Hard Coatings and Vapor Deposition Technologies
Room Pacific D - Session B7-ThA

Plasma Surface Interactions, Diagnostics and Growth Processes

Moderators: Dr. Yin-Yu Chang, National Formosa University, Taiwan , **Prof. Arutiun P. Ehiasarian**, Sheffield Hallam University, UK, **Dr. Yolanda Aranda Gonzalvo**, University of Minnesota, USA

1:20pm **B7-ThA-1 On (simple) Measurement of Energy and Momentum Transport Between Process Plasmas and Substrates***, **Holger Kersten**, T. Trottenberg, M. Klette, L. Hansen,* IEAP, U Kiel, Germany*; F. Schlichting,* IAEP, U Kiel, Germany **INVITED**

For optimization of plasma-based processes as thin film deposition or surface modification, respectively, suitable diagnostics are required. In addition to well-established plasma diagnostic methods (e.g. optical emission spectroscopy, mass spectrometry, Langmuir probes, etc.) we perform examples of "non-conventional" low-cost and simple diagnostics, which are applicable in technological plasma processes. Examples are the determination of energy fluxes by calorimetric probes and the measurement of momentum transfer in sputtering by force probes [1].

In particular, energy and momentum transport through the plasma sheath by charge carriers as well as by energetic neutrals are of interest and can be detected by these diagnostics. Total energy fluxes from plasma to substrate are measured by special calorimetric sensors. A typical method is the passive thermal probe (PTP) based on the determination of the temporal slope of the substrate surface temperature (heating, cooling) in the course of the plasma process. By knowing the calibrated heat capacity of the sensor, the difference of the time derivatives yields the integral energy influx (deposited power) to the surface. Simultaneously, the electrical current to the substrate can be obtained and by variation of bias voltage the contributions of charge carriers can be determined. Moreover, the use of a PTP as collector of a retarding potential analyzer (RPA) allows for energy-selective measurements and studying even the energy influx due to neutrals.

Furthermore, for thin film deposition by sputtering it is essential to determine the sputtering yield as well as the angular distribution of sputtered atoms. In addition to simulations (TRIM, TRIDYN etc.) an experimental determination of the related quantities is highly demanded. For this purpose, we developed a suitable interferometric force probe. The sensitive probe bends a few µm due to momentum transfer by the bombarding and released particles, i.e. sputtered target atoms and recoiled ions. By knowing the material properties of the cantilever and by measuring its deflection, the transferred momentum, e.g. the force in µN range, can be determined experimentally.

[1] Benedikt, J., Kersten, H., Piel, A., Plasma Sources Sci. Technol. **30**(2021), 033001.

2:00pm **B7-ThA-3 Chemical Stability of Sputter Deposited Silver Thin Films***, **Diederik Depla**,* Ghent University, Belgium

Thin silver films are used in a wide range of applications including antibacterial coatings and different optical devices. Silver thin films are deposited on a large scale as part of spectral selective thin films to improve the insulating properties of glazings. These multilayers consist of a stack of a metal layer sandwiched between two dielectric layers such as aluminum doped zinc oxide, TiO_2. The multilayer acts as an optical filter to control the heat flux through architectural glazings. The filter must combine a high visual with a low infrared transmittance. The optical properties of silver makes it the preferred metal in this application. The fabrication of a thin silver film is challenging due its inherent three-dimensional growth on substrates such as most oxide films in the multilayers. Due to the tendency for 3D growth, continuous films can only be obtained at relative high mean film thicknesses. Therefore, strategies have been developed to overcome this problem. The most common approach is the deposition of metal seed layers prior to the silver deposition. The seed layer is typically a non-continuous thin film which affects the silver film growth.

Silver films are vulnerable to humid air. Therefore, the multilayer is deposited on the interior of the double glazing. Double glazings will normally fail due to internal fogging, when moisture appears between the panes. With an anticipated 20 year lifetime of double glazing, the long term chemical stability of silver thin film is an important feature.

