## Hard Coatings and Vapor Deposition Technologies
## Room On Demand - Session B8

## HiPIMS, Pulsed Plasmas and Energetic Deposition

**B8-1 INVITED TALK: Evolution of Ionization Fraction of Sputtered Species in Standard, Multi-pulse and Reactive HiPIMS**, *M. Fekete, K. Bernatova, P. Klein, J. Hnilica,* ***Petr Vasina (vasina@physics.muni.cz)***, Masaryk University, Brno, Czech Republic **INVITED**

High power impulse magnetron sputtering (HiPIMS) technology attracts the interest of the industry as the coatings deposited by HiPIMS exhibit enhanced properties compared to conventional dc magnetron sputtered (dcMS) coatings. This is because HiPIMS generates very dense plasma, which results in a large fraction of ionized sputtered particles. However, a significant drawback of HiPIMS is a lower deposition rate compared to dcMS, which can be mitigated by operation of HiPIMS in multi-pulse mode (m-HiPIMS). M-HiPIMS further changes the coating structure and resulting properties due to the enhanced ion flux to the substrate because of the interaction of the preceding and the subsequent pulse. The evolution of the sputtered species ionization fraction is studied using a recently developed effective branching fraction method. This non-invasive method utilizes the optical emission signal to quantify the absolute ground state number densities of the sputtered titanium species. Influence of the preceding pulse on the subsequent pulse in the non-reactive m-HiPIMS process is examined as a function of delay between two successive pulses.

The sputtered species ionization fraction plays an important role also in reactive processes. In reactive HiPIMS process, the hysteresis curve is generally reduced in width and shifted towards lower reactive gas supplies compared to reactive dcMS. We report on the evolutions of the sputtered species ionization fraction in reactive HiPIMS discharges in oxygen, nitrogen and acetylene gases for a constant mean power and pulse duration, when varying the repetition frequency. The ionization fraction of the sputtered species increases with the partial pressure of the reactive gas, which was attributed to a combination of different effects taking place in HiPIMS plasma. Further, the hysteresis curve shape changes with the change of the repetition frequency. Larger ionization fraction of the sputtered species leads to larger difference in the hysteresis curve shape. The hysteresis behavior of reactive HiPIMS is modelled utilizing a modified Berg model. The back-attraction of the sputtered species to the target is incorporated into the modified Berg model. The results from simulations prove that the back-attraction of sputtered metal ions is the main effect causing the hysteresis curve reduction and shift in reactive HiPIMS compared to reactive dcMS.

**B8-3 Dynamics of the Titanium Ground State Atoms and Ions in HiPIMS Discharge**, ***Jaroslav Hnilica (hnilica@mail.muni.cz)***, *P. Klein, P. Vasina,* Masaryk University, Brno, Czech Republic*; R. Snyders, N. Britun,* University of Mons, Belgium

High power impulse magnetron sputtering (HiPIMS) is a very attractive physical vapor deposition technique, which has been of great interest over the last two decades. Continuous development of the HiPIMS-based sputtering discharges is tightly related to the more profound understanding of the undergoing physical processes, a crucial factor for the optimization of thin-film growth as well as for further development of sputtering technology in general.

In our study, we combined various optical diagnostic methods for in-situ characterization of HiPIMS discharges. Special attention was dedicated to the visualization of the ground state titanium neutrals and ions in the discharge volume as their direct imaging above the magnetron target is a straightforward way to obtain information about their number density. Two-dimensional time-resolved density mapping of the sputtered particles in a HiPIMS discharge was performed by laser-induced fluorescence (LIF) technique. Atomic absorption spectroscopy (AAS) measurements were utilized in parallel to LIF to follow the number density evolution of sputtered species. Above mentioned methods were used to study effects such as plasma-on time, plasma-off time, gas pressure, pulse energy, or oxygen addition on density evolution of sputtered particles.

As a result of discharge characterization, the number densities, as well as temporal propagation of the neutral and ionized sputtered titanium atoms were determined. The result shows that atoms always remain in the discharge volume, the plasma-off time duration mainly alters the amount of background sputtered atom densities at which the successive pulse starts. At the same time, the plasma pulse duration together with the pulse energy, significantly affect ionization degree of the sputtered titanium above the magnetron cathode, especially shortly after the HiPIMS pulse. On the other hand, the observed titanium atom and ion density dynamics are weakly sensitive to the plasma pulse duration which implies that the initial stages of HiPIMS pulse have a stronger influence on the sputtering process evolution.

The results obtained in this study can be utilized to control the ionization degree, sputtering rate, as well as the other discharge parameters in industrial deposition processes involving HiPIMS discharges.

