have been developed to control in real-time the interface during the growth process. Reflection High Energy Electron Diffraction (RHEED), which is widely used in Molecular Beam Epitaxy and Pulsed Laser Deposition, is not compatible with Magnetron Sputtering (MS) due to the presence of electromagnetic fields near the substrate. Therefore, in-situ moni-toring of the growth process in MS is a challenging task.

Grazing Incidence Fast Atom Diffraction (GIFAD) [1] has been used for over a decade as a surface analysis technique for all types of materials [2-4]. In GIFAD, neutral He atoms with primary energy of 0.2 to 5 keV, are scattered at small angle of incidence (< 1°) from the surface. The soft scattering and surface sensitive property of GIFAD allows one to observe the surface structure and phase transitions during the growth process. So far, the diffraction of atoms from the surface has been studied under UHV conditions and up to $10^{-6}$ mbar to limit degradation of the diffraction signal due to gas phase collisions.

We have developed a new high-pressure GIFAD (HP-GIFAD) system that can cur-rently operate at pressures up to ~$10^{-2}$ mbar (figure 1). This innovation opens new perspec-tives in high-pressure deposition processes such as MS. In the particular case of HiPIMS, where many parameters need to be controlled and optimized, HP-GIFAD should help re-vealing the role of each of these parameters in both the growth dynamics and the final film properties. A deposition apparatus combining HiPIMS and HP-GIFAD is currently under development.

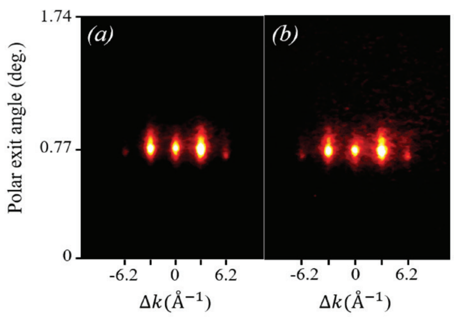


**Figure 1**: He atom diffraction from LiF(001) surface at (a) $10^{-8}$ and (b) $8.9\times10^{-3}$ mbar of Ar

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# Hot Magnetron Sputtering with an Nb Target Studied by Emission Spectroscopy

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Magnetron sputtering with a thermally insulated target has been attracting the interest of researchers for the last decades since it allows reaching several times higher deposition rates as compared to the classic, cooled-target, approach [1, 2]. However, a comprehensive study of this kind of discharge is still required.

In the present work, we studied and compared the hot and cold dc magnetron sputtering (HMS and CMS) discharges with a Nb target by means of optical emission spectroscopy (OES). Particularly, the target heating process was related to the discharge electrical parameters, the spectral line behaviour, and the target surface temperature. The latter has been measured by OES, i.e., by fitting the baseline of the optical spectrum using the Planck's radiation law, as well as by pyrometry.

In the HMS system, when the applied power density is 20 W/cm$^2$ and the target surface temperature reaches 1900 K, the current is significantly affected by thermionic emission. Using time-resolved OES, the lines of $Nb^0$, including those coupled to its five ground states (GS), $Nb^+$, $Ar^0$, and $Ar^+$ are clearly detected, and the significant increase of the peak intensities during the target heating is revealed. Moreover, in the HMS case, the intensity growth rate linked to both Nb and Ar ions surpasses the rate of the corresponding neutrals. This behaviour is presumably related to a higher ionization of those species during HMS as compared to the CMS case. In addition, a population inversion of the GS levels as well as corresponding excited electronic states is discovered for Nb neutrals due to the gradual gas heating. Finally, in the HMS system, a deposition rate of 0.1 μm/min is achieved at 32 W/cm$^2$ (i.e., at a target temperature of 2100 K). This is three times higher than the maximum value attainable in the CMS case.

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# HiPIMS With Novel Reactive Gas Control Method and Positive Voltage Reversal to Deposit AlScN

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Scandium doped aluminum nitride (AlScN) is a material of interest due to its enhanced piezoelectric property. The development of this material is essential for many applications, including use in the telecommunication industry. A reactive pulsed DC sputter process was initially explored, and then a HiPIMS process with a novel reactive gas control method was developed. It was found that the reactive HiPIMS process of a diffusion bonded AlSc (60/40 at%) target deposited AlScN films with near theoretical optical properties and the film stress can be tuned using the positive voltage reversal parameters. Ultimately, the HiPIMS process deposited AlScN films microns thick with a highly c-axis oriented hexagonal wurtzite crystal structure.