To get a better understanding of the degradation of silver thin films, silver films with a thickness below 50 nm were deposited on glass using DC magnetron sputtering. The chemical stability of the films was investigated by exposure of the film to a droplet of a HCl solution in a humid atmosphere. The affected area was continuously monitored with a digital microscope. The affected area increases approximately linearly with time which points to a diffusive mechanism. The slope of the area versus time plot, or the diffusivity, was measured as function of the HCl concentration and film thickness. The diffusivity scales linearly with the HCl concentration. The role of a aluminum seed layer was also investigated. It is shown that the diffusivity for Al seeded Ag films is much lower. The film growth process is studied based on AFM, resistivity measurements, SEM and transmission measurements. The behavior as function of the film thickness is more complex as it shows a maximum, and seems to challenge the understanding of this straightforward stability test as no strong correlation was found with the aforementioned film diagnostics.

2:20pm **B7-ThA-4 Electron Drift and Electron Property Studies in HiPIMS by Incoherent Thomson Scattering***, T. Dubois, S. Tsikata,* CNRS-ICARE, France*; **Tiberiu Minea**,* Université Paris-Saclay, France

Magnetized laboratory sources such as planar magnetrons exhibit rich physics beyond their broad interest for various applications. There is increasing evidence for the complex role played by the electrons during the high-power impulse operation of the planar magnetron discharge.

This work discusses recent findings from a high-performance non-invasive incoherent Thomson scattering implementation on a planar magnetron in HiPIMS (High Power Impulse Magnetron Sputtering). The technique probes the electron properties (electron temperature, density) and dynamics (drift velocity) in the ionization region with an unpreceded time and space resolution.

The electron temperature is observed to be isotropic during pulsing (identical radial and azimuthal temperatures, measured, respectively, along the magnetic field and parallel to the ExB drift). However, the electron drift shows clear anisotropy and the azimuthal electron drift evolves according to a changing balance of E x B and diamagnetic electron drifts. In contrast, the radial movement of electrons (measured parallel to the magnetic field) can be attributed to plasma expansion/contraction and centrifugal forces. Additional information on particle dynamics during pulsing and relaxation in the afterglow are presented. Two time scales characterize the variation of plasma properties in the afterglow. The differences in the discharge behavior in argon and helium will be discussed.

2:40pm **B7-ThA-5 Engineered Phase Differences between HIPIMS Power and Substrate bias for Improved Mechanical Properties of TiN and CrN***, **Ying-Xiang Lin**, P. Liu,* National Chung Hsing University, Taiwan*; D. Wuu,* National Chinan International University, Taiwan*; W. Wu,* National United University, Taiwan

In order to enhance the hardness, density, and adhesion of the deposited film, a substrate bias was normally applied during the deposition to attract ions to the substrate to increase the bombardment of the Ar+ on the film. However, an excessive ion bombardment also causes an extremely high compressive residual stress of the film and leads to peeling off. Therefore, adjusting the substrate bias voltage to obtain a proper ion impact on the film is an important factor in the process. High-power pulsed magnetron sputtering (HiPIMS) is an advanced technology of conventional magnetron sputtering. The plasma density of HiPIMS is three levels higher than conventional magnetron sputtering due to its high ionization rate. Therefore, a high amount of charged particles are generated in the HiPIMS process. Applying a DC bias voltage in HiPIMS process helps these charged particles reach the substrate, but a high amount of charged particles also causes the bias fail instantaneously. Meanwhile, two groups of high-energy ions of gas and target were observed when the pulse is turned on and off, respectively. Therefore, adjusting the phase differences between HiPIMS power and substrate bias becomes critical in a HiPIMS deposition process. However, the effect of applying synchronized and phase difference bias on the film deposition between CrN and TiN has not been detailed discussed.

In this study, different phase difference bias of HiPIMS deposited TiN and CrN layer was individually investigated. A DC substrate bias was also used for comparison. The plasma composition in front of the target and substrate was individually analyzed by optical emission spectroscopy (OES), and it was found that Ti^+, Cr^+, N_2^+, and Ar^+ increased significantly at the

substrate after applying DC bias and pulsed bias. According to the XRD, SEM, and AFM results, the grain size and surface roughness of TiN and CrN decreased when a DC bias was applied. The N/Ti and N/Cr ratio of TiN and CrN samples with a phase difference of 100 µs pulsed bias and synchronized pulsed bias was 0.99 and 0.96 respectively. The residual stress of the film can be reduced by applying a phase difference bias during the process. It has been found that the ion signal strength in the plasma can affect the nano-hardness and corrosion resistance. In the TiN process, the Ti^+ and Ar^+ intensity increases at a phase difference of 100 µs, and the hardness and polarization resistance increase. CrN plasma is dominated by Cr^0, and the strength of both Ar^+ and Cr^+ plasma decreases with phase difference bias.