**B8-4 The Single-Shot Spatial-Resolved OES of the Spoke in Non-Reactive HiPIMS**, ***Marta Šlapanská (slapanska@physics.muni.cz)***, *M. Kroker, J. Hnilica, P. Klein, P. Vašina,* Masaryk University, Czechia

The rotating plasma patterns, also known as ionisation zones or spokes, firstly observed in non-reactive high power impulse magnetron sputtering discharges (HiPIMS) are at certain conditions present in direct current magnetron sputtering (dcMS) and radio frequency magnetron sputtering discharges (rfMS) as well. The spokes are investigated due to their high impact on the deposition process and sputtered species' transport. To better understand the spoke phenomena, it is necessary to acquire comprehensive data of the plasma parameters inside the spoke; however, in HiPIMS, preferably by non-invasive diagnostics.

This contribution presents the non-invasive spatial-resolved optical emission spectroscopy (OES) of the plasma inside the spoke conducted in non-reactive HiPIMS discharge. The pulses have a duration of 100 µs with a repetition rate of 5 Hz. The 3-inch titanium target was utilised. The experiment was run at argon pressures of 0.4 Pa, 1.0 Pa, and 1.6 Pa to investigate both triangular and round spokes.

The fast photodiode and the cylindrical probe were used to capture and determine the passing spoke position. The photodiode's signal and the probe signal were synchronised with the optical emission spectrum acquisition by the intensified charge-coupled device (ICCD) detector with a gate time of 100 ns. By processing these three signals and creating the normalised time scale for each spoke, the unified spoke (UNI-spoke) has been created. Consequently, the evolutions of the selected emission lines can be shown within the UNI-spoke.

The spatially resolved emissions of Ar atom and ions and Ti atoms and ions spectral lines were investigated within the UNI-spoke. The spatial resolved OES measurements have shown that the Ar and Ti atoms and ions spectral lines have the characteristic evolution of a specific species' intensity and is the same for all observed spectral lines of this species within the spoke independently of applied pressure. The Boltzmann plot method was utilised to determine the excitation temperatures within the UNI-spoke. The excitation temperatures obtained using the Ar ions and Ti atoms and ions are 13000 K, 8000 K, and 19000 K. The ionisation fraction has been calculated from the selected spectral lines of titanium atom and ion. The ionisation fraction reaches approximately 40%, and its evolution and excitation temperature evolutions remain constant in the margin of standard error within the UNI-spoke for all investigated working pressures.

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**B8-5 Understanding and Influencing the Energy Delivered to the Film in Bipolar HiPIMS**, ***Tomas Kozak (kozakt@ntis.zcu.cz)***, *A. Pajdarova, J. Capek,* University of West Bohemia, Czech Republic*; M. Cada, Z. Hubicka,* Institute of Physics, Academy of Sciences of the Czech Republic*; P. Mares,* HVM Plasma, s.r.o., Czech Republic

Benefiting from high degree of ionization of process gas and, especially, target material atoms, the high-power impulse magnetron sputtering (HiPIMS) technique provides increased energy delivered to the film resulting in hard, dense and defect-free coatings [1]. Asymmetric bipolar pulsed magnetron sputtering is one of the major techniques used for deposition of dielectric films allowing the neutralization of charge on the target during a positive voltage pulse on the magnetron. Moreover, the positive magnetron voltage causes an increase of plasma potential leading to enhanced energies of ions incident on the growing film [2]. Using the positive pulse in a HiPIMS discharge, where the degree of ionization is much higher, can result in substantial increase of energy delivered to the film and improvement of film properties [3]. Additionally, this technique might be more suitable for the industry than using separate substrate bias source.

This paper presents a systematic study of ion energy spectra in a bipolar HiPIMS discharge employing a rectangular positive voltage pulse (with controllable amplitude, delay after the main negative pulse and pulse length). The time-averaged spectra of ions measured at the substrate position exhibit a prominent high-energy peak corresponding to the ions accelerated by the increased plasma potential during the positive pulse. The position of the peak can be varied by positive pulse amplitude, its size scales with the pulse length and its width can be slightly influenced by the delay of the positive pulse. Moreover, time-resolved mass spectroscopy has been used to analyze the time of arrival of ions at various energies. Features of the energy spectra related to the magnetron voltage transients were identified. They indicate changes of the plasma potential in front of the substrate. To fully understand the ion energy spectra, the mass spectroscopy results are supported by Langmuir probe measurements of plasma and floating potential, and also electron density and temperature, at several positions in the discharge.