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# On Microstructure and Mechanical Characteristics of TiAlSiN Deposited by High Power Impulse Magnetron Sputtering with Variable Silicon Content

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In recent years, High Power Impulse Magnetron Sputtering (HiPIMS) PVD deposition technology has emerged as a superior alternative to direct current magnetron sputtering (DCMS) due to better substrate-coating adhesion [1]. High peak power with a small pulse duration is used in HiPIMS technology to achieve a much denser plasma in the order of $10^{18}$ $m^{-3}$ [2], which results in dense, defect-free, and good quality smoother coating [3]. Cutting tools with superior properties like higher hardness, better oxidation resistance, and lower friction would have been an alternative to TiAlN for high-speed cutting applications. Since traditional nitride coatings can no longer fulfill the requirements, nano-composite TiAlSiN could be a promising alternative to this problem. The coating morphology changes from columnar to spherical [4] for the presence of Si. Hardness increases due to Si3N4 phases, which have higher Vickers hardness than 40 GPa [5]. These $Si_3N_4$ phases have high thermal stability and reduce friction [6]. The coefficient of friction (CoF) of the Si-based coating can also be potentially reduced by increasing the percentage of Si. This silicon forms of self-lubricating top-film of $SiO_x$, which helps in lowering the CoF value [7–9].

In the current study, TiAlSiN coatings have been deposited on WC-10Co substrates with two different Si contents by state-of-the-art HiPIMS technology. Two types of target TiSi23 and TiSi34, along with TiAl60 in common, were used for the deposition. The effect of Si% on the microstructure and mechanical properties of the coatings were characterized by energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), 3D-surface profiler, nano-indentation, Rockwell indentation-adhesion, and scratch test. The thickness and deposition rate of the coating was calculated from the cross-section morphology. It was identified that the crystalline TiAlN phase is likely to be wrapped in the amorphous phase of Si3N4 in TiAlSiN coatings. With the increase of Ti atomic percentage in the coating, the hardness was achieved up to 42 GPa. In addition, coating surface roughness decreased from 14.3 nm to 10.9 nm, as shown in Fig.1, and grain size from 16.2 nm to 12.4 nm. The adhesion strength observed under the Rockwell-indentation test was of HF1 classes in both cases (Fig.2). Patterns of cracks were very similar to one another. However, a significant improvement in coating-substrate adhesion was realized with the increase of Ti content, as investigated through the Scratch test. The scratch test achieved a maximum load of 173 N during full delamination (Lc2) of TiAlSiN from the carbide substrate.

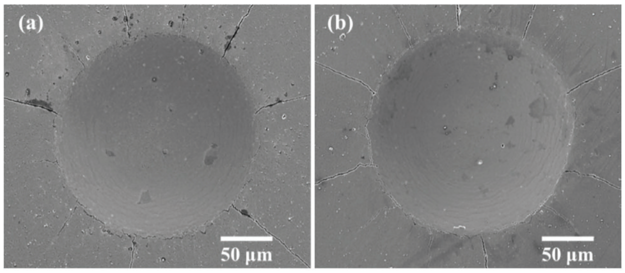


**Figure 1**: Rockwell adhesion test conducted at 60 kg load on TiAlSiN coated surface deposited with higher Ti content b) lower Ti content

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## Poster 1

# Growth of Nuclear Fusion Materials using a Bipolar-HiPIMS Discharge

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A production of nanostructured tungsten occurs when the material surface is bombarded by helium ions at high surface temperatures. Thicknesses of nano-tendril fibre extending from nm to 1 mm [1,2], the porosity of Fuzzy surfaces in excess of 95% [3], and the optical reflectivity of fuzzy layer is about 1%. Fuzzy tungsten was grown on Langmuir probes located in the Alcator C-Mod W divertor and Pilot- PSI LPD tokamak [4].

The growth of nanostructured tungsten in a HiPIMS magnetron sputtering discharge is recorded for the first time at department of Electrical Engineering and Electronics, university of Liverpool. Fuzzy W layers were produced in an conventional and a bipolar-HiPIMS discharge at a surface temperature of 1150 $K^0$, an average He ion fluence of 6 $\times 10^{24}$ $m^{-2}$ , and an average helium ion bombarding energy of 60 eV. After six hours of exposure to a HiPIMS discharge, the tungsten substrate became optically black.

