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Correlation Between Pulse Parameters and Coating Growth During S3p™ Deposition of TiAlN

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Nowadays reactive cathodic arc evaporation is a well established physical vapour deposition process (PVD) for industrial production of wear resistant coatings. On the one hand the cathodic arc deposition is a very robust and stable process providing high degree of ionization of the deposition fluxes, on the other hand a significant amount of macroparticles is usually emitted from the cathode surface which in turn leads to the degradation of the surface quality of the produced coating. Significant improvement of the surface quality of the deposited coating can be achieved by using the magnetron sputtering technique. However, in many cases the process window is very narrow, particularly during the reactive sputtering, and the degree of the ionization remains low. During the last decade the high power impulse magnetron sputtering technique (HIPIMS) has been developed intensively. This novel PVD method is supposed to combine the advantages of both cathodic arc and conventional magnetron sputtering techniques for deposition of smooth, wear protective coatings utilizing highly ionized deposition flux. Despite the continuous development activities, there are still some limitations for process window and industrial implementation of the HIPIMS technique.

Oerlikon Balzers has developed a HIPIMS approach, which offers high flexibility in terms of applied pulse power density and pulse duration. Using the S3p™ technique - scalable pulse power plasma, the degree of ionization can be balanced together with the deposition rate to achieve an optimum between coating properties and productivity. In this paper we report about the possibilities of the S3p™ deposition technique based on the example of TiAlN coatings. The coatings have been deposited using melting metallurgical $Ti_{50}Al_{50}$ targets. The sputter power density and the pulse length were varied in a broad range. The plasma chemistry and degree of ionization were studied using optical emission spectroscopy (OES). The chemical composition of the coatings was investigated by means of energy dispersive X-ray spectroscopy (EDX). The evolution of the growth morphology and crystallographic structure as a function of plasma characteristic was studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Nanoindentation methods were used for determination of the elastic modulus of the coatings. The variation of the pulse parameters was found to have a strong impact on the coating growth. A strong dependence of the coating structure and properties on the plasma characteristic was observed. Finally the correlation between growth conditions and the cutting performance of the coatings is exemplarily discussed.

Key words: PVD, magnetron sputtering, HIPIMS, wear protective coatings

Novel Deposition of Multi-Compositional Aluminum Titanium Nitride (AlTiN) Coatings by High Power Impulse Sputtering (HIPIMS+) Technology

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Aluminum Titanium Nitride (AlTiN) coatings have been deposited from targets consisting of tiles with 4 different aluminum/titanium ratios using High Power Impulse Sputtering (HIPIMS+) technology. In such a configuration, the material properties such as hardness and crystal orientation can be analyzed for many coating compositions while keeping the plasma conditions constant. The peak cathode current has been used as the control variable as this has a strong influence on the metal ion content within the plasma and the plasma density. As the peak cathode current is increased, the crystal size and structure change significantly. It is shown that a pure cubic phase is maintained for aluminum content up to 65 atomic percent.

TiN Coatings for Machining: Can HIPIMS Stand the Test?

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The use of protective wear-resistant coatings is well established in the industry with TiN coatings as the breakthrough coating for machining resulting in a factor 10 prolonged lifetime compared to uncoated tools. With the invention and development of the HIPIMS technology, these coatings are believed to perform even better due to an improved adhesion, a more conformal deposition and a denser microstructure. For a customer, TiN coatings are deposited on cutting tools using an Hauzer Flexicoat PVD machine equipped with Arc-cathodes, magnetron sputter cathodes in a closed field configuration and HIPIMS technology on one of the cathodes.

Machining tests are performed using the different coated tools and the machining results are compared. The wear on the tools is analyzed.

Can HIPIMS stand the test by increased performance compared to today’s techniques, knowing it has a lower deposition rate and consequently an increased deposition cost?

Introduction Of ICIS - A Novel Technology for Ionised Sputtering of Magnetic Materials

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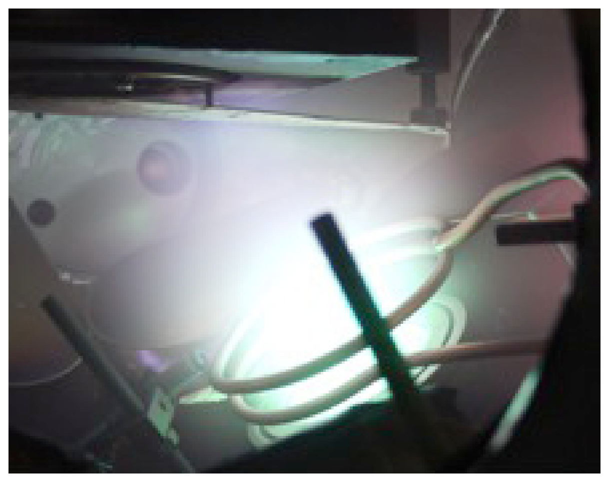
Magnetron sputtering is a successful deposition technology with a wide application field. However, there are inherent challenges that the technique has never fully resolved.

Magnetron sputtering is unable to sputter magnetic materials, which shunt the field of permanent magnets that confine the plasma. Film thickness uniformity is dependent on the shape of magnetic confinement zone and is usually achieved using rotating magnets. Target utilisation is typically <40% with expensive magnetic field design. Finally, the microstructure density of films is low due to insufficient ion-to-neutral ratio and energy of species on the surface.



Inductively Coupled Impulse Sputtering (ICIS) is a new technology for ionised physical vapour deposition based on sputtering without magnetic fields in the environment of high-density plasma. The sputtering plasma is generated in front of the target via an inductively coupled coil driven with a radio frequency (RF) power supply. The target is then biased to a high voltage to initiate sputtering. The RF power density is raised to >30 Wcm^{-2} to produce plasma density of the order of 1012 cm^{-3} and ionise the sputtered flux. In specific configurations, a target power density of 1.5 $kWcm^{-2}$ (current density 1.5 Acm^{-2}) is achieved, corresponding to plasma densities of 10^{13}-10^{14} cm^{-3} near the target surface. A low duty cycle of < 25% is used to achieve high peak powers and plasma densities.

The degree of ionisation of Cu, Ti, and Ni were evaluated using optical emission spectroscopy. Plasma density increased proportionally to the applied RF Power in the coil. Metal ionisation degree was influenced strongly by both gas pressure in the system and RF power. Penning ionisation was the dominant ionisation mechanism with the metal ion-to-neutral ratio being determined by Ar metastable density. Uniform erosion was observed across the target surface.

Film microstructure changed from globular to large-grain columnar as ionisation degree increased. Coverage of semiconductor vias with aspect ratio of up to 4:1 was studied with cross sectional SEM.

History of Vacuum Deposition Using Energetic Ions

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Historically the most important single use of energetic ion deposition was probably the enrichment of uranium (^{235}U) for the first atomic bomb using magnetic sector ion sources (Calutrons). Many kilograms of ^{235}U ions were deposited. Pure and mixed energetic ion fluxes of condensable, reactive and inert ions have been used for about 50 years to deposit films and coatings as diverse as diamond-like-carbon (DLC) and Ti-Al-C-N. Continuous or periodic bombardment effects on deposition include: in situ cleaning, modification of the nucleation stage of growth, influence on interface formation, structure modification during growth (stress, crystallographic orientation, density, hardness, chemical composition), chