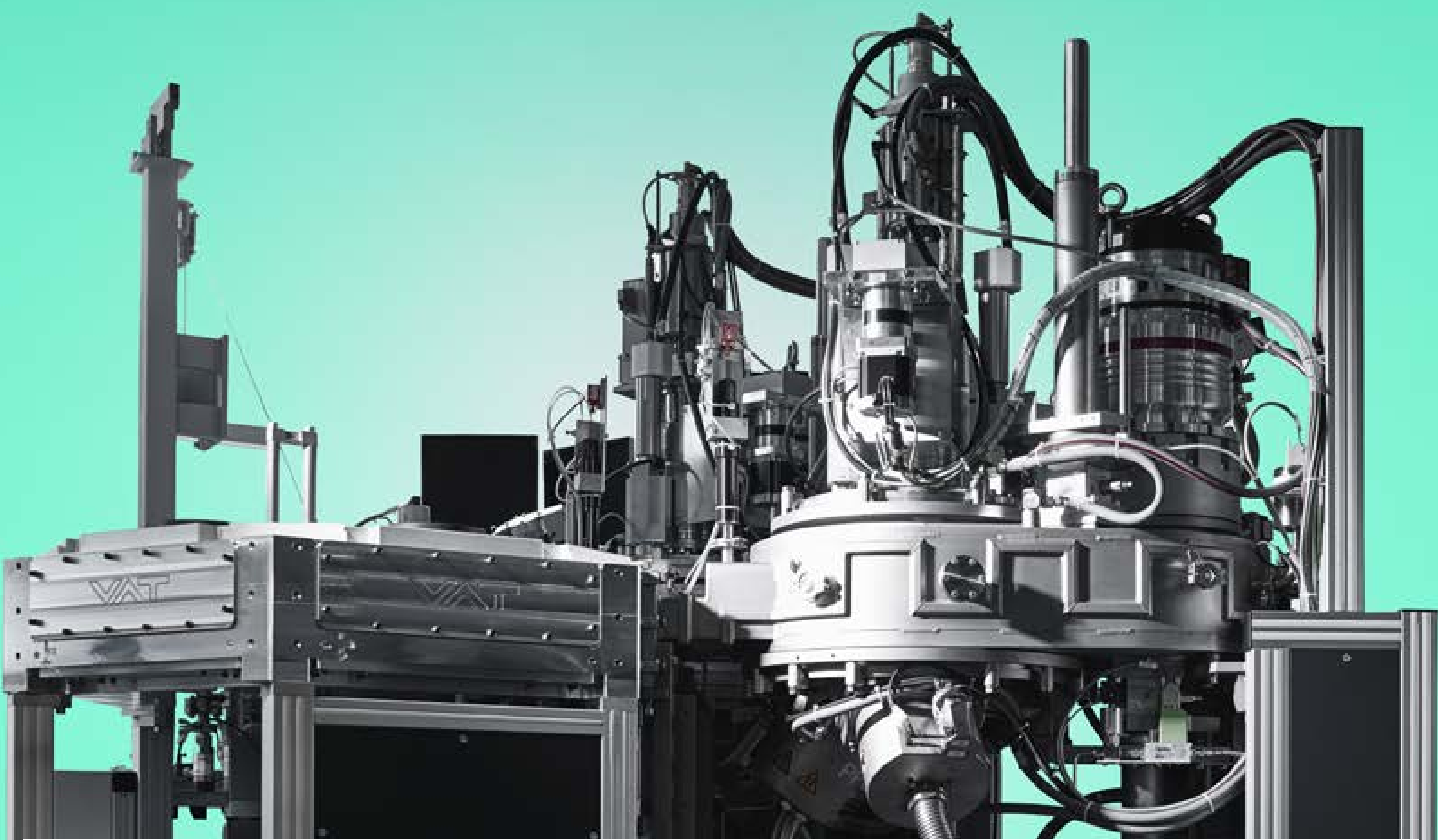
Eleventh International Conference on HIPIMS

Abstract Book



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SELF

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Surface Engineering: The key to a Sustainable Future?

David Elliott

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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 industrial and financial well-being is beyond question. So why is surface engineering so often overlooked by Governments around the world when they are developing manufacturing strategies for the future?

This presentation will examine why surface engineering is so often overlooked and the role that SELF – the Surface Engineering Leadership Forum is undertaking to ensure that the UK surface engineering sector remains a world leader both academically and industrially.

The presentation will focus on the overall goal of SELF to deliver the ecosystem for future growth:

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A low friction route to Net Zero

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There is a call to arms for the manufacturing community in delivering net zero GHG emissions through the products that we engineer across energy, transport, infrastructure and the manufacturing processes and supply chains we use to deliver them.

Over 60% emissions in manufactured goods are embodied in the materials extraction and primary processing stages. One of the greatest opportunities we have to reduce emissions is to look at life extension and end of life repurposing of engineered products. Surface engineering and advanced coatings play a crucial role in life extension of high value engineered products in service, and of the tooling and equipment used in the manufacturing processes that produce them. The value proposition for life extensions of critical wear components becomes even more attractive when we consider a shift toward through life engineering and servitisation of high value assets. Surface coatings also provide the opportunity to enhance bulk properties of less energy intensive materials to deliver required in service performance and reduce embodied emissions for these components.

HIPIMS has a clear role to play in enhancing performance and extending life for critical components in some of the evolving clean technology markets. The demand for the solutions that HIPIMS offers should accelerate the innovation and market pull.

From a UK perspective the government's 10-point plan to deliver net zero 2050 and the Industrial Decarbonisation policy provide a clear focus and purpose for the manufacturing research and innovation community. At the HVM Catapult we intend to work with world leading researchers in the UK and beyond to develop and fast track these solutions into deployment with HIPIMS providing a great example.

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Some current and future coating challenges in aero-engines

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As the aerospace industry continues the drive towards more fuel efficient and greener engines, without compromising safety and performance, materials will continue to be pushed to their limits to deliver these requirements. Combine this with increasing the service intervals and one can understand the need for robust tribological solutions to enable bulk materials to safely operate in extreme environments. Another aspect to consider is the challenge of a carbon neutral engine by 2050; will this be through the use of bio fuels, electrification or the use of hydrogen as a fuel? Each of which will come with its own unique set of challenges that will need to be overcome.

From a thermal efficiency perspective hotter and faster is better; hence the relentless increase in turbine entry temperature such that engines now operate at temperatures exceeding the melting point of nickel based superalloys. This is only possible with the use of internal cooling and thermal barrier coatings. But these systems are now reaching their limits; hence the planned introduction of ceramic matrix composites (CMCs) but even these need protection in the form of environmental barrier coatings.

On the other hand, improve propulsive efficiency there is a desire to decouple the fan from the LP turbine via a gearbox. This power gearbox (PGB) has a whole new set of challenges for the surface engineering and coatings community. What coatings are required and where? How will the oil interact with the surface engineering solutions? Are new coatings required for the bearings? And if we look towards electrification and electric motors all these questions are still valid.

This paper looks to highlight and discuss some of these issues and the potential for coating technologies to mitigate some of the current and future challenges faced in achieving design intent for highly complex modern aero-engines.

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Surface engineering of the leading edges of turbomachinery blades

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Blade leading edges in turbomachinery are critical to performance and therefore fuel efficiency, emission, noise, running and maintenance costs. Leading edge damage and therefore roughness is either caused by subtractive processes such as foreign object damage (bird strikes and debris ingestion) and erosion (hail, rain droplets, sand particles, dust, volcanic ash and cavitation) and additive processes such as filming (from dirt, icing, fouling, insect build-up). Therefore, this paper focuses on the changes of controlling the topography induced by during service to blade leading edges and the effect of roughness and form on performance and efforts to predict and model these changes. A range of applications are considered focused on wind, gas and tidal turbines and turbofan engines.

The surface engineering needed and microstructural design as well as the current options to limit roughness change and protect the leading edge will be presented along with emerging technology that offers protection such as HIPIMS coatings.

The main focus will be on water droplet erosion (WDE) with a review of the known physics of droplet impact, current testing and modelling capabilities, mechanism-microstructural interactions seen in actual damage of ex-service Ti-64 fan blades and surface engineering solutions for blade protection. Solutions include HIPIMS CrAlYN/CrN nanostructured multilayer systems, Ti/TiN multilayer and NiCrAlTi PVD coatings, CVD nanostructured W/WC coatings as well as electroplated hard coatings and the more conventional polyurethane and PACVD boron phosphide coatings. Where possible comparisons in erosion performance will be discussed along with their detailed erosion mechanisms.

Recent work where modelling and machine learning is used to predict coated wind turbine blade leading edge delamination and the effects this has on aerodynamic performance is also presented. The paper concludes that understanding the coated material response to additive and/or subtractive mechanisms and thus the roughness/ form evolution over time is essential going forward. This is turn would allow better understanding of the effects these changes have on aerodynamic/ hydrodynamic efficiency and the population of stress raisers and distribution of residual stresses that result. These in turn influence erosion rates, fatigue strength and remaining useful life of the blade leading edge as well as inform new designs, coating selection, maintenance and repair needs.

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Surface engineering in Renewable Energy: Mapping the weather on wear maps

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In studies of wind and tidal turbine energy conversion, there has been much interest in understanding the effects of the environment. This includes parameters relating to rain, hail and UV exposure. As these vary significantly globally, it follows that materials requirements for components associated with such engineering systems may change accordingly.

In Europe, there is significant energy capture afforded by the high wind speeds surrounding coastal areas in the Western part of the continent. Whilst these speeds improve energy efficiency, they also have may limit the lifetime of materials associated with wind turbines. This is especially true for leading edges of wind turbine blades.

In this paper, a review of laboratory raindrop erosion test results is presented on coated and uncoated surfaces and the conditions linked to those experienced by turbine blades in the environment. Erosion maps are generated showing patterns of wastage. Future trends in materials and surface coatings for exposure around coastal areas in Europe are discussed bearing in mind changes in environmental conditions as experienced in such locations.

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Understanding tribological contact: how a detailed understanding can help design wear resistant materials

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The impact of tribology (friction and wear) on the economies of developed nations is a substantial 5-8% of GDP. Friction and wear play a central role in life; in transport, in manufacturing, in process engineering, in medical devices and in everyday human activities. 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. It is these dynamic changes that determine the success or failure of the component. In many cases, distinct surface structures are generated by the sliding contact. Of these, the formation of so-called tribofilms is perhaps the most important. The formation of tribofilms can be engineered, for example through additives in oil lubrication. However, evidence is mounting that tribofilms play a crucial role in the success of many components, ranging from articulating surfaces in hip joints through to ultra-low friction coatings. This talk will show case studies that detail the importance of the formation of tribofilms. Examples will be taken from coatings and bulk materials. The structure of the tribofilm will be considered in detail, down to the atomic scale. The way in which this can drive the design of wear resistant materials will be considered.

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SiAlN coating produced with magnetron sputtering on metal substrate for aero-engine and nuclear industry applications

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SiAlN coatings consisting of Si_3N_4 and AlN phases with Mo interlayers were produced by magnetron sputter deposition on both Ti and Zr alloys. With the coating on Ti substrate, inter-diffusion and inter-reaction at the interface during cyclic oxidation at 800°C form a multilayer nitride coating system. A novel nitride interlayer exhibits adaptive conformability via mechanical twinning, thereby accommodating the thermal mismatch strain between the coating and substrate. This along with a high bond strength confers excellent thermal cycling life with no cracking, spallation and oxidation of the coating evident after hundreds of hours of cyclic oxidation (>40 cycles) in air at 800°C. This work provides a design pathway for a new family of coatings displaying excellent bonding, adaptive conformability and superior environmental protection for Ti-alloys at high temperature used in aero-engine industry.