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**B8-6 The Use of HiPIMS with Positive Pulses to Tailor Film Ion Assistance and the Resulting Microstructural Properties***, **Ivan Fernandez (ivan.fernandez@nano4energy.eu)**, J. Santiago, A. Wennberg, A. Mendez,* Nano4Energy SL, Spain*; F. Papa,* GP Plasma, USA

*Recently, it has been demonstrated that the addition of a positive voltage pulse adjacent to the negative HIPIMS sputtering pulse allows the increase of film ion assistance and thus, the improvement of coating properties on both biased and insulating substrates. Also, the energy of the incoming ions is proportional to the amplitude of the positive voltage. Some examples of experiments carried out in industrial coating machines will be presented in this study, such as the improvement on film density, mechanical properties and deposition rate in an industrial batch coater for metal nitrides, or the increased barrier performance of films deposited on PET in an industrial scale (330 mm wide web) web coater.*


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**B8-7 Measurements and Modeling of Residual Stress in Sputtered Nitride Films: Dependence on Growth Rate and Gas Pressure***, **Zhaoxia Rao (zhaoxia_rao@brown.edu)**, E. Chason,* Brown University, USA

Transition metal nitride films (e.g. TiN, ZrN and TaN) are often used as coatings because of their exceptional physical and mechanical properties. However, the residual stress induced during deposition can significantly alter their performance and reliability, leading to failure by cracking or buckling. Therefore, it is of critical importance to understand and control the stress evolution during deposition in nitride films. In this work, we investigate the stress evolution in nitride coatings deposited by physical vapor deposition. We report on the dependence of stress on the growth rate and gas pressure coupled with microstructure characterization. The experimental data is interpreted in terms of a kinetic model which includes the effects of film growth kinetics and energetic processes. The ultimate goal is the development of a model for predicting and optimizing stress in sputtered nitride films.

**B8-9 Wafer-scale Metallic Nanotube Arrays (MeNTAs): Fabrication and Application***, **Alfreda Krisna Altama (d10904819@mail.ntust.edu.tw)**, J. Chu,* National Taiwan University of Science and Technology, Taiwan*; A. Purniawan, S. Wicaksono,* Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia

Sputter deposition has been widely used in the manufacturing of high-performance on-chip interconnect. The metal connecting lines at each layer can be formed by filling trenches and vias in the interlayer dielectrics (ILD). High-power impulse magnetron sputtering (HiPIMS) techniques as a novel ionized physical vapor deposition (IPVD) technology has been developed in view years for metallization in integrated circuits and nanostructures manufacturing with high aspect ratio (AR). HiPIMS is an IPVD technique based on pulsed power technology where the peak power exceeds the time-averaged power by roughly two orders of magnitude so. HiPIMS deposition offers a route for depositing uniform coatings onto complex-shaped substrates and structures. In this research, we formed high AR trenches using photoresist lithography on silica wafers. The deposition process was performed using a 6 inch diameter metallic alloy target using HiPIMS and DCMS. The plasma properties were measured using a Langmuir probe at a distance of 70 mm from the target face and below the racetrack. The measurement results show that the plasma produced by HiPIMS has a higher ion and electron density value compared to DC plasma. We consider the experimental condition of high density plasma as the favorable process condition for the trench deposition. In this condition, the film was deposited at different power and working pressure. The cross-sectional pictures performed by scanning electron microscopy (SEM) shows that the film had good trench step coverage and amorphous structure. Furthermore, the results of this study can be used as a reference for trench filling and the manufacture of nanostructures with high aspect ratio using HiPIMS.

**B8-10 Plasma Chemistry, Crystal Growth and Mechanical Properties of CrAlYN / CrN Nanoscale Multilayer Coatings Deposited by High Power Impulse Magnetron Sputtering***, **Arutiun Ehiasarian (a.ehiasarian@shu.ac.uk)**, A. Sugumaran, P. Hovsepian,* Sheffield Hallam University, UK

Nanoscale multilayer coatings based on CrAlYN / CrN find applications in manufacturing, automotive components, power generation turbines and petrochemical industry. To perform well in these different environments, the coating microstructure must be tailored via the deposition process. In High Power Impulse Magnetron Sputtering (HIPIMS), which provides a high degree of ionisation of the metal flux and activation of the reactive gas, the relation between process parameters, microstructure and coating properties is not well understood.

We report on the effect of unbalancing magnetic field on species-dependent transport of metal and gas species to the substrate and its influence on film growth, texture formation and mechanical performance of nanoscale multilayer CrAlYN/CrN films. Experiments were carried out in an industrial-sized coater with four cathodes arranged in a closed magnetic field configuration, two of which were operated in HIPIMS mode and two in conventional sputtering.

In a balanced configuration, the magnetic null height was $h_m$ = 12 cm and the volume of plasma near the target was the greatest and resulting in a high metal-to-gas ion ratio ($J_{Me}$+ / $J_G$+) observed by optical emission spectroscopy. The transport to the substrate, as measured by the ion saturation current ($J_i$), was the lowest due to the absence of magnetic field lines connecting to the substrate. The 4-micrometre-thick films exhibited competitive growth and a strong [111] texture evidenced by XRD due to the relatively low flux of dissociated nitrogen to the surface. SEM observations showed that the [111] texture resulted in dome-shaped column tops and clearly defined column boundaries where vacuum impurities were segregated.