The experimental results revealed, the thickness of fuzzy tungsten grown in a bipolar HiPIMS plasma (50 V kick pulse) was 701 nm, 140 nm (25%) higher than the thickness of corresponding fuzzy layer produced in a conventional HiPIMS plasma for the same surface temperature (1150 $k^o$). The thickness difference between the two cases may be due to that the deposition rate in modified HiPIMS plasma is greater than that one generated in a conventional HiPIMS discharge. The positive kick pulse was used to eject sputtered metal fractions at the tungsten target surface (self-sputtering), allowing the increase in a highly energetic W ions toward a substrate . furthermore, the increase in the flux of tungsten ions at the substrate lead to the increase in a deposition rate [5] as well as the presence of auxiliary deposition enhance the growth of fusion materials [6]

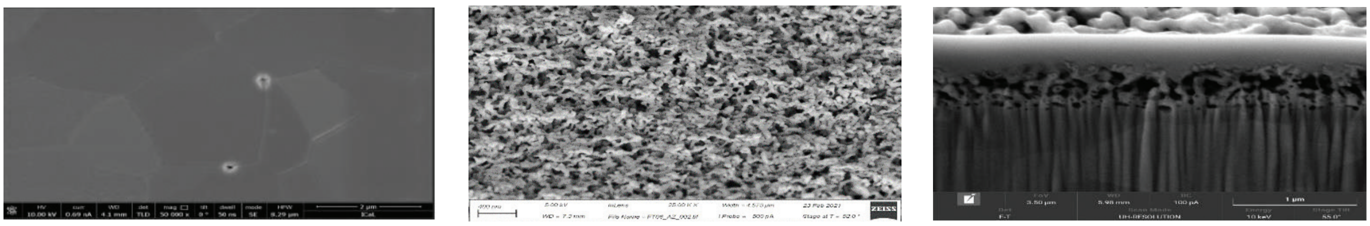

**Figure (1)** : SEM & FIB-SEM cross section images of fuzzy W surface before and after an exposure of a helium bipolar-HiPIMS discharge at a surface temperatures of 1150 $K^0$.

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## Poster 2

# Improving Tribocorrosion Resistance Through HIPIMS Low Pressure Plasma Nitriding Process

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Research has indicated that tribocorrosion resistance (combined wear and corrosion resistance) demands a higher precedence while choosing materials for prosthetic joints and medical implants. Better individual wear and corrosion resistance of a material does not guarantee better tribocorrosion resistance as it is system dependent and complex tribo-corrosive mechanisms reign. Most of the implant materials do not inherent favourable attributes and need engineered surfaces to improve their longevity. Recently, a novel nitriding process based on the plasma generated by the High Power Impulse Magnetron Sputtering (HIPIMS) technique has been developed.

Previous works demonstrated that this technique successfully nitrided medical grade (F75) CoCrMo alloys resulting in significant improvement in mechanical properties, wear and corrosion resistance of these alloys. Current work analyses the tribo-corrosion performance of these HIPIMS nitrided alloys with the help of a pin-on disk tribometer. Sliding wear experiments have been carried out in a simulated body fluid environment (Hank's solution) with simultaneous corrosion monitoring. Under the Open Circuit Potentials (OCP), both HLPN nitrided and the untreated specimens exhibited a near similar values ($K_{SWC} = 6.52 \times 10^{-15}$ and $K_{SWC} = 3.95 \times 10^{-15}$ respectively). However, the benefits of HLPN were clearly visible under the accelerated corrosion (anodic potentials) conditions where the HLPN treated specimens exhibited an order of magnitude higher wear resistance ($K_{SWC} = 6.41 \times 10^{-15}$) as compared to the untreated alloy ($K_{SWC} = 3.40 \times 10^{-14}$). This work focuses on explaining the significant improvement in tribocorrosion performance from microstructural perspective.

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## Poster 3

# Investigation of Solid Particle-Surface Interaction of Powder Metallurgically Manufactured Pure Tantalum (Ta) under Aqueous Conditions

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Tungsten (W) is widely used as a spallation target material (source) for generating neutrons. At Rutherford Appleton Laboratory (RAL), the target design consists of a tungsten core with Tantalum (Ta) cladding, which facilitates water-cooling of the target. The target (Ta-W) system is currently experiencing rapid deterioration, susceptibly due to the erosion-corrosion phenomenon reducing its operational life significantly. The current work investigates, previously unreported, aqueous erosion response of powder metallurgically manufactured pure Tantalum (Ta) using laboratory experiments, with an emphasis on identifying mechanisms of material removal. Results indicate that tantalum exhibits classical ductile erosion behaviour with higher mass erosion at oblique impact angles (peak at 30°). Plastic deformation and micro cutting form the main material removal mechanisms, both of which results in perforated lips formation prior to its fracture. Micro-perforation, usually unobserved during lip formation for ductile materials, was prominently visible in for Ta and can be attributed to the weakened grain boundaries arising from its manufacturing process (powder metallurgy).