The SiAlN coatings were applied to the Zr alloy with the 750 nm or 300 nm Mo interlayers and then were exposed to the steam environment at 1000°C. After 1 hour exposure, no detectable oxide scale forms on SiAlN/Mo (750 nm) coatings whereas SiAlN/Mo (300 nm) forms oxide scale. The downward diffusion of Si followed by relatively faster downward diffusion of N generates excessive Si and lean N, forming Si-Si bond in outermost surface of SiAlN, thereby resulting in oxidation. The degradation mechanism of amorphous nitrides is determined by elemental composition instead of reported amorphous or crystalline status. The coatings have demonstrated potential for application of coated Zr alloy for application in nuclear reactors.

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Thin film refractory plasmonic materials: deposition, optical properties, and temperature stability

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In this presentation, I will summarise the results of the research work carried out in my group.

Materials such as W, TiN[1], and $SrRuO_3$ (SRO)[2], have been suggested as promising alternatives to Au and Ag in plasmonic applications owing to their stability at high operational temperatures. In this study, thin films of W, Mo, Ti, TiN, TiON, Ag, Au, $SrRuO_3$ and SrNbO3 with thicknesses ranging from 50 to 105 nm are deposited on MgO, $SrTiO_3$ and Si substrates by e-beam evaporation, RF magnetron sputtering[1] and pulsed laser deposition [2,3,4]. Their properties are investigated to evaluate their potential use in the advancing field of plasmonics and nanophotonics by means of AFM, XRD, spectroscopic ellipsometry, and DC resistivity.

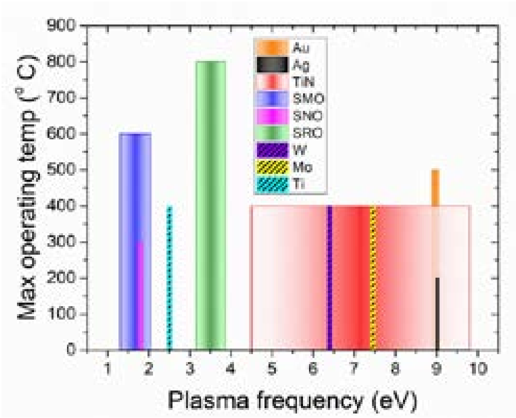

Fig 1. The proposed operating regimes for the investigated materials [5].

All samples are measured before and after annealing in air at temperatures ranging from 300 to 1000° C for one hour, to establish the maximum cycling temperature and potential longevity at elevated temperatures for each thin film materialv. It is found difficult to produce reliably the commonly reported refractory materials W, Mo and Ti, owing to the apparent influence of surface oxides. Meanwhile, the real part of the dielectric permittivity of Au was found to be stable up to 500° C when deposited on MgO, though the optical losses increased gradually with annealing temperature. After annealing at 600° C, significant changes to the morphology of the Au film were shown to result in a loss of connectivity across the film.

The optical properties of both TiN and TiON have been observed to change significantly upon annealing in the air before a loss of metallic behaviour after annealing at 500° C. However, unlike the noble metals, changes to the material properties appear a result of oxidation rather than changes to the surface morphology. It may therefore be concluded that, while Au may be more suitable for high temperature applications in air, TiN and TiON are better suited to high temperature applications operating under vacuum conditions or after suitable protective capping layers are identified.

Finally, the optical properties of SNO and SRO are considered, with the results showing that metallic behaviour is lost in SNO after annealing at 400° C due to a phase transition while being retained in SRO after annealing at 800° C. However, the degradation above this temperature appears a result of the agglomerate formation of the film. Therefore, although SRO may be an attractive alternative to Au for some high temperature applications, TiN and TiON may be expected to exhibit superior thermal stability in an encapsulated environment.

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Abstract Book

HIPIMS of transition metal nitrides for CMOS-compatible optoelectronic applications

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Transition metal nitrides (TMNs) display increased mechanical stability, thermal stability and spectral tunability when compared to the noble metals gold and silver and as such have emerged as viable alternative materials for plasmonic and optoelectronic applications.[1,2]

In order to successfully develop TMN-based optoelectronic devices it is necessary to deposit high quality thin films at CMOS compatible temperatures. Furthermore, deposition parameters of TMN thin films must be correlated with film optical properties in order to determine the suitability of various transition metal nitrides for use within a range of applications and operating environments. Key factors to consider include temperature stability and compatibility with application-specific substrate materials.

In this work, we investigate the applicability of transition metal nitride thin films (TiN, NbN, $Ti_{(1-x)}Nb_xN$) for use within plasmonic and optical devices. TMN thin films were deposited by High-Power Impulse Magnetron Sputtering (HIPIMS) onto a variety of semiconductor and industrial-standard substrates including Si, MgO, glass and steel. Optical properties were characterised using spectroscopic ellipsometry and correlated with the crystalline structure and surface morphology of the thin films. Additionally, the spectral tunability of these materials was investigated with respect to film stoichiometry.

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Towards Digitalised Surface Manufacturing: The EPSRC DSM NetworkPlus

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A study by a Special Interest Group (SIG), set up by the KTN, identified that compared to other High Value Manufacturing sectors, the coatings industry has tended to lag behind in terms of the level of digitalisation achieved. This, coupled with the drive towards Industry 4.0 and "Made Smarter" thinking has prompted moves within UK academia and industry to encourage the wider adoption of digitalisation. The Engineering and Physical Sciences Research Council (EPSRC) has supported the creation of an academic network (the Digitalised Surface Manufacturing (DSM) NetworkPlus) and at the same time, industry has joined forces to create "SELF" (the Surface Engineering Leadership Forum). This talk explains the background to the DSM Network, its mode of operation and provides an insight into its progress. This includes the distribution of biddable research funds, regular webinars and discussion groups as well as engagement with leading laboratories around the world to identify best practice and make that available to UK academics and industrial practitioners.

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Towards Creation of a Digital Twin of the Plasma Synthesis of Functional Materials by High Power Impulse Magnetron Sputtering and Other PVD Processes

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Optical emission spectroscopy (OES) has been used to monitor all stages of both HIPIMS and conventional magnetron sputtering processes and has been shown to provide a robust method of determining process repeatability with the potential to provide a reliable means of process control for quality assurance purposes. Using suitably designed probes it has been possible to identify relevant emission lines for monitoring the progress of chamber evacuation, substrate/source cleaning/conditioning, together with coating related aspects such as thickness, composition and morphological development of film and interlayer deposition. In addition, OES has been shown to provide a reliable means of system condition-monitoring, including early identification of air and water leaks, to support process optimisation and equipment utilisation.

The methodology has been shown to be highly relevant to sputter processes, including HIPIMS with a range of magnetron magnetic field configurations, for the deposition of 'conventional' nitride and carbonitride coatings, i.e. those of fixed composition. Challenges have been experienced with identifying suitable parameters for monitoring and control of films deposited using varying processing conditions, e.g. continually changing gas composition/pressure, frequently used in the control of, e.g. decorative coatings. Work is underway to determine if and how machine learning protocols can be applied to facilitate and optimise monitoring and control of these and other processing activities, including coatings development and the use of alternative deposition techniques, e.g. arc evaporation.

The work reported provides essential elements for the creation of a digital twin of the sputtering process which can be used both to monitor the process and predict outcomes such as sample and chamber wall contamination whilst incorporating physical models allowing calculation of film thickness in real time and the prediction of film texture.

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Computational Engineering and Cyber-Physical Systems

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Coatings and surface engineering are essential enablers for sustainable products and processes. They have the potential to drastically reduce environmental impacts per functional unit. A holistic approach is required to support engineering decisions from a system perspective and to avoid problem shifting. Such a holistic approach spans from process and machine level to factory level.

Two individual process examples for digitalization are shown. Using sputtering deposition for precision optics the EOSS(R) from Fraunhofer IST is a great example for application of digital data and digital twin. Using real time monitoring and feedback control the coating process is tuned during operation. The second example considers the tensidic cleaning line at Fraunhofer IST where all data is provided in real time digitally. The wide data basis is used for trend analysis and predictions.

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Unravelling the ion-energy-dependent structure evolution and its implications for the elastic properties of (V,Al)N thin films

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Ion irradiation-induced changes in the structure and mechanical properties of metastable cubic (V,Al)N deposited by reactive high power pulsed magnetron sputtering are systematically investigated by correlating experiments and theory in the ion kinetic energy (Ek) range from 4 to 154 eV. Increasing Ek results in film densification and the evolution from a columnar (111) oriented structure at Ek ≤ 24 eV to a fine-grained structure with (200) preferred orientation forEk ≥ 104 eV. Furthermore, the compressive intrinsic stress increases by 336 % to -4.8 GPa as Ek is increased from 4 to 104 eV. Higher ion kinetic energy causes stress relaxation to -2.7 GPa at 154 eV. These ion irradiation-induced changes in the thin film stress state are in good agreement with density functional theory simulations. Furthermore, the measured elastic moduli of (V,Al)N thin films exhibit no significant dependence on Ek. The apparent independence of the elastic modulus on Ek can be rationalized by considering the concurrent and balancing effects of bombardment-induced formation of Frenkel pairs (causing a decrease in elastic modulus) and evolution of compressive intrinsic stress (causing an increase in elastic modulus). Hence, 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.

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Energy flux measurements at magnetron sputtering

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A summary is given of different elementary processes influencing the thermal balance and energetic conditions of substrate surfaces during magnetron sputtering. The discussed mechanisms include heat radiation, kinetic and potential energy of charged particles and neutrals as well as enthalpy of involved chemical surface reactions. The energy and momentum of particles originating from the plasma or target, respectively, influence via energy flux density and substrate temperature the surface properties of the treated substrates [1,2]. For comparison of different sputtering devices or for upscaling of the plasma process, respectively, as well as for the estimation of critical thermal loads of the substrate the determination of the energy influx is a crucial need [1,3].

Measurements of energy fluxes from plasma to substrate during sputter deposition of thin films were carried out in different magnetron sputter deposition systems using calorimetric probes at typical substrate positions. By variation of the probe bias the different contributions originating from the kinetic energy of charge carriers, the recombination of charge carriers at the surface as well as the contributions from the impact of neutral sputtered particles and subsequent film growth have been determined. Radial scans in the substrate plane were recorded to obtain information about spatial distribution in the total energy influx and film properties.

In one example, the correlation between thin film growth of Cu and NiTi in a tilted magnetron cluster sputtering system [4] and the energy flux from plasma to substrate is studied. The special design of the sputter system with a fixed angle of 45° between targets and substrate enables a homogeneous coating of 200mm wafers with 100mm targets. The passive thermal probe measurements were made radially across the substrate area for two different magnetron positions. Depending on the static position of the probe, a significant change in the incoming energy flux towards the substrate was found. By using several surface analysis techniques, changes in deposition rate and morphology were correlated with the energy input.

In another example, crucial parameters of the magnetron plasma for thin film deposition, such as floating potential, electron temperature, and the energy flux to the substrate, are correlated with the I-V characteristics of sputtered memristive devices [5]. Strong differences in the oxidation state of the niobium oxide layers were found by transmission electron microscopy. Furthermore, kinetic MC simulations indicate the role of defect concentration within the NbO_x layer on the I-V hysteresis due to negative ion impact. The findings may enable a new pathway for the development of plasma-engineered memristive devices tailored for specific application.

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Ionization of Sputtered Particles in HiPIMS Discharges

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Coatings deposited with high power impulse magnetron sputtering (HiPIMS) discharges usually feature higher density and hardness than those deposited with traditional direct current magnetron sputtering (DCMS). However, this increase in coating quality comes at the cost of deposition rate, which is often found to be much lower for HiPIMS processes, compared to DCMS [1].

The main reason for this lower deposition rate is thought to be the so-called return effect: A large share of sputtered particles gets ionized close to the target surface. There, they are back attracted towards the target surface by the strong electric field present in the magnetic trap region of HiPIMS discharges. Only a small minority of particularly fast ions may overcome the electric field and reach the substrate [2].