As the magnetic field grew more unbalanced, the confinement volume decreased whilst transport to the substrate was enhanced, resulting in both $J_{Me}$+ / $J_G$+ and $J_i$ reaching their maximum values. Weakly unbalanced fields with $h_m$ = 10 cm provided sufficient flux of activated species to cause the grains to switch to [220] and then to [200] texture and allowing them to absorb impurities interstitially. This resulted in the elimination of dome-shaped morphology, drastic reduction in roughness, parallel column boundaries and increase in grain size.

Highly unbalanced fields ($h_m$ = 4 cm) constricted the height of the confinement volume, reducing the ionisation of metal and dissociation of nitrogen as evidenced by the significant reduction in $J_{Me}$+ / $J_G$+. The loss of dissociation switched the texture back to a strong [111]. Grain sizes were significantly larger than for the balanced configuration due to a higher $J_i$.

The hardness and dry sliding wear rates are discussed.

**B8-12 On the Influence of the Micropulse on Nb Thin Films Deposited by MPPMS and DOMS: A Comparative Study***, **Y.G. Li (ygli@dlut.edu.cn)**, Z. Jiang, H. Yuan, N. Pan, M. Lei,* Dalian University of Technology, China

Nb thin films deposited by modulated pulsed power magnetron sputtering (MPPMS) and deep oscillation magnetron sputtering (DOMS) were comparatively studied under similar average power by controlling the micropulse duty cycle. It was found that DOMS discharge showed both higher discharge peak current and peak voltage, time delay between the current and voltage was much shorter with respect to a MPPMS discharge. All Nb thin films were observed with Nb(110) preferred orientation and compact columnar structure with DOMS Nb thin films hardness with higher hardness and elastic modulus. The increase of micropulse duty led to the gradually movement of Nb(110) to the high scattering angle direction, meanwhile the DOMS Nb(100) diffraction peaks were all on the left of MPPMS Nb(110). An anomalous increase could be observed for compressive residual stress s of Nb thin films for both techniques. The anomalous increase in s also led to the deterioration of scratch adhesion. Despite, the grain sizes of DOMS Nb thin films were all smaller than MPPMS Nb thin films, s in DOMS Nb thin films generated by the adatom diffusion and ion irradiation still overwhelmed the tensile stress generated by the volume shrinkage of the growing grains. The special afterglow of DOMS in microsecond time scale gave a new dimension controlling the grown thin films.

**B8-13 The Effect of Metal Transition Dopents on Mechanical Properties TiBCN Based Coatings Deposited by CFUBMS-HiPIMS***, Ihsan Efeoglu* 
***(iefeoglu@atauni.edu.tr)**,* Ataturk University, Turkey*; N. Aksakalli,* Atatürk University, Turkey*; B. Gumus, E. Tan,* Aselsan Inc., Turkey

Ternary and quaternary hard coatings based on carbonitrides of transition metals with amorphous matrix have many advantages; these have high hardness, adhesion, abrasion, oxidation, and corrosion resistance. Functional properties can be gained by adding definite amounts of different transition elements to carbonitride-based coatings**.** In this study, mechanical and tribological properties were investigated by adding Nb and Zr transition elements to TiBCN based coatings. The coatings were deposited on 4140 tool steel and the silicon wafer. TiBCN-based coatings with high adhesion and dense microstructure were synthesized with CFUBMS (Pulsed-dc+HiPIMS) using Cr, Ti, $TiB_2$, Nb, Zr targets and Ar, $N_2$, $C_2H_2$ gases. Microstructural properties of the coatings were obtained from the coatings on the silicon wafer and 4140 steel using SEM, XRD, and XPS. The mechanical properties of coatings synthesized on 4140 steel base materials have been characterized by Microhardness and Scratch tests. The hardness and adhesions of TiBCN-based coatings, which were grown by adding Nb and Zr, respectively on Cr:CrN graded structure (~200nm) as the transition layer, were optimized depending on the process parameters. Scratch test results showed that the adhesion strength varied as a function of the Nb and Zr target negative bias voltages. The highest adhesion strength was obtained as Lc:80N at -800V with adding Zr. In the case of the Nb adding, the highest adhesion strength was obtained as Lc:57N. Adhesion and microhardness test results showed that the utilization of bias-voltage with HiPIMS to the targets and pulsed-dc to the base material was the most effective coating parameter in the critical load and the hardness properties. Friction coefficients were observed as the lowest value, $\mu \approx 0.163$ in TiBCN-Nb coatings, while it was observed as $\mu \approx 0.337$ in TiBCN-Zr coatings.

**Keywords:** TiBCN:Zr/Nb, Adhesion, Microhardness, CFUBMS-HiPIMS,

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