3:00pm **B7-ThA-6 Influence of Microwave Power and Substrate Biasing on the Structure and Properties of Zinc Tin Nitride Films Deposited via Microwave Plasma-Assisted R-HiPIMS**, ***Caroline Hain***, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Swiss Cluster AG, Bern University of Applied Sciences, Switzerland; *K. Wieczerzak, D. Casari, A. Sharma, A. Xomalis,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland; *P. Sturm,* Tofwerk AG, Switzerland; *J. Michler,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland; *A. Hessler-Wyser,* EPFL, Switzerland; *T. Nelis,* Bern University of Applied Sciences, Switzerland

Zinc tin nitride (ZTN) is a semiconductor, which has been gaining in interest in the field of optoelectronics (including photovoltaics) due to the possibility to vary the bandgap within the ultraviolet to infrared range. It is considered as a possible replacement for InGaN, as it includes Earth-abundant and cost-efficient Zn and Sn, is non-toxic and has a band gap up to approx. 2.0 eV, which has been reported to be relatively insensitive to disorder[1–3]. Different fabrication approaches have been used, including molecular beam epitaxy (MBE), direct-current (DC) and radiofrequency (RF) magnetron sputtering and reactive sputtering[1,4–8], where the structure and optoelectronic properties of the obtained films were investigated. However, there remain questions regarding the influence of deposition conditions on these aspects of ZTN films. To this end, series of ZTN films of the same chemical composition but different structuring were deposited via microwave plasma-assisted high power impulse magnetron sputtering (MAR-HiPIMS), which has previously been used by us to produce high quality nitrides. The structure was modified by varying the applied microwave power and substrate bias. The obtained films were analysed using X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM) and UV/Vis spectrometry. The obtained differences in film structure and properties were linked to the changes in the deposition environment, which was characterised through *in situ* diagnostics, including studying HiPIMS I(*V,t*) curves, time-resolved optical emission spectroscopy (OES), time-of-flight mass spectrometry (ToF-MS), time-resolved Langmuir probe and retarding field energy analyser (RFEA).

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3:20pm **B7-ThA-7 Influence of Duty Cycle on Microstructure of TaN Coatings Prepared by High-Power Pulse Magnetron Sputtering Technique**, ***Yung-Chi Chang***, National United University, Taiwan; *F. Wu,* National United University,, Taiwan

Nowadays quality requirements, such as higher hardness, wear resistance, sufficient toughness and adhesion strength are gathering much more attention for transition metal nitride, TMN, hard coating field. The selection of materials among various possible coating systems and related manufacturing processes is quite a challenge and requires careful consideration on the properties in the developing choices. Among TMNs, with high hardness, excellent tribological behavior, thermal and electrical performance, TaN has been chosen as a good protective layer for working components in versatile applications. In this study, TaN thin films are sputtered through high-power pulse magnetron sputtering, HPPMS, at different duty cycle. At a fixed power of 200 watt and a Ar/N_2 ratio of 18/2 sccm/sccm, the frequency and pulse off time, the related duty cycle and the shape of the current and voltage are manipulated. With the decrease of the duty cycle, the peak power increases when the high energy is applied in a short period of time, leading to an increase in ionization rate and plasma density. For such increase in plasma density, the grain size of TaN film is reduced within a well-defined columnar structure. This leads to the improvement in mechanical behavior, elastic modulus, and wear resistance of the films.