How many sputtered and ionized particles may reach the substrate does not only depend on the strength of the electric field but also on where the particles are ionized: If a sputtered particle is ionized close to the target surface, it has to cross nearly the entire magnetic trap and, thus, needs to possess initial kinetic energy larger than the complete potential drop across the magnetic trap region to reach the substrate. However, if ionization occurs closer to the magnetic null position, only a small part of the complete potential drop has to be overcome by the ion. Consequently, a much larger share of ions could reach the substrate in this case.

In this contribution we investigate the position of ionization for three different target materials, using Abel inversion spectroscopic imaging and probe measurements.

These measurements reveal rapid ionization of sputtered material and subsequent depletion of neutral density when using titanium as the target material. The same effect can not be observed for aluminium or chromium as the target materials. A simple radiative model is applied to estimate the rate of titanium neutral ionization and the position where the ionization occurs.

The difference between the three target materials is further investigated using probe measurements [3] which reveal vastly different electron temperatures. Based on the sputter yields of the target material, general trends about the position of metal ionization and the consequences for the deposition rates may be surmised.

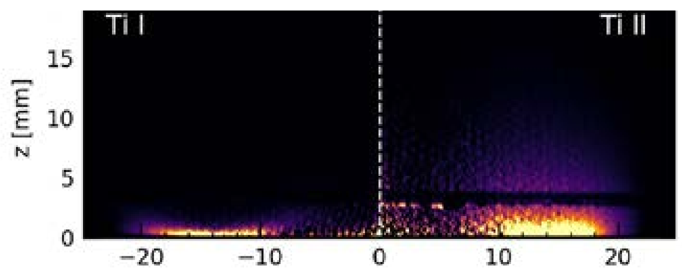

Fig 1. – Abel inverted false color image of titanium neutral emission (left) and titanium ion emission (right) at the end of a HiPIMS pulse. Titanium neutral emission is only observed close to the target because of neutral depletion by strong ionization.

Acknowledgments

This work has been supported by the German Science Foundation (DFG) within the frame of the collaborative research center SFB-TR 87.

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Multifunctional carbon-based nanocomposite HiPIMS coatings

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Carbon-based nanocomposite films offer the option to tailor protective coatings. These films consist of nanocrystalline carbon or carbon nitride hard materials which are embedded in an amorphous carbon-based network. The properties can be selectively adjusted by varying the process parameters and by choosing a specific film design. Important process parameters are the ion energy and the flux ratio of ions to film-forming particles during film growth as well as the substrate temperature. The film design finally provides the grain size of the hard material and the proportion of the hard material to the carbon-based matrix. The carbon-based matrix can be again modified by hydrogen and other elements. These aspects are discussed in detail in terms of thin film development in the system Ti-Zr-C-N-H. The fabrication of films is carried out by means of a materials combinatorial approach which is flanked by SRIM- and SIMTRA- modelling. Concerning the intricate determination of the film composition ERD, microprobe analysis, SEM, XRD, (HR)-TEM and -SEM is used.

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Abstract Book

Antibacterial activity of DLC Films with zinc, copper and silver

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Diamond-Like Carbon (DLC) films have a lot of interesting mechanical, chemical, and biological properties, therefore it has been extensively applied in different areas. The incorporation of other elements in these films can increase these properties, expanding their applicability as a coating for biomedical devices. Therefore, in this work, DLC films were grown with copper, silver, and zinc. The film was deposited via a combined Plasma Enhanced Chemical Vapor Deposition (PECVD) / Physical Vapor Deposition (PVD) technique driven by a High Power Impulse Magnetron Sputtering (HIPIMS) power with a metallic target in an atmosphere of Ar / C_2H_2. In the process, parameters such as gas flow, peak current, and deposition pressure were varied. Thus, the films were obtained with different compositions and structural qualities. The chemical composition, structural quality, and coating thickness were analyzed by Electronic Probe Microanalysis (EPMA), Raman spectroscopy, and profilometry, respectively. The analysis of the antibacterial activity of DLC films with metals was realized following the standard ISO 22196. The antibacterial test was carried out with *Escherichia coli* with different incubation times. Preliminary results show that adding metals in the DLC film structure increases its antibacterial activity against *Escherichia coli*.

Acknowledgments

The authors want to thanks to the Fundação de Amparo à Pesquisa do Estado de São Paulo – FAPESP (grants n. 2020/12450-4, 2017/08899-3, and 2012/15857-1), CNPq and Capes.

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Effect of positive pulse voltage in bipolar reactive HiPIMS on crystal structure, microstructure and mechanical properties of CrN films

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CrN films were prepared using three different configurations of the HiPIMS discharge mode and the substrate holder potential. We investigate the effect of a positive pulse voltage (30–400 V) in bipolar HiPIMS on the crystal structure, microstructure and resulting mechanical properties of the films, and compare it to the effect of a standard DC bias voltage applied to the substrate holder in unipolar HiPIMS. We find that when the substrate holder is at a floating potential, its charging causes the loss of the plasma-substrate potential difference, necessary for ion acceleration, and no obvious evolution is thus observed with increasing positive pulse voltage. However, when the substrate holder is grounded, the effect of the positive pulse voltage is apparent and different from the effect of the DC bias substrate voltage. That is mainly due to differences in energies delivered into the growing film by bombarding ions. Films prepared using bipolar HiPIMS at a positive pulse voltage of 90 and 120 V exhibit the most interesting properties, namely high hardness (23.5 and 23.1 GPa, respectively) at a relatively low residual compressive stress (1.7 and 1.5 GPa, respectively). The results indicate that as long as the growing film is conductively connected with the ground, bipolar HiPIMS is a suitable method to tailor and improve the film properties.

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Abstract Book

More than 30 year of Evolution of Cr-Al-N – from conventional sputtering to HIPIMS for industrial applications

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Since the first investigations in the metastable coating system Cr-Al-N at the end of the 80s by conventional sputtering took place, a lot of papers had been published in the last 30 years on this topic. Most of the early papers dealing with the deposition parameters and preparation of a possible phase diagrams for this system. Later the system was transferred to Arc machines and the aluminum rich side which is often described as AlCrN became an industrial standard for many applications in tool applications like milling or hobbing.

The metastable system Cr-Al-N offering compared to other ternary systems like Ti-Al-N or Zr-Al-N a high hot hardness and a higher wear resistance and make it ideal for different high temperature industrial applications due to the dense formation of (Cr,Al)oxides during the use in e.g. cutting applications.

However improvements in the deposition technology can widen the horizons in terms of application oriented properties. It has been reported when changing form ARC to HIPIMS, that HIPIMS technology not only offering smoother surface, also the microstructure as well as the phase composition can be changed, giving better properties e.g. for tool applications. In terms of the later performance not only the deposition technology is important, but also the equipment to deposit these type of coatings in an industrial way. Today's industrial production of coated parts require not only good coating properties also production related topics like reliability, easy maintenance, cost per part and flexibility of the coating unit itself plays an important role.

In this regard a historic overview of the system Cr-Al-N is giving and showing the latest results, what is possible in HIPIMS in terms of performance and deposition technology and showing that this technology is ready for serial production in a modern production environment.

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12 µm PVD in HiPIMS

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Coating development focussed for decades on the film's composition in an endless endeavour for increasing the hardness of the coating. On the other hand it was taken for granted that the thickness of tool coatings is limited to 3-4 µm. More than 6 µm is for traditional technologies not a viable option due to excessive intrinsic stress. No real improvement are the usual workarounds such as bond coats and multilayers with soft intermediate layers. The process gets slower and more prone to failures. There was no technology available to deposit the extra thick coatings for heavy-duty metal cutting applications. This paper will shine a light on a new direction for protective coatings: managing intrinsic stress and a dense morphology of the film.

HiPIMS is a good candidate since it is known for a dense structure without any droplets resulting in toughness and hardness at the same time. The real innovative leap is stress management by synchronising the HiPIMS pulses on the cathodes with the substrate bias. This paper will introduce the concept of selective ion biasing. Plasma analytics reveal that the flux arriving at the substrate per HiPIMS pulse is composed of the wanted metal ions coming from the target and other ion portions which highly influence the intrinsic stress of the growing film. Selective ion biasing is a fully new tool and allows to precisely select certain ion portions out of the pulse while suppressing unwanted species. Now the coating developer can actively tune the intrinsic stress of the film by setting the synchronisation parameters.

Full control on the process, the morphology and the intrinsic stress growing film – that's the quantum leap of selective ion biasing. And this for different HiPIMS frequencies and pulse data for each and every cathode – tailored for the respective target material.

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.

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Abstract Book

Pulsed Arc plasma of ta-C and doped ta-C

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Hydrogen free DLC (ta-C) coating is attracting a lot of attention recently. It can be produced with extremely high hardness; it has a low friction coefficient, and it has a temperature stability ~ 300°C higher than hydrogenated DLC. To obtain a sufficiently high sp3 to sp2 bonding ratio, C atoms must arrive with sufficient energy to penetrate the surface and thermalize at a depth of a number of atom layers. To achieve this requirement most of the C atoms must be ionized. ARC is suitable to reach a good ionized fraction, and pulsed ARC is known to achieve multiple ionization. In literature experiments have been reported, where the used pulse length is between 0.1 and 1 ms. We have focused on a short pulse duration of 5 µs. The produced coatings were ta-C and ta-C doped with different levels of W. OES experiments were completed to investigate the plasma during the pulse. Indications are showing that indeed double ionized C and multiple ionized W are present in the plasma. In our experiments a high-speed camera installed and was synchronized with the ARC pulses. It was found that during the pulse time the ARC splits. Despite the steep rise rate of the ARC current splitting follows the rule, that at currents above 60 A the ARC splits in several sub-arcs. Coatings deposited by this technique were studied by TEM, HRTEM and Raman. It was found that even for a W dopant level of 1 at%, Raman analyzes showed an indication of presence of WC. The HRTEM displayed clearly smaller WC particles than observed when growing a-C:H:W by magnetron sputtering, also for W dopant levels of around 8 at.%.

An explanation for this is the higher ionization degree of W, whereby W is implanted with an energy derived from the bias Voltage. SRIM calculations show that 50 eV W implanted into C reaches a depth of 1.3 nm, equivalent with a depth of 5 atom layers. This will effectively suppress movement, whereas with magnetron sputtering W atoms arrive with much lower energy, remain at the surface and allow a little bit more re-arrangement.

Key words: DLC, protective coating, doped ta-C, pulsed arc discharge

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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, N2, CH4 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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Measurement of momentum transfer in ion beam sputtering

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In today's industry, thin film coatings are an essential component to enable functionality of tools and electronics and act as catalysts for chemical reactions. Processes using physical vapor deposition are often used to produce high quality thin films. Ion beam sputter deposition allows a strict control of the coating process and is particularly well suited for systematic experiments to understand the underlying physical phenomena in order to optimize coating processes. Deposition rates can be determined by quartz crystal microbalances, and charged particles in the sputter plume can be characterized by Faraday cups or retarding field analyzers.

However, much of the sputter plume consists of neutral particles. Characterizing these requires much more complex diagnostics, such as optical emission, laser-induced fluorescence [1], or mass spectrometry [2].

A more direct measurement can be archived using interferometric force probes. Here, the force exerted by all particles of the sputter plume, including neutrals, onto the probe's surface is analyzed. In previous works, these probes have been used to determine the thrust of electric space propulsion engines, forces exerted by a low-temperature plasma onto a solid boundary [3], or the recoil of reflected and sputtered particles at a sputter target [4].

In this work, a rotatable copper target is irradiated by an ion beam. A directionally resolved momentum profile of the resulting sputter plume is obtained by circling the target with a force probe at a fixed distance, measuring the current and momentum transferred to the probe surface. The obtained profiles are then compared with numerical simulations using SRIM [5] and SD.SRIM.SP [6]. Both, measurements and simulations, are carried out for different angles of incidence, ion energies, gases, target materials, and working pressures [7].

In general, force probe measurements are not limited to specific plasmas and should work for all kinds of particle fluxes.