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# Poster 4

# A New Approach Towards Performing Plasma Nitriding Of CrCoMo Medical Grade Alloys Using HIPIMS Discharge

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CoCrMo alloy, although an acceptable choice for metal-on-metal prosthetic implants, requires enhancement of its mechanical and tribological properties. In this work, HIPIMS discharge was utilised to perform a low-pressure plasma nitriding (HLPN) process. XRD studies revealed the formation of a compound layer consisting of a desirable mixture of $Co_{2-3}N$ and $Co_4N$ phases and a (111):(200) [43:57] texture. The process led to a higher rate of nitrogen diffusion, (case depth of 2.5μm in 4 hours) than that observed for a conventional dc plasma nitriding process (DCPN) (2.1μm in 18 hours). The HLPN treatment resulted in a higher hardness of 23 GPa as compared to 20 GPa achieved for DCPN and substantially higher than that measured for the bare alloy (7.9GPa). Consequently, a significant improvement in dry sliding wear resistance ($K_C=1.18\times10^{-15}$m3$N^{-1}m^{-1}$) and lower friction coefficient (μ=0.6) was achieved as compared to the untreated specimens ($K_C=6.0\times10^{-14}$m3$N^{-1}m^{-1}$) and μ=0.8). The defined H/E and $H^3/E^2$ values of 0.078 and 0.135 respectively indicated that the HLPN process enhances toughness. Potentiodynamic polarisation tests in Hank's solution showed a significant improvement in corrosion resistance; $E_{Corr}$ value of -218mV was considerably nobler compared to the untreated alloy ($E_{Corr}$=-775 mV) whereas corrosion current densities of $I_{Corr}$= $5\times10^{-5}$ mAcm$^{-2}$ were found to be two orders of magnitude lower as compared to the untreated CoCrMo alloy with ICorr= $2\times10^{-3}$ mAcm$^{-2}$. Metal ion concentration studies using ICP-MS analysis revealed that the plasma nitrided layers present a reliable barrier against Me-ion release from CoCrMo alloy. Enhancement of mechanical and corrosion properties and favorable Me-ion release performance combined with the significant reduction in process time makes HLPN a powerful technique for surface treatment of medical grade CoCrMo alloys.

### Keywords

Plasma nitriding; HIPIMS discharge; Low pressure; expanded austenite; corrosion resistance, medical grade alloys.

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## Poster 5

# Performance of CuAg Doped TiN/NbN Antimicrobial Coatings Deposited by High Power Impulse Magnetron Sputtering

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Pathogens that cause healthcare-associated infections (HAIs) pose an ongoing and increasing challenge to hospitals, both in the clinical treatment of patients and in the prevention of the cross-transmission of these pathogens. HAIs result in more deaths than AIDS, auto accident and breast cancer deaths combined in U.K. hospitals. This had led to an increased interest in medical coatings with antimicrobial protection for devices in continuous contact with patients. In this study, monolithic CuAg and four CuAg doped TiN/NbN multilayer coatings with varying CuAg content were deposited in Ar+$N_2$ reactive atmosphere using combined HIPIMS/DCMS technology. An industrial size Hauzer HTC 1000-4 system enabled with HIPIMS technology was used for the deposition of the coatings. The CuAg content in the TiN/NbN multilayer coating was altered by changing the target power. Energy dispersive X-ray (EDX) analysis was done to study the composition of the coatings. Knoop hardness tests revealed that the hardness value of CuAg doped TiN/NbN coating was 2.5 times higher than that of monolithic CuAg coating. X-ray diffraction was done to study the structural characteristics of the coatings. Scanning electron microscopy (plan-view and cross-section SEM) was used to analyse the microstructure of the coatings. The surface roughness measurements using a Dektak profiler showed that the TiN/NbN multilayer coating with the highest CuAg content was the roughest (Ra = 0.26 μm) amongst five coatings, including the monolithic CuAg coating. Pin-on-disc tribo tests at ambient conditions showed that the coefficient of friction reduced with increasing CuAg content in the CuAg doped TiN/NbN multilayer coatings. CuAg monolithic and CuAg doped multilayer coatings deposited on glass substrates tested for antimicrobial activity via a 45 min room-temperature exposure to a 10-fold PBS dilution of an overnight culture of *Escherichia coli* DH5α revealed that all of the coatings had strong antimicrobial activity.