3:40pm **B7-ThA-8 Synthesis of Vanadium Dioxide and Vanadium Pentoxide Nanoparticle Films Using Magnetron-Based Gas Aggregation Source**, *A. Kuzminova, N. Khomiakova, J. Prokes, T. Kosutova, M. Prochazka,* ***Ondrej Kylian***, Charles University, Prague, Czech Republic

Nanoparticles and nanoparticle-based films have nowadays become one the most studied classes of materials. The popularity of this family of materials is foremost due to their unique physicochemical properties and high surface-to-volume ratio that makes them highly attractive for use in various technological fields such as (bio)detection, catalysis and photocatalysis or gas sensing. This is especially true in the case of metal-oxide nanoparticles. Naturally, the critical step is the controlled, cost- and time-effective and reliable synthesis of nanoparticles with the required structure/functionality. One of the possible strategies that receive increasing importance is the use of magnetron-based gas aggregation sources, i.e., the technique in which the nanoparticles are formed as a result of spontaneous nucleation of supersaturated vapors generated by the sputtering of a solid target. While the majority of so far reported results dealt with metallic NPs, we investigate in this study the applicability of such nanoparticle sources for the synthesis of metal-oxide nanoparticles, namely vanadium oxide ones. A two-step process for the production of vanadium oxide nanoparticles was followed. In the first step, the metallic nanoparticles are produced by a conventional GAS system. Such produced nanoparticles are subsequently annealed in the air. It is shown that the proper selection of the deposition and annealing conditions allows the production of highly porous vanadium dioxide or vanadium pentoxide nanoparticle films, as witnessed by detailed characterization of the resulting materials by electron microscopy and X-ray spectroscopic techniques (XPS and XRD). Furthermore, it was found that while the coatings with a high fraction of VO_2 phase exhibit thermally induced switching of electrical conductivity, V_2O_5 nanoparticle films are suitable for use as substrates for non-plasmonic surface-enhanced Raman spectroscopy (SERS) that offer not only a high detection limit but also excellent spectral reproducibility and stability, i.e., features problematic for conventionally used metallic SERS substrates.

This work was supported by the Czech Science Foundation through the project GAČR 22-16667S.

4:00pm **B7-ThA-9 Diagnostics with an Optically Trapped Microparticle in the Sheath of an Asymmetric CCP**, ***Viktor Schneider***, *J. Schleitzer, H. Kersten,* Institute of Experimental and Applied Physics, Kiel University, Germany

Applications of low-temperature plasmas range from etching processes and coatings of solids to plasma medicine and basic research. Important plasma parameters such as density, temperature or composition of the species are diagnosed using many established methods [1]. However, it is difficult to probe the extremely important sheath region, which is only a few millimeters thick and, thus, not accessible with macroscopic probe methods, as they themselves change the plasma. In recent years, therefore, microparticles have been qualified as probes for so-called non-conventional plasma diagnostic purposes. Due to their size and their behavior in the plasma, they, in particular, are well suited for increasing the spatial resolution and, thus, providing information in addition to common diagnostics [2].

In this study SiO2 microparticles are in an optical trap to manipulate them in the environment of a capacitively coupled asymmetric radio frequency discharge. In contrast to common plasma diagnostic tools (e.g. Langmuir probes, calorimetric probes, mass spectrometers etc.), in the µPLASMA (microparticles in a discharge with laser assisted manipulation) experiment particles can be regarded as noninvasive single probes [3]. The displacement of the particle in the laser trap is observed to measure a force while it is moving relatively to the plasma, either deeper into the sheath or into the plasma bulk.

Force profiles at different pressures and rf-powers have been performed in the sheath of an asymmetric capacitively coupled plasma. The force is

mainly determined by the particle charge and the electric field in the sheath region. Thus, the measured force while moving a single particle from the bulk plasma towards the electrode surface show a characteristic profile with a maximum and a descrease close to the electrode.

Furthermore, the benefit of the presented technique is the possibility to retain the particle even after the plasma is turned off providing the possibility to perform additional studies, e.g. on the rediual particle charge.

[1] J. Benedikt, H. Kersten and A. Piel 2021 Plasma Sources Sci. Technol. 30 pp 033001
[2] H. R. Maurer, V. Schneider, M. Wolter, R. Basner, T. Trottenberg and H. Kersten 2011 Contrib. Plasma Phys. 51 pp 218-227
[3] V. Schneider and H. Kersten 2018 Rev. Sci. Instrum. 89 pp 103505

4:20pm **B7-ThA-10 Investigating the Plasma Physics of Plasma-Enhanced Pulsed Laser Deposition of Photocatalytic Thin Films***, Matthew Hill,* University of York, UK