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Impact Fatigue and Fracture Toughness Analysis of CoCrMo Alloy Nitrided using HIPIMS Plasma

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CoCrMo alloy specimens were plasma nitrided using a HIPIMS discharge. In this work, we have investigated the effect of plasma nitriding voltage (-700 V to -1100 V) employed during nitriding on the microstructure, surface hardness, impact fatigue resistance and fracture toughness (K_{Ic}) of the alloy.

Results revealed that the specimens treated at lower nitriding voltages (-700 V and -900 V) develop a nitrided layer consisting of a mixture of Co_4N+$Co_{2-3}N$. As the nitriding voltage increased, this transformed into a thick layer consisting mainly of Co2-3N with a minor contribution from CrN/Cr2N phases. Accordingly, surface hardness test showed a significant improvement in hardness value (H= 23 GPa) as compared to the untreated specimen, (H= 7.9 GPa). The impact resistance of the alloy also increased with the nitriding voltage. Impact crater profiling of the specimens showed that the depth of the crater decreased drastically when nitrided with higher nitriding voltages. At the end of the impact test (one million impacts), the crater depth for an untreated alloy (12.78 µm) was found to be twice to the crater depth measured for the specimen nitrided at -1100 V (7.1 µm). Results indicate that the load-bearing capacity of the CoCrMo alloy increased linearly and considerably with nitriding voltage. HIPIMS plasma nitriding also improved the fracture toughness (K_{Ic}) of the surface where values of K_{Ic} could reach 988 MPamm$^{1/2}$ as compared to 908 MPamm$^{1/2}$ calculated for the untreated specimens. *H/E* (elastic index or elastic strain to failure) and H^3/E^2 (plastic index) results of the nitrided layers were calculated using surface hardness, *H* and elastic modulus, *E* values obtained with the help of nanoindentation tests. Systematic improvement in the values of *H/E* and H^3/E^2 ratios calculated for all nitrided specimens validate the increase in K_{Ic}, toughness and impact fatigue resistance of the nitrided specimens.

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Abstract Book

Me-DLC based strain sensitive materials

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Sensors are essential component of the digitalization (Internet of Things, Industry 4.0, …). There are challenges arising in integrating sensors in existing workpieces and machines. Besides the integration boosting the sensitivity is an essential challenge.

In the case of strain gauges a gauge factor of 2 is standard. Increasing the sensitivity mostly is connected with higher thermal sensitivity of the investigated materials. Furthermore, the applied process can influence the performance of the sensing materials. Therefore, this contribution will address development of metal containing diamond-like carbon films for strain sensing films with enhanced sensitivity while at the same time considering the thermal coefficient of resistance. As best solution a highly strain sensitive film with low or no thermal sensitivity is desired.

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Diamond-like carbon coatings by HIPIMS

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Diamond-like carbon (DLC) coatings are a multifunctional materials which exhibits excellent mechanical, electrical and optical properties making it suitable for wide range applications from tribological, biomedical to optical fields. Because of its wide range of application in various fields, over last two decades, the industry and scientists were focusing on diamond-like carbon (DLC) coating improvements. Recent trials on diamond-like carbon show high demand on high transparency with low friction and wear rate DLC coatings for protection of electrical, optical and decorative components.

Essential properties of DLC thin films are determined by the bonding configuration - sp3/sp2 fraction of its carbon atoms. In order to prepare DLC thin films for desired applications, it is essential to control and estimate the sp3/sp2 fraction precisely. The bonding configuration can be controlled with the ionization energy of the sputtered carbon atoms.

Moreover, other process variables (e.g., bias voltage, etching, current, precursor gas, time, and substrate temperature), also affect the tribological characteristics of DLC coatings as surface roughness, hydrogen incorporation or coating thickness.

In this research utilization of High Power Impulse Magnetron Sputtering (HIPIMS) for control of the DLC thin films parameters is instantiated. First the influence of HIPIMS (peak current, voltage, power, pulse time and frequency) and process (pressure, gas follow) parameters are investigated. Next effect of incorporation of hydro-carbon gas during deposition process is studied.

Following, DLC film properties were investigated with the Raman Spectroscopy. The ID/IG carbon peak ratio is found in the range of 0.2-1.49. However, certain samples don't show characteristic carbon peak in range of 800-2200 cm-1. Microscopic analysis reveals that most of coatings has non homogeneous coating distribution along the sample, which was confirmed by the Raman Spectroscopy. Optical parameters changes with an increase of deposition energy. For low ionization (low power or current) samples have low optical transmittivity in the visible spectrum. With increasing ionization the transmittivity increase, however for high ionization it starts to decrease. This behavior is consistent with the sp3 content depending on energy per carbon ion of 100 eV.

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Pulsed Arc non-equilibrium process effects on the properties of doped and pure ta-C coatings

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It is well known that thin films made of diamond-like Carbon (DLC) exhibit high hardness, low friction, and low wear rate. Due to their excellent mechanical and tribological properties, the DLC films are often used in form of protective coatings. Hydrogenated Diamond Like Carbon films have been utilized widely. However, their thermal stabilities at elevated temperature restrict many potential applications as high temperature lubricating coatings. Now in the focus of many industries is Hydrogen-free DLC. These coatings are prepared from solid graphite targets. Important features of non-hydrogenated films are their high hardness (>4.000 HV), high operational temperature (up to 600°C) and large internal compressive stress. To form hard tetrahedral-amorphous Carbon films requires high energy of all impinging ions. These conditions are met by a cathodic arc plasma deposition process.

Extensive research has been done in the past whereby the effect of impact energy, angle of incidence, substrate temperature and deposition rate on properties of ta-C were studied. We have shown in earlier presentations that we can modulate the sp^2/sp^3 content in the film at nanoscale if the right conditions are chosen.

Presently we report about ta-C coatings prepared from pure and doped graphite targets using pulsed Arc evaporation, whereby a pulsed discharge gives a steep rise rate of the ARC current. In all the cases the samples were tightly fastened to an Al block fixture with a temperature monitoring.

A Hardness in a range of 5.000 to 7000 HV was routinely achieved. An anomalous effect was observed about the film hardness; it is influenced negatively by the deposition rate. Despite the substrate being kept at a low temperature, the energy applied at the film surface during the pulse apparently causes a non-equilibrium temperature excursion at the outer surface. A semi-quantitative analysis was done to check at which deposition rate per unit surface area this effect occurs.

Two doping elements were chosen, Boron and Tungsten, with target dopant level varying between 0.5 and 4 at.%. The results for films with the two dopants as well as for pure ta-C films are described in detail.

Key words: DLC, protective coating, doped ta-C, pulsed arc discharge, sp^2/sp^3 modulation.

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Ionization region model for Ar/Cr in a high power impulse magnetron sputtering discharge

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Magnetron plasma discharge s are widely used in several technological applications, especially in semiconductor manufacturing. Metallic, oxide and nitride thin film are deposited by sputtering used in different steps of device manufacturing. One of the avenues explored is the application of power in the form of very short pulses High Power Impulse Magnetron Sputtering HiPIMS. It represents an alternative to DC or RF PVD processes. Therefore, the injection of a high power about 150 Watts/cm^2 during a very short pulse time allows to avoid t he high heat increase during the thin film deposition process. It also allows the improvement of the ionization degree and the dissociation rate of the injected reactive gaz.

To better understand about the pulsed high power discharge, a time dependent global plasma model is developed for the ionization region in a HiPIMS discharge of Ar/Cr. The model is based on solving a nonlinear equation system composed of the continuity equations of neutral and charged species in the Ionization Region (considered in the reaction scheme coupled to the power continuity equation. The advantage of our kinetic model is its ability to quantify the densities of neutrals and ions considered in the reaction scheme as well as their fluxes into the substrate. It is also possible to evaluate the electron density and temperature evolution with time.

A good agreement is shown between the calculated time current evolution and that measured. The simulations results show the effects of the main machine parameters on the neutral and the ion densities evolution versus time, by varying the pressure from 5 to 30 mTorr and the pulse width from 10 to 100 µs. Also, they contribute to understand the phenomena observed experimentally and to quantify the created population from HiPIMS discharge, particularly in the IR.

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Abstract Book

Ion-induced secondary electron emission coefficient of metal surfaces analysed in an ion beam experiment

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1. Introduction

In glow discharges the generation of secondary electrons at surfaces plays an important role for ignition and maintenance of a plasma. The ion-induced secondary electron emission coefficient (iSEEC) γ depends on the chemical state of the surfaces and is defined as number of released electrons per incident ion. The iSEEC varies depending whether metal surfaces are clean or oxidized [1]. In magnetron sputtering discharges e.g. knowledge about the interaction of plasma and metal ions with the metal target, described by γ, is important for the occurrence of different discharges regimes [2]. Moreover, γ is an important input parameter for many plasma simulations. The coefficients of some metals are already published in literature and measured by different techniques [3]. As the applied techniques measure often directly in the plasma, the determination of the iSEECs remains rather indirect though. Moreover, any energy dependence is mostly missing. The unique feature of the here presented experiment is the possibility of analysis of surface processes induced by single and multiple ionized argon ions impinging on metals or their oxides within a broad energy and mass range.

2. Experiment

The elementary plasma processes on surfaces are mimicked by sending quantified beams of ions to metal foils in an ultra-high vacuum reactor. Different thin metal foils are exposed to a beam of argon ions, which are extracted from an inductively coupled plasma. This ion beam is mass and energy selected before reaching the metal foil. The iSEEC is measured by comparing target currents with currents on a biased collector surrounding this target [4]. We will present γ of different clean and oxidized metal surfaces in a broad energy range and compare them with calculations.

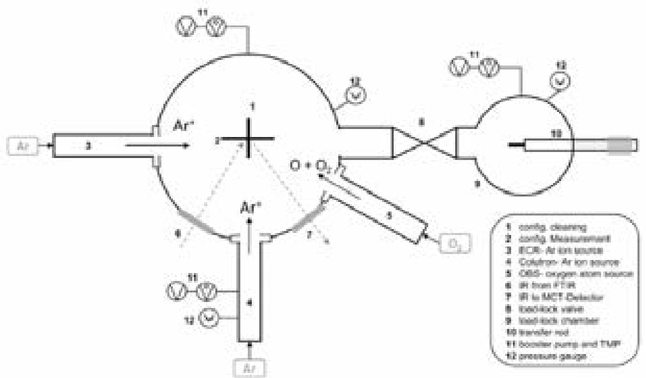

Figure 1: Schematic top view of the ion beam reactor.

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Keywords: ion beam experiment, ion-induced secondary electron emission, oxidized metal surfaces

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PVD coatings for Aluminium die casting applications: an experimental realistic approach

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Aluminium parts are widely used in Automotive, design and general mechanics applications and their most common production process is die casting. Moulds designed must foresee extremely high thermal and mechanical loads, due to molten alloy and cooling agent effects on tool skin, in conjunction with wear and abrasion taking place during injection of the Aluminium alloy. PVD coatings are a strong valid solution in order to increase tool lifetime by reduction of metallization and thermic insulation to steel substrate. Of course, there are important differences from one coating formulation to a different one and these are investigated in this work.

Furthermore, surface finishing of the mould plays an important role in tool performance. In addition, substrate pre-treatment, like plasma nitriding, can have a big influence referring to fatigue mainly.

In this extensive work, an innovative testing bench had been created where the probe undergoes an alternation between hot molten Aluminium alloy bath and spray cooling made of silicone based liquid. These two conditions are the most representatives in order to simulate thermal loads and fatigue of the probe. About mechanical loads, intended as high stresses generation; a small deep grove is created along the length of the probe: on the edges of this channel, there is a natural concentration of stresses that can evolve in crack formation and propagation.