**Key words**

DLC, protective coating, doped ta-C, pulsed arc discharge

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# Poster 6
# High Entropy Alloy Coatings for Geological Disposal Facilities

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One of the current proposed strategies for the Isolation and containment of intermediate level radioactive waste involves storage within stainless steel canisters in underground geological disposal facilities (GDF), backfilled with a cementitious grout. Post closure, re-saturation of a GDF will result in highly alkaline, anoxic environment. Under these conditions, cellulosic materials degrade to smaller, microbially available substrates including isosaccharinic acid and volatile fatty acids. Intruding sulphate reducing bacteria (SRB) are likely to use these substrates, generating free sulphide, leading to microbially induced corrosion of the containers. These corrosion events may potentially lead to a compromised containment, leading to release.

High entropy alloy thin films (HEA) were used as a strategy to supress microbially induced corrosion. Thin films containing Cu, Fe, Al, Cr and Ni we produced by deposition by ion beam sputter deposition onto grades 304 and 316 stainless steel test pieces (Dia. 13mm). Test pieces were then placed within a bioreactor containing an alkaliphilic SRB culture derived from the soil of lime kiln waste site. The impact of the biofilms on HEA and their subsequent impact on preventing corrosion of the base material were determined using CLSM, SEM and AFM.

The role of heavy metal on biofilm repression is demonstrated and discussed within this paper.

**Keywords:** Heavy metal, Biofilm, Disposal facilities, Corrosion.

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## Poster 7

# High Entropy Metallic Coatings for Oil Extraction Infrastructure

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It has been shown that some highly concentrated alloys, also known as High Entropy Alloys (HEAs), demonstrate good corrosion resistance. In this study, AlFeMnNiC, (in close to equimolar composition), was produced by arc melting and in the form of thin films. The thin film was deposited by Ion Beam Sputtering from elemental targets onto silicon and ferrous alloy substrates. The elemental chemical composition was determined by Energy Dispersive X-Ray (EDX) analysis. X-Ray Diffraction (XRD) was employed to determine atomic structures. The bulk alloy has a multiphase structure with the elements predominantly segregating into iron manganese carbides and nickel aluminium phases. An amorphous single-phase thin FeMnNiAlC films were created. The corrosion resistance of the materials was evaluated by potentiodynamic polarization in sodium chloride solution and compared to reference materials with good corrosion resistance such as 304 Stainless Steels in the same environment. The sintered alloys show better than stainless steel corrosion resistance.

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# *Poster 8*
# Coatings for the Next Generation of Turbochargers

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Modern high-output diesel engines have exhaust temperatures above 800 °C and there are demands to grow this temperature even further. The hot exhaust gas flow puts significant demands on general turbocharger engineering and used in turbocharger materials.   The exhaust gases have complex composition and, coupled with high temperature, they lead to corrosion and to material loss. Corrosion initiated cracks quickly spread below the surface of the material, accelerating turbocharger failure.

This presentation shows the design, testing and analysis of coatings, produced for use in contemporary and future turbocharger environment.

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# Poster 9
# Me-DLC Films in Textures via PECVD-HIPIMS: Analysis of Antimicrobial Activity and Cytotoxicity Evaluation

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The incorporation of metals in Diamond-Like Carbon (DLC) films makes it possible to combine the excellent tribological properties of this material with high antimicrobial activity. Therefore, in this work, DLC films were grown with Ag, Zn, and Cu via a combined Plasma Enhanced Chemical Vapor Deposition (PECVD) and High-Power Impulse Magnetron Sputtering (HIPIMS) process with a Balzers BAS 450 sputtering system. The films were deposited on textiles in an atmosphere of Ar (99.999%) and $C_2H_2$ (99.6%). The percentage of metal in the DLC was varied by controlling the flow of the acetylene gas. The working pressure was kept constant at 0.5 Pa and the peak current was adjusted for each type of target and varied from 100 to 400 A. Whereas, the average power was 500 W for the Zn-DLC films and 1500 W for the Cu-DLC and Ag-DLC films. EPMA analysis and Raman spectroscopy were used to evaluate the composition and structural quality of the material. Also, the morphology of the samples was characterized by SEM-FEG analysis. In addition, to analyse the antimicrobial activity, the AATCC100 (2019) standard method was used. The effectiveness of the film was evaluated against a Gram-negative (*Escherichia coli*) and a Gram-positive (*Staphylococcus aureus*) bacteria, and a fungus (*Candida albicans*), after a 24 h contact. The films showed excellent inhibitory effects against these microorganisms, with 100% effectiveness in some cases. Afterward, the cytotoxicity of the samples was evaluated by indirect contact. For this, the samples were soaked into the growth media (ISO 10993-5) for 1 and 7 days and then the extracts were collected and put in contact with keratinocytes for 24 h. The pure extracts obtained from all the samples with incorporation of metals were cytotoxic ($p<0.05$). Despite that, the cell viability after contact with some Zn-incorporated diluted extracts (10%) was not different from that observed in the control group.

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