Photoelectrochemical water splitting is one of the many applications of thin films in modern technology, producing hydrogen fuel from water using sunlight. Photoelectrodes are a key part of this technology, which use solar energy to dissociate water molecules into hydrogen and oxygen. Metal oxides such as titanium dioxide have been established as the most prevalent materials for thin films applied to photocatalysis due to their active and efficient photocatalytic properties. Pulsed laser deposition (PLD) is a widely accepted method of producing high-quality metal oxide thin films. However, PLD has limitations which make it suboptimal for depositing thin films as the process limits the control of the stoichiometry of the deposited film, usually requiring additional background oxygen gas to improve thin film growth. Plasma-enhanced pulsed laser deposition (PE-PLD) is a novel method which uses a metal target instead of a metal oxide target, and oxygen plasma instead of oxygen gas, which reacts more readily with the ablated material, allowing for greater control of the stoichiometry. Despite its promising potential, PE-PLD remains an active area of research. The overarching goal of this particular research is to develop a deeper understanding of the underlying plasma physics and chemistry of thin films such that they can be created according to specific criteria rather than empirical observations. This contribution presents results from modelling the laser ablation of different photocatalytic materials using the 2D hydrodynamic laser ablation code POLLUX as well as measurements of the densities of O and N in the background plasma using Two-photon Absorption Laser-Induced Fluorescence (TALIF). For the laser ablation, we investigate the evolution of key parameters such as plasma density and temperature when the target material is changed from titanium to e.g., tantalum, zinc, copper, aluminium and gold. The results showed that the atomic number of the material significantly affected the electron temperature and mass density of the subsequent plasma plume, with both parameters increasing with atomic number, whilst the mass density of the material appeared to have no effect on the electron temperature or particle density of the plumes. The TALIF measurements gave absolute measurements of the reactive N and O species in the background plasma for a range of N_2/O_2 mixtures, allowing control of the ratio of reactive O and N species in the plasma interacting with the plume ablation. These results provide an understanding of the underpinning processes of PE-PLD as well as the design of specific metal-oxide and oxynitride thin films.

4:40pm **B7-ThA-11 Thin Film Modification in a DC Microplasma – Understanding the Importance of Ions under Atmospheric Pressure Conditions for the Plasma Surface Interaction***, Luka Hansen,* Institute of Experimental and Applied Physics, Kiel University, Germany*; N. Kohlmann, L. Kienle,* Institute of Materials Science, Kiel University, Germany*; H. Kersten,* Institute of Experimental and Applied Physics, Kiel University, Germany

The plasma surface interaction is one of the most discussed topics in plasma technology. The large number of interacting (plasma) species and simultaneously running processes aggravates the understanding of the plasma surface interaction. For low-pressure thin film deposition, structure zone diagrams visualize the most important parameters and their influence on the growing thin film [1]. Substrate temperature and the energy flux from the plasma to the surface strongly influence the grain structure and the texture of the film. The energy flux is composed from multiple components such as kinetic and recombination energy of ions, fast neutrals and radiation [2]. The expression of the different components should also influence the film structure, as large kinetic contributions also transfer momentum to the surface and densify the film.

For atmospheric pressure plasmas a highly collisional environment is present. Therefore, no large kinetic energies and momentums of individual ions or fast neutrals are expected. The difference in the energy flux composition may change the thin film properties and the transferability of the universal structure zone diagrams has to be questioned.

A normal glow atmospheric pressure DC microplasma was developed and characterized [3]. Its design enables the utilization of thin film coated TEM grids as electrodes to study the plasma-induced surface modifications of the electrode surfaces. Significant differences between the thin films used as either anode or cathode have been found, stressing the importance of ions despite the atmospheric pressure conditions. Further, these differences depend on the working gas (Ar or He) and correlate with the measured energy fluxes to the surfaces. Combination of different plasma diagnostics resulted in a postulated energy balance at the cathode, showing the important ion power transfer mechanisms. The different power transfer mechanisms explain the differences in the thin film modification [4].

In the near future *in situ* experiments with the microplasma being integrated into the TEM similar to previous proof of principle experiments [5] are planned. The *ex situ* observed surface modifications should be visible in real time. The current state of these experiments as well as the design of the *in situ* microplasma cell will be presented in addition to the obtained *ex situ* results.

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