Tool steel probes (1.2343 – AISI H11) were strategically prepared with different surface meshes on the same sample, one more close to near polished while the second one higher in Ra (trying to combine equal Rp and Rv values). The half of the probes were nitrided by a plasma process with the scope of increasing hardness from the surface to depth of about 80µm. All these preparation steps were just the bases for the application of PVD coatings that, as shown by preliminary flat coupons releasing force tests, are the only possible solution to overcome metallization and wear typical of uncoated samples.

The experiment was carried out on both sets of probes up to a total of twelve thousands cycles, with intermediate steps where surfaces were investigated by visual inspection for evaluation of the metallization effect and by scanning electron microscopy, researching fatigue cracks and monitoring their evolution during subsequent cycle.

In conclusion, with this setup we created a realistic a reliable method for die casting process simulation. Moreover, a specific design of the probes allowed for very adherent to real working conditions results. Fatigue cracks were found on samples with different preparations and their evolutions were followed showing very interesting outcomes.

A combination of roughness, material pre-treatment and PVD coating results as the best performing solution, showing minimum suffering from metallization point of view and best resilience, in relation to fatigue defects phenomena creation and propagation.

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Investigation of spokes in reactive Ar/N_2 atmosphere

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Plasma in high-power impulse magnetron sputtering (HiPIMS) discharge, similarly to other discharges utilizing ExB field (Hall thrusters, homopolar devices), undergoes self-organization into the ionization zones rotating in the ExB direction, called spokes [1]. Many studies were conducted focusing on the characterization of their appearance, number, rotational velocity, merging and splitting events in different experimental conditions. Nevertheless, only very little research was conducted in the case of reactive sputtering, where only general spoke characteristics were evaluated [2].

A dual-image fast camera screening was utilized to capture plasma emission on 3” Nb target in a reactive mixture of nitrogen and argon. Spoke characteristics were evaluated while overall pressure and supplied power was kept constant and the ratio of N_2/Ar was varied. The shape, velocity and spoke number were significantly affected by higher ratio of N_2 in the mixture. To distinguish between the effects of the poisoned target and reactive gas present in the plasma on spoke behaviour and appearance, plasma emission was screened as the Nb target was cleaned in pure Ar atmosphere. Additionally, obtained spoke characteristics were compared to those made on a fully compound NbN target.

Acknowledgements

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

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Control of Spokes in Magnetron Discharges

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Magnetron Sputtering is a Plasma Vapour Deposition (PVD) process widely used in industry and scientific communities. HiPIMS (High Power Impulse Magnetron Sputtering) produces plasma pulses of very high density of the order of 10^{19} m^{-3} without overheating the target. The plasma appears to be homogeneous to the human eye, but shows localised zones of high brightness rotating in the E x B direction when observed with an ICCD camera with exposure times below 1μs [1][3]. These local ionization zones, also called 'spokes' are assumed to play a role in the transport of particles and energy away from the target [2]. This anomalous transport results in an enhanced deposition rate by counteracting the return effect [4]. The primary objective of this project is to control spoke frequency in HiPIMS in-order to study its influence on the IEDF and metal ion flux from the target. Controlling metal ion flux from the target would lead to a better deposition rate and quality of the film. DCMS was chosen for the development of spoke control as an initial test object since the spokes in DC regime are more uniform compared to HiPIMS. Amplified rectangular signals are applied to a Langmuir probe to draw electron current from the plasma at the highest gradients in the E x B direction. The responses of the spoke frequency and intensity to the applied signal are measured with a flat probe. The metal ion flux from the target surface is measured time and energy resolved with a mass spectrometer. This study is then further extended to HiPIMS spokes by applying signals on multiple probes to achieve an effective control of spokes.

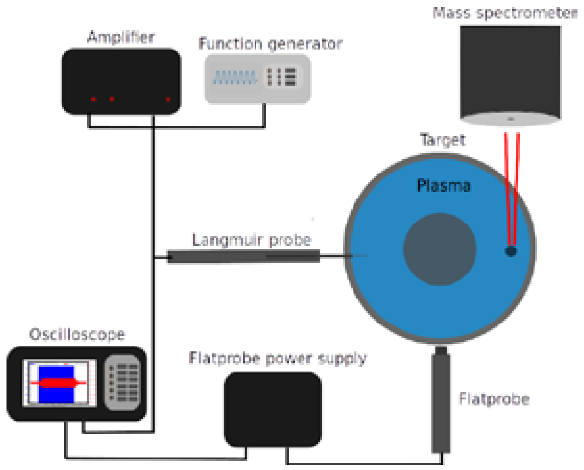

Fig 1. Schematic depiction of the experimental setup.

Keywords: Anomalous transport, local ionisation zones, overheating, DCMS, HiPIMS, control, spoke frequency, mass spectrometer, Langmuir probe, applied signal, ion flux, deposition rate, magnetron.

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Abstract Book

Time-Resolved Electron Energy Distributions and Plasma Potentials During HiPIMS Processes

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In this paper, we demonstrate a method for computing a set of temporally resolved plasma parameters taken in the vicinity of the substrate during a HiPIMS process. Further, a set of time-dependent plasma parameters, computed using the method described here, is presented for a Zr target with an unbalanced magnetron driven by a Starfire Industries IMPULSE® 2-2. This work, which employs a measurement technique first demonstrated in the early 1990's, [1], allows for the plasma potential, electron energy-distribution function, and normalized plasma density to all be resolved with μs-resolution. Figure 1 shows a set of temporally resolved parameters extracted using this method. This data corresponds to a 4" diameter Zr target at 10 mTorr with the substrate (probe) located 8" from the target. Under these conditions, we observe a ~5 μs delay between the onset of the kick pulse and the arrival of this change in plasma potential at the substrate. Further, although there is a sharp, distinct change in the plasma potential during the kick pulse, there is virtually no observable change in the electron energy distribution—both the mean and median electron energy are seemingly unaffected by the positive voltage reversal.

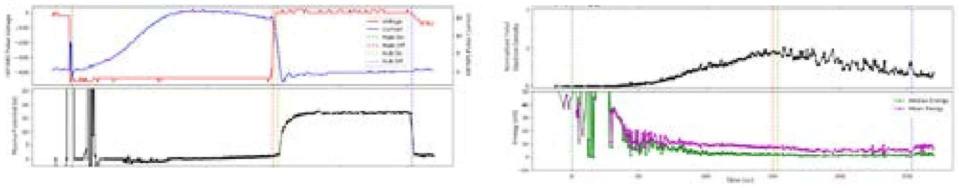

Fig 1. The HiPIMS voltage and current waveforms, plasma potential, normalized plasma density, and mean/median energies of the time-dependent EEDF are all plotted as functions of time.

Since the first commercial supplies appeared on the market in 2006, [2] there has been a dramatic increase in research aimed at exploring and leveraging the capabilities of HiPIMS processes. A major innovation here was the introduction of the Positive Kick™ by Starfire Industries in 2017, which applies a positive bias to the magnetron following the main HiPIMS current pulse (see Refs. [3] and [4] for some of the first published literature on this topic). Although a growing body of evidence exists in support of the benefits of HiPIMS w/ Positive Kick™ (see Refs [3]—[5]for some examples), relatively little is known about the plasma parameters that exist during the various phases of the HiPIMS pulse. The method used for extracting time-dependent plasma parameters, the parameters themselves extracted during various HiPIMS processes, and a discussion of the observed trends will be presented here.

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HIPIMS deposited nanoscale CrN/NbN multilayer coating for tribocorrosion resistance

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Recycling equipment (waste/ sea water/chemicals) need high tribocorrosion resistance. In this work High Power Impulse Magnetron Sputtering technique deposited nanoscale CrN/NbN multilayer coating for tribocorrosion resistance is explored. Sliding-wear experiments are performed under corrosive atmosphere (3.5% NaCl solution) in potentiodynamic and potentiostatic conditions. Results reveal that coated substrates exhibited (by a factor of 3) lower corrosion currents and high sliding wear-corrosion resistance (K_C = 1.1 x 10^{-14} $m^3N^{-1}m^{-1}$) as compared to uncoated HSS specimens. Superior adhesion and dense microstructure consisting of flat and well-defined hard nitride nanolayers leads to stable friction coefficients and retain the unique nanoscale layer-by-layer wear mechanism without delamination. Effect of corrosion on friction coefficients, wear mechanisms and vice versa has been presented.

Key words: HIPIMS; Tribocorrosion resistance; nanoscale multilayers; CrN/NbN.

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Abstract Book

Characterisation of a High-Power Impulse Magnetron Sputtered C/Mo/W Wear Resistant Coating by Transmission Electron Microscopy

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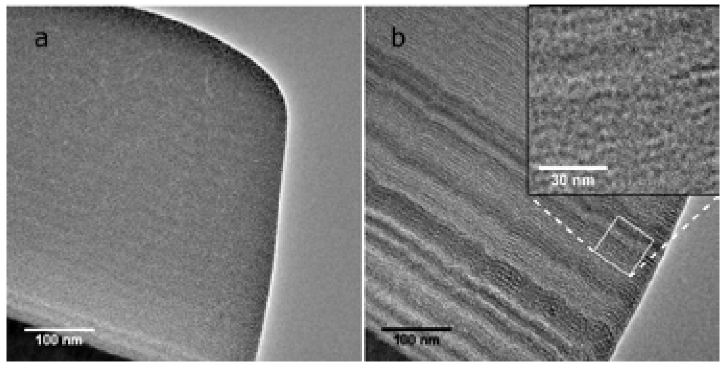
Thin films of C/Mo/W deposited using combined UBM/HIPIMS sputtering show 2-8 nm clusters of material richer in Mo and W than the matrix (found by EDS microanalysis), with structures that resemble graphitic onions with the metal atoms arranged regularly within them. EELS microanalysis showed the clusters to be rich in W and Mo.

As the time averaged power used in the pulsed HIPIMS magnetron was increased, the clusters became more defined, larger, and arranged into layers with amorphous matrix between them. Films deposited with average HIPIMS powers of 4 kW and 6 kW also showed a periodic modulation of the cluster density within the finer layers giving secondary, wider stripes in TEM. By analysing the ratio between the finer and coarser layers, it was found that this meta-layering is related to the substrate rotation in the deposition chamber but in a non-straightforward way. Reasons for this are proposed. The detailed structure of the clusters remains unknown and is the subject of further work.

Fluctuation electron microscopy results indicated the presence of crystal planes with the graphite interlayer spacing, crystal planes in hexagonal WC perpendicular to the basal plane, and some plane spacings found in Mo2C. Other peaks in the FEM results suggested symmetry-related starting points for future determination of the structure of the clusters.



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Complex 3D Nano Structures in HIPIMS $Ti_{1-x}Al_xN$–Coatings, an Electron Microscopic Study

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Complex 3D nanostructures with feather like morphology were found in HIPIMS $Ti_{1-x}Al_xN$ coatings with high Al-content (x>0.7). Reports of feather like structures during gas phase deposition are rare and refer to processes like R.F. Magnetron Sputtering [1, 2], Arc Discharge [3] und CVD techniques [4]. However, we have observed 3-dimensional feather-like nanostructures in a different system: HIPIMS $Ti_{1-x}Al_xN$ coatings on cemented carbide substrates. The following investigation refers to the characterization of the morphology, crystal structure and chemical composition of the complex arranged phases because influences of these parameters on the mechanical performance of a coating are expected. STEM/EELS Analysis show that the novel structures consist mainly of Wurtzite phase and are embedded in a matrix of cubic $Ti_{1-x}Al_xN$.Three-dimensional reconstructions of the feather like structures by STEM-Tomography show a foliate to cone like arrangement of the Wurtzite branches. A growth model to explain the formation of the complex structures with respect to the coating parameters is proposed.

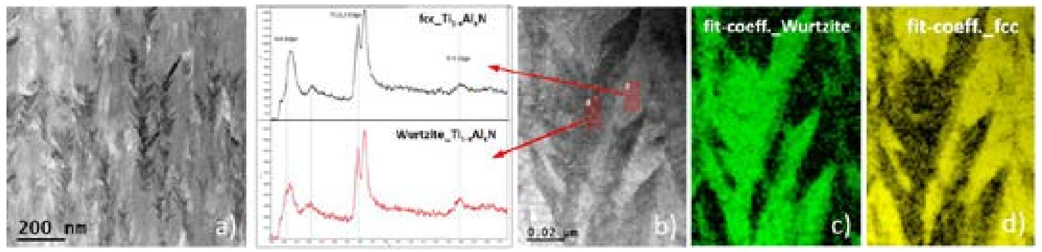

Fig.1 a): STEM-image of the feather like structures b): ADF-image with corresponding EELS-Spectra of the different phases c) mapping result after MLLS Fit with Wurtzite spectra d): mapping result after MLLS Fit with fcc spectra

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Controlled reactive HiPIMS: Effective technique for low-temperature deposition of tunable oxynitrides and thermochromic oxides

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Reactive high-power impulse magnetron sputtering (HiPIMS) with a feedback pulsed reactive gas (oxygen and nitrogen) flow control and to-substrate reactive gas injection into a high-density plasma in front of the sputtered metal target was used for a low-temperature deposition of highly optically transparent Al-O-N films (substrate temperature of 120 °C) and thermochromic VO_2-based films (substrate temperature of 330 °C) onto unbiased substrates.

A modified version of HiPIMS, called Deep Oscillation Magnetron Sputtering, was used to produce high-quality Al-O-N films with a gradually changed elemental composition (from Al_2O_3 in AlN), structure and properties. We give the basic principles of this controlled deposition, maximizing the degree of dissociation of both O_2 and N_2 molecules in a discharge plasma, which leads to a replacement of very different reactivities of the O_2 and N_2 molecules with metal atoms on the surface of growing films by similar (high) reactivities of atomic O and N.

We developed a low-temperature scalable deposition technique for high-performance durable thermochromic $ZrO_2/V_{0.982}W_{0.018}O_2/ZrO_2$ coatings. The $V_{0.982}W_{0.018}O_2$ layers were deposited by controlled HiPIMS of V target, combined with a simultaneous pulsed DC magnetron sputtering of W target (doping of VO_2 by W to reduce the transition temperature to 20-21 °C), in an argon-oxygen gas mixture. The effective pulsed oxygen flow control of the reactive HiPIMS deposition makes it possible to utilize the enhanced energies of the ions bombarding the growing $V_{0.982}W_{0.018}O_2$ layers for the support of the crystallization of the thermochromic phase in them at the low substrate surface temperature of 330 °C and without any substrate bias voltage. We present the basic principles of this controlled deposition.

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Amorphous and crystalline ReOx thin films deposited by reactive HiPIMS

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Rhenium oxides are known to exist in the three main phases ReO_2, ReO_3, and Re_2O_7, corresponding to the oxidation states Re^{4+}, Re^{6+}, and Re^{7+}, respectively. ReO_3 sometimes is called a “covalent metal”, because it has a high metallic conductivity comparable to metals due to the delocalized nature of the *d* electrons.[1]

The thin films of ReO_x (≈ 150 nm) on fused quartz substrates were deposited by reactive high power impulse magnetron sputtering (R-HiPIMS, t_{ON}=50 μs, t_{OFF}=9 ms, I_p≈0.8 A/cm^2) from a metallic Re target in an Ar and O_2 atmosphere. The substrate temperature and the oxygen-to-argon flow ratio were varied to determine the influence on film’s properties. In addition, as-deposited films were annealed at 250 °C in air for 3 hours to obtain a crystalline ReO3 structure. During the annealing, a clean piece of quartz was placed on the sample surface to avoid the evaporation of rhenium oxide.[2] The films were studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), UV-Vis-NIR absorption spectroscopy and conductivity measurements.

The films were stored in an inert atmosphere till the characterisation to avoid the possible film’s degradation in the ambient conditions. All the films exhibit an atomic concentration ratio close to 1:3 (Re:O) and a mixed-valent composition of Re^{2+},Re^{4+}, Re^{6+}, and Re^{7+} regardless of the deposition conditions. However, some correlations have been observed between the composition and the deposition parameters. The as-deposited films either have an X-ray amorphous structure (a-ReO_x) or contain a nano-crystalline ReO_2 phase if deposited at room or elevated temperatures (150 or 250 °C), respectively. It is possible to convert a-ReO_x into the crystalline ReO_3 upon annealing (Fig.1(a)). A dense surface without voids forms when the deposition temperature is increased (Fig.1(b)). Crystallites with the size of approximately 500 nm have been observed on the surface of the films deposited at 150 °C after the annealing. The conductivity of the films is in the range from 10^{-4} to 10^{-3} Ωcm. Absorption in the visible light due to free electrons results in the characteristic transmittance peak around 500 nm for the crystalline ReO_3 films (Fig.1(c)).

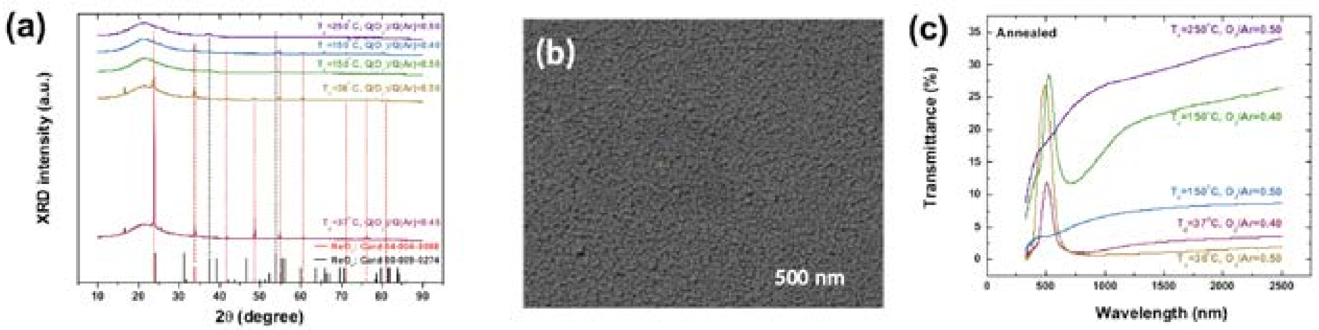

Fig. 1. X-ray diffractograms of the annealed rhenium oxide films (a), SEM image of the film deposited at 250 °C (b), and transmittance spectra of the annealed films (c).

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Financial support was provided by ERDF Project no. 1.1.1.1/ 18/A/073.

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High-speed slot-milling of 304 stainless steel by end mill cutters coated with HiPIMS deposited AlTiN

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In the recent years, High Power Impulse Magnetron Sputtering (HiPIMS) PVD deposition technology has emerged as a superior alternative to DC magnetron sputtering (DCMS) due to better substrate-coating adhesion. TiAlN coated cutting tools are often used for machining stainless steel. Earlier it was deposited using unbalanced magnetron sputtering. Literature reveal that HiPIMS deposited TiAlN coating has better wear resistance than the one deposited by conventional DCMS. It was also reported that the HiPIMS coating morphology was quite smoother with a smaller grain size than the DC magnetron sputter coating. There are literature on the milling of duplex stainless steel, maraging steel and 420 stainless steel using AlTiN coated tool below 100 m/min cutting speed which revealed the difficulties of machining these steels. Present study focuses on high-speed machining performance of the HiPIMS deposited AlTiN coated end mill cutters under small quantity lubrication medium. 4-fluted end mill cutters having a diameter of 10 mm with flute length of 19 mm and helix of 45° was used. Slot-milling operation was carried out on a block of 304 stainless steel. In the deposition process, the average power of 5 kW and pulse duration of 100 μs were set. The coating service has been outsourced. The Al and Ti were present in the coating layer as atomic percentages of 24% and 16% respectively. It was also observed that the coating was quite smoother and uniformly deposited on the cutting edge. As such, flood cooling is recommended for such tool during machining. Present research group intended to explore the feasibility of the minimum quantity lubrication (MQL) in such applications. The MQL adopted in the present study consumes cutting fluid (soluble oil) in the range of only 250 ml/hr. MQL the cutting fluid is atomized with the help of a compressed air jet and sprayed at the cutting zone in the form of an aerosol. Objective was to see if these coated tools performs effectively with such a low consumption rate of flow rate of MQL. On the other hand, cutting fluid was delivered at 300l/hr. in flood cooling mode The cutting speed in the range of 150-350 m/min and feed rate in between 956-2229 mm/min were varied both at a constant depth of cut of 0.5 mm so that the load per tooth can be kept constant.

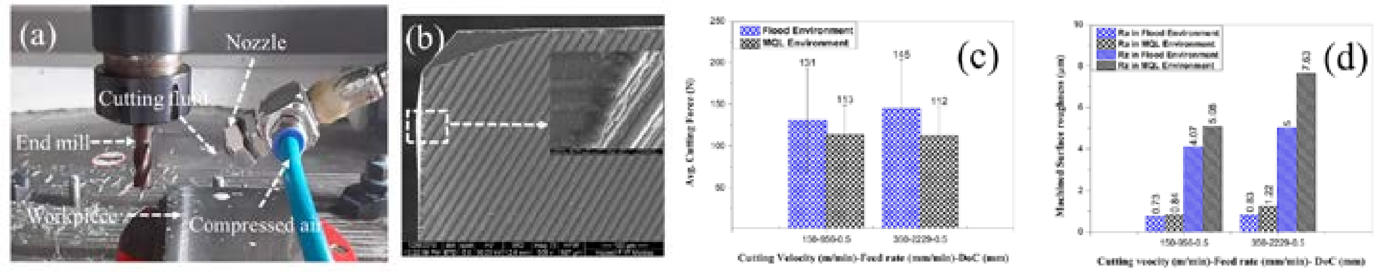

Fig. - (a) MQL set up, **(b)** coated tool before machining **(c)** cutting force variation in Flood and MQL environment at minimum and maximum process parameters and **(d)** machined surface roughness variation in Flood and MQL environment at minimum and maximum process parameters.

MQL could effectively arrest BUE formation, as efficiently as flood cooling. The cutting force level was comparable, although there was a marginal increase in surface roughness. The heat load was well managed by the HiPIMS deposited AlTiN coating and it performed without any sign of failure by flaking and aggressive wearing. Thus, when environment friendliness gains priority in machining industries, these HiPIMS deposited AlTiN coated end mills exhibits its potential to work under a sustainable environment like MQL, even for high-speed machining of an austenitic stainless steel grade

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Industrialization of Plasma Technology: Requirements for the Power Supplies When Moving to the 100 kW Range

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Industrial plasma processes today require power supplies in the 100-kW range and above. Thus, these devices are a critical component of the plasma processing system. Consequently, cost effectiveness and reliability are essential features of the design. To illustrate this, power supplies for different frequency ranges are described here: middle frequency (kHz), high frequency (MHz) and, as a possible future perspective, microwaves (GHz). A change from monolithic designs to modular structures is taking place in all areas.

MF power supplies are used for the large-area sputter coating of architectural glass. These coatings give building facades the desired functionality (e.g. sun protection or energy conservation). The coatings are applied over a width of more than three meters. Dielectric layers require dual magnetrons and power supplies with up to 150 kW output. The MF is generated with a single load commutated IGBT inverter bridge, followed by the output resonant circuit for load matching. A problem with this architecture is that the provision of different power ranges always requires a new design. Modern bipolar generators are built from of individual 20 kW power modules that can be interconnected up to 180 kW of total power.

HiPIMS sputtering has in recent years made a successful transition from research into industrial applications. Even with slightly lower rates compared to some established coating technologies, HiPIMS coatings can provide unique properties such as low defect densities and stress control. Today growth rates are sufficient for high-quality decorative and protective hard coatings up to about 10µm in thickness. Introduction HIPIMS into i.e. large-area sputter coating of architectural glass requires scaling up the power supply ratings to the few-kA range. Such high currents may require re-qualification of the end blocks to assure long-term reliable operation. The modular design of state-of-the-art HIPIMS power supplies allows industrial operation with peak current as high as 8 kA.

RF power supplies in the multi-kilowatt range are used for PECVD and especially for plasma etching of the backplanes in flat panel displays. Up to GEN 6 (1.5 x 1.8m) glass, generators with a single output tube were used, which were driven by a transistorized driver stage. A 90-kW generator is currently available for GEN 10.5, which is based on the interconnection of 8 semiconductor modules each of 12 kW. This technology change has numerous advantages in terms of costs, availability, and throughput. A particular challenge to the load matching is the provision of high reactive voltage and current to the capacitive load in case of dry etching.

A transition to modular semiconductor power supplies is also gradually taking place in the field of microwave generators. In this field, the power supplies of particle accelerators are already quite advanced and a good indicator for what will be the future of microwave plasma technology. Instead of the previously used klystrons, individual semiconductor power modules, each with an output power of 1.2 kW are connected via an isolator to a system of combiners to sum them to the desired output power.

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Abstract Book

Presence of a reverse discharge during long positive voltage pulses in a bipolar HiPIMS discharge

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Bipolar HiPIMS discharges attract great attention because the application of a positive voltage pulse (PP) after the main negative voltage pulse (NP) which sputters the target may be beneficial for the film formation, e.g., for a higher hardness, improved adhesion to the substrate and/or increased density. Especially, a longer PP may produce a significant flux of ions to conductive films on the grounded substrates. In our case, the presence of a reverse discharge (RD) was observed for PP with a longer duration.

All our measurements were carried out in a vessel build from a DN 200 ISO-K 6-way cross piping equipped with an unbalanced circular magnetron (Ti target, a diameter of 100mm) powered by a self-build bipolar HiPIMS pulsing unit. The duration of NP was 100µs, the averaged target power density in NP was around 1kWcm^{-2} and the argon pressure was 1Pa. Here we present the results for PP with the positive voltage pulse amplitude of 100V, the duration of 500µs, and the delay between the end of NP and the beginning of PP of 20µs. The time-resolved Langmuir probe (cylindrical, a diameter of 0.15mm and length of 10mm) measurements were performed at the discharge axis (the probe tip parallel with the target surface) for the distances from the target z = 35, 60, and 100mm. The time-resolved imaging was carried out in a perpendicular direction to the discharge axis using the intensified CCD camera with electron multiplication on the chip (emICCD, Princeton Instruments PI-MAX4 1024EMB) for Ar and Ti atoms and ions (using appropriate band-pass filters).

It was found that around time t = 230µs from the initiation of NP (110µs after the beginning of PP) a decrease in the plasma and floating potentials (U_s and U_f, respectively) by up to 40V appears at z = 35mm. This potential decrease moves with time to higher distances from the target and around t = 270µs it is also registered at z = 100mm. The potential drop is accompanied by a local increase in the electron temperature (T_e) from around 0.5eV before the ignition of RD to values over 10eV and by a local decrease in the electron density (n_e) from 4×10^{17}m^{-3} to 1×10^{17}m^{-3}. From t = 350µs up to the end of PP, the RD stabilizes and T_e ranges between 1 and 2.5eV. During this time, the value of U_s slowly rises by about 4V and its average value may be estimated to be around 85V (an average over time and distances) which is lower by 10V in comparison to the average value before the RD ignition. The value of n_e also slowly decreases from roughly 2×10^{17} at z = 100mm to 7×10^{16}m^{-3} at z = 35mm. The emICCD camera revealed that the light emission of Ti^+ ions starts to increase around t = 265µs at the discharge axis near the target. After t = 285µs, the similar light emission is observable also for other species (Ar atoms and ions, and Ti atoms). This emission spreads out in space and persists up to the end of PP. Here it should be noted that these results are consistent with our mass spectroscopy measurements carried out for PP with the duration of 200µs.

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Electron property measurements in a Bipolar HiPIMS discharge by laser Thomson scattering

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Laser Thomson Scattering (LTS) is a non-perturbing diagnostic tool that is unaffected by magnetic fields, meaning that electron properties can be measured with precision and the data analysis is unambiguous and simple to implement. Using an LTS system, developed at the University of Liverpool, time resolved measurements can be made throughout the HiPIMS waveform, both in the active-glow and after-glow. Results have been published in [1] by P.J. Ryan and in this contribution, the study is extended to the asymmetric bipolar configuration, where a positive voltage is delivered to the target immediately after the HiPIMS pulse.

The LTS system has an excellent temporal resolution of ~ 5μs with a spatial resolution of 3mm. In this study the laser beam was aligned on the centre line with respect to the tungsten target surface, focused at two points; one corresponding to the magnetic null of the unbalanced magnetron at 61mm from the surface and another at 15mm. Different magnitudes and lengths of positive pulses (PP) were delivered to the target, with a fixed HiPIMS pulse of duration 50μs repetition rate of 50Hz and ~ 8μs delay between the delivery of the PP and the HiPIMS pulse termination. Two different operating pressures were also investigated. The electron density reached values above $3.8\times10^{18}\,m^{-3}$ during the HiPIMS on time, with a maximum temperature exceeding 2.4 0 eV. Without the addition of a PP, these values fell to below $3.8\times10^{17}\,m^{-3}$ in the afterglow with electron temperatures below 0.2 eV. However, at certain conditions, the temperature measurements in the PP began to rise again, often matching the temperature measured in the initial HiPIMS pulse and the density decayed comparatively faster. Shown here is the effect the PP has on the electron properties measured by LTS for different gas pressures, length and magnitude of PP.

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Diagnosis of Be-Ne-D magnetron plasma operated in bipolar HiPIMS mode

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Disruptions are an inherent problem of the tokamak fusion reactor design. On early devices it was considered a nuisance but on large devices like ITER it can pose a serious threat to the structural integrity of the plasma facing components. To address the disruptions problem a solution can be represented by the massive gas injection (MGI). Through MGI systems, gas impurities (noble gases or nitrogen) are seeded into the vessel to mitigate disruptions and in order to protect the PFC's from thermal loads higher than their engineering limit. As one of the main candidates, neon (Ne) could be used as a seeding gas in ITER to perform this task. However, by introducing a new gas into the vessel can further complicate the material-mixing and tritium retention problem. In this context it is important to study the retention and release kinetics of Ne from beryllium co-deposited layers and to asses through future studies its influence of nuclear fuel retention and release from this type of layers. As a first step this contribution is focused on establishing a precise control over the parameters of the deposition process in terms of ion current and energy. The Be-Ne-D magnetron plasma was operated in bipolar HiPIMS mode and electrical diagnosis was performed in order to optimize de Ne and D inclusion in Be layers. Measurements of I-V characteristic of the pulses, temporal distribution of plasma potential and ion saturation current respectively, were performed to establish in what manner the controllable parameters (target voltage amplitude, the pulse configuration, the length of the negative and positive pulses, pressure inside the deposition chamber) can impact the plasma density, the ion current to the substrate and ion energy respectively. It was observed that the ion current to the substrates (in this case a biased planar probe) increases with the negative pulse width up to 20 μs. In relation to the pressure inside the vacuum vessel the ion current decreases quasi-linearly with the increase of pressure (0.7-3 Pa range) due to ion scattering at the collision with neutral gas particles. Also, the increase of the width of positive reversal voltage applied on the target immediately after the negative pulse also indicate a gain in regards to the ion current. In the same manner the pulse energy also leads to an increase of the ion current, but in this case the ion return effect can play a major role in ion flux composition due to the fact that at high operating voltages in bipolar HiPIMS the deposition rate decreases but the electron density increases leading to an ion flux dominated by the process gas ions. In terms of ion energy, the main interest process parameter is represented by the positive pulse voltage amplitude. Measurements performed showed that during the negative pulse only, the ion energy has a value ~ 5 eV, however this energy can be fine-tuned between 5-200 eV by changing the amplitude of the positive pulse. The research performed here could help in the future with the improvement of reference coatings similar in composition with the layers resulted during the functioning of a fusion reactor with Be as a PFC.

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/ CCCDI–UEFISCDI, project PN-III-P1-1.1-PD-2019-1024, no. PD 107/2020 , within PNCDI III programme.

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Bipolar HiPIMS: Correlating plasma parameters to thin film properties

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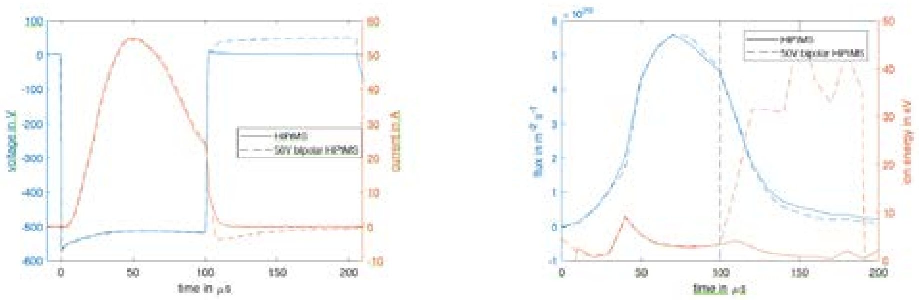
Retarding Field Analyzer (RFA) and Langmuir probe measurements were carried out in a 3 inch magnetron system with a niobium target operating in argon to determine how positive polarity pulses in the HiPIMS voltage waveform can change the dynamics of the plasma and influence thin film properties.

The positive voltage pulses were introduced in the early afterglow with heights U_{pos} between 10 and 100V and a variation of durations between 10 and 100 µs. Operating argon pressures were varied from 5 to 24mTorr. The plasma parameters were determined with a time-resolution of 10 µs for the RFA at a typical substrate position 10 cm away from the target. The time-resolution for Langmuir probe measurements was 1 µs at different position along the centre line of the magnetron and above the racetrack.



(a) Waveform of a 50V bipolar HiPIMS pulse

(b) Ion flux and energy of Figure a

Fig 1. Waveform of a 200W HiPIMS pulse with and without a 50V positive polarity pulse. The average ion energy in Figure b shows an increase in ion energy during the positive polarity pulse.

RFA measurements, like in Figure 1, show a clear increase in ion energy when a positive polarity pulse is applied. In contrary the ion flux is identical for both cases. Since the ion flux is the product of ion density and ion energy a faster decay in ion density is required, which was verified by Langmuir probe measurements. To correlate the effects a bipolar HiPIMS pulse has on the crystal structure and the superconductivity of thin films, Niobium films were analysed by SEM, XRD and Squid measurements.

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The plasma potential structure in a bipolar pulsed HiPIMS plasma

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One of the most promising recent innovations in HiPIMS sputtering is a technique known as bipolar HiPIMS (BP-HiPIMS), where a positive “kick” bias is applied to the target immediately after the end of the pulse. This positive bias has the effect of ion bombarding the substrate without the need for sample biasing [1]. The ion bombardment was initially attributed to high plasma potential during the afterglow accelerating ions through the sheath at the grounded substrate. This was challenged by V. Tiron *et al*. [2] who found evidence of ions actively accelerated away from the target by a moving double layer. However, there is an inconsistency in the appearance of this moving double layer: No such potential wave was observed for a positive bias below +150 V by V. Tiro *et al*. [2]. This is despite there being evidence for a moving double layer presented in work by F. *Avino et al* [3] at +50 V kick an inconsistency noted by the authors of [2].

Investigations of BP-HiPIMS using an emissive probe at the University of Liverpool also failed to find a moving double layer using a 105 mm diameter circular magnetron, even when the system delivers a +200 V kick. However, when a smaller 50 mm magnetron is used in the same system, a moving double layer is clearly evident. In this contribution, we attempt to understand the fundamental plasma physics linking target to the wall surface area ratio and plasma potential. This understanding can then be used as a guide to designing the BP-HiPIMS systems most capable of ion bombardment.

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Sputtering onto liquids for Nanoparticle Synthesis

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Magnetron Sputtering onto liquids allows obtaining high purity dispersions of nanoparticles (NPs - Fig.1). We studied the sputtering of Cu, Ag, and Au onto castor and rapeseed oil and its polymers as these vegetable oils are low cost, ecologically friendly, can be stored in air, and withstand vacuum. The effect of sputtering time and power, Ar pressure, type of sputtering plasma (dcMS vs HiPIMS), and viscosity of host liquid are studied. The formation of a cloud of particles underneath the oil surface is observed (Fig.1) while films form for high viscosity oils. The scenario of NPs formation is inferred from experimental and theoretical analyses. Cu-NPs oxidize rapidly in castor oil with formation of stable copper oxide NPs (3-10 nm for dcMS). Au-NPs (2.4 - 3.2 nm for dcMS) have higher stability in castor oil than Ag-NPs (1 - 4 nm for dcMS [1]) but secondary growth processes take place (Fig. 2). HiPIMS processing promotes the formation of NPs twice larger than those obtained in dcMS mode.

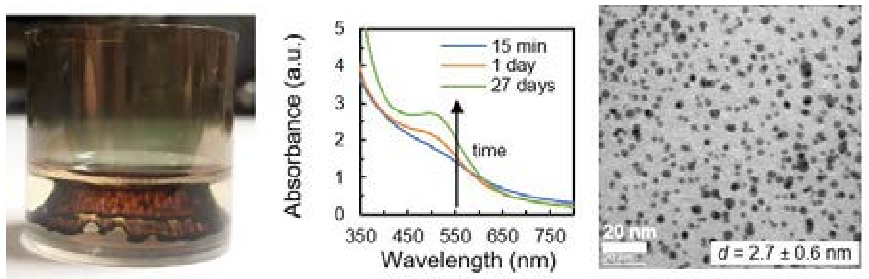

Fig 1. UV-VIS and TEM characterization of Au-NPs obtained by sputtering Au on castor oil.

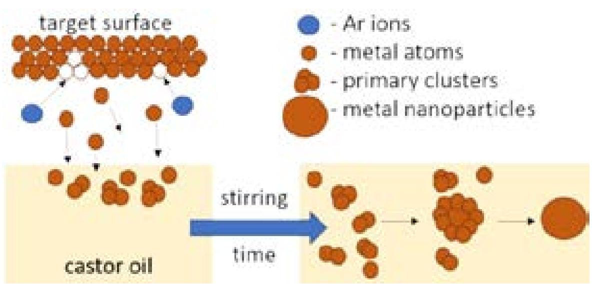

Fig 2. Scenario of Au-NPs formation in castor oil.

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The effect of magnetic field configuration on structural and mechanical properties of TiN coatings deposited by HiPIMS and dcMS

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The quality of coatings deposited by magnetron sputtering is known to depend on, among others, the magnetic field strength (Φ) and the magnetic field configuration. Furthermore, high power impulse magnetron sputtering (HiPIMS) is known to result in low defect - high density coatings, and is therefore used to deposit barrier coatings against wear and corrosion. The influence of varying the Φ, on deposition rate (*R*), structure and hardness of titanium nitride coatings prepared by HiPIMS and dc magnetron sputtering (dcMS) was investigated. At 22mT, the ratio between HiPIMS deposition rate and dcMS deposition rate (R_{HiPIMS}/R_{dcMS}) was almost equal to 1. As Φ was increased from 22mT to 35mT, R decreased by 28% for HiPIMS and increased by 15.6% for dcMS, and R_{HiPIMS}/R_{dcMS} was reduced from 1 to 0.63. From 35mT to 44mT, the decrease in *R* slowed to 6% for HiPIMS and to 12.5% for dcMS. The (111) orientation was dominant over (200) orientation for both HiPIMS and dcMS, and become less dominant with the Φ in the case of dcMS. The residual stresses and surface roughness were determined and their evolution with Φ is highlighted. Mechanical characterization of the deposited coatings was performed, where the hardness tests showed that on average the HiPIMS coatings (29-34GPa) were some 5 GPa harder than dcMS coatings (25-27GPa).

Keywords: HiPIMS, dcMS, magnetic field strength, hardness, deposition rate, TiN

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HiPIMS : A side of the story

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Cathodic sputtering is a story that begins at the end of the 19th century (grove) and whose evolutions follow technological progress (pumps, electric power supplies, etc.) and scientific progress, in particular the knowledge and understanding of cold plasmas. D. M. Mattox[1], A. Anders[2] and many others[3] have traced its history.

Paradoxically, although having shown and modeled the importance of additional magnetic fields and different excitation modes (DC, RF, Pulsed, High Power Pulsed) there are always new ideas and improvements brought by experimenters. As Andre Anders says[2] : due to the complex, often non-linear and non-equilibrium nature of plasma and surface interaction, there is still a place for the experienced ion and plasma "sourcerer." The work on magnetic fields has been remarkable: magnetron, unbalanced magnetron[4], outer field[5], induction coil[6,7].

The history of HiPIMS is one of them, from Kustnetsov to the latest developments, with incessant back and forth between experiences, understanding and modeling. I will try to show how a whole young generation of researchers (Konstantinidis, Ehiasarian, Lundin, Minea, Bandorf, Sarakinos, Hecimovic, Gudmunson, Kubart, Ferrec, Keraudy, Greczynski, Shimizu...) have appropriated this technique through of the European COST HiP program. Finally I will talk about our contribution first, with the fast HiPIMS[8,9] and for a few weeks with a new generation of HiPIMS power supply with different tunable stages.

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Abstract Book

Role of energetic ions in the growth of fcc and ω crystalline phases in Ti films deposited by HiPIMS

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The present work aims at investigating how to control the nucleation of uncommon crystalline phases in Ti films by adding and properly tailoring a Ti ion flux to the film-forming species.

Due to their interesting properties such as high mechanical strength, good corrosion resistance, excellent chemical and thermal stabilities, Ti films have been largely exploited for many applications (e.g. aerospace, production of medical implants, microelectronics). Ti films commonly show the hcp (α) phase [1], whose preferential orientation depends on whether the surface energy or the deformation energy is minimized [2].

The formation of a specific phase in the growing film is influenced by the energies of the particles striking the substrate, but also by the type of incident species, both those of the working gas and the metal ones [3, 4]. Thus, having good control of energy and type of the film forming species is crucial to affect both the microstructure and phase composition of the growing films [5]. To achieve this goal, the HiPIMS technique proved to be an ideal tool [3, 4, 6]. Indeed, through a suitable choice of the process parameters, it is possible to tune the composition of the HiPIMS plasma and, through the application of substrate bias voltage, it is possible to vary the energy of the species impinging to the substrate.

In the present work, we show how to obtain the conditions for which, in addition to the growth of Ti α-phase, the nucleation of fcc [7] and ω-Ti phase [1] is observed. Since the film phase evolution is affected by the type of impinging species, Optical Emission Spectroscopy (OES) has been used to monitor the HiPIMS plasma composition with the aim to maximize the Ti ion flux by varying the peak power. On the other hand, the energy of the species has been set by applying different values of a bias voltage synchronous with the pulse during the film depositions. Specifically, HiPIMS depositions with three different substrate bias voltage US (0 V, -300 V and -500 V) have been performed. Moreover, conventional Direct Current Magnetron Sputtering (DCMS) films have been deposited as a reference.

The microstructure, morphology and residual stress of the deposited films have been analysed with different characterization techniques (i.e. X-Ray Diffraction Spectroscopy, Scanning Electron Microscope and Wafer curvature method). The DCMS samples, where the film forming species are mostly low energy atoms, exhibit the Ti α-phase with preferential orientation along the (002) reflection. As far as HiPIMS samples are concerned, films deposited in low energy environment (U_S = 0 V) initially show the presence of the Ti fcc phase which gradually, as the thickness increases, transforms to the Ti α-phase orientated along to the (002) reflection. Differently, films deposited under high energy conditions (US = -300 V and -500 V) show the (100) reflection of the Ti α-phase during the initial stages and, for higher thicknesses, the nucleation of the Ti ω-phase is observed.

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Time Resolved Ion Energy Distribution Functions during a HiPIMS Discharge

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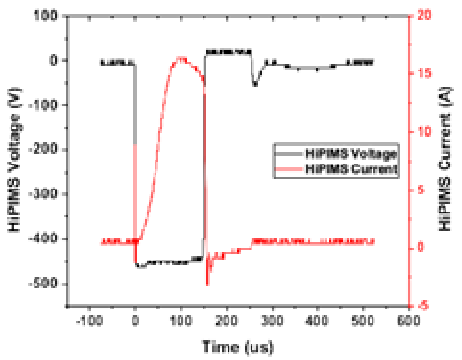
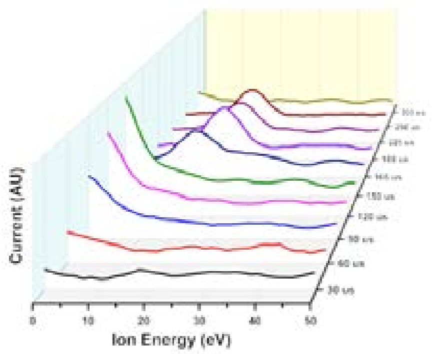
The expansion of HiPIMS as both a research and production technique has demonstrated the need to better understand transient events inherent to the discharge, specifically the Positive Kick™ pulse, first commercialized by Starfire Industries, responsible for imparting ion energy to the workpiece at low gas temperatures. Previous research has shown that sputtered metal ions arrive at the workpiece with tunable ion energies depending on the conditions of the discharge, while limiting ion energies of working gases. Much remains to be understood about the nature of the plasma responsible for this.

In the current work, a Starfire Industries 2-2 Impulse® with Positive Kick™ was utilized in conjunction with an Impedans Semion gridded energy analyzer to determine the transient nature of the ion energy distribution during the positive kick pulse. The time for ion energies to match that of the kick pulse bias voltages were recorded for a 4" Zr target on an unbalanced magnetron for a variety of gas pressures, pulse lengths, kick pulse lengths and amplitudes.

Ion energies within 5% of the kick pulse bias voltage are consistently observed at the detector within several μs of the beginning of the kick pulse indicating rapid transit times for the plasma across the chamber. Time delays were strong functions of pressure, but not of pulse lengths or amplitudes. Additionally, decay times for ion energy distributions occurred on similar time scales suggesting the plasma expansion enabled by the kick pulse is short lived. Ion energies above the kick pulse bias voltage are consistently absent over the conditions tested (Semion detection maximum for this configuration is 150 eV) indicating that the pulse conditions may be suitable for the minimization of instabilities that may be deleterious to both film quality and uniformity of deposition. These and other results will be discussed in conjunction with time resolved electron energy distribution measurements to provide an understanding of plasma dynamics and the effect of the magnetron's magnetic trap.





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Abstract Book

Bipolar HiPIMS Thruster: Effective propulsion of metal ions for increased flux and enhanced coating characteristics

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The dense plasma created in HiPIMS owing to the applied high voltage pulses enables the deposition of superior quality coatings compared to conventional direct current magnetron sputtering and cathodic arc. However, the coating characteristics such as hardness, wear resistance are enhanced in HiPIMS by compromising deposition rate because a major fraction of ions of sputtered materials are attracted back to the target due to the magnetic trap. The problem with low deposition rate in HiPIMS can be counteracted by applying a positive potential to the target following every negative HiPIMS pulse to accelerate the depositing ions towards the substrate through raised plasma potential. The accelerated depositing ions are well-thermalized before reaching the substrate. In this work, a retarding field analyser is used to study the bipolar pulse induced modulations in the temporal and the spatial distribution of ion flux and ion energies, and electron temperature in the HiPIMS plasma. This study helps to understand and tune the right pulse characteristics based on the sputtering target materials to enhance the deposition rate and important coating characteristics such as hardness, wear resistance and tool functionalities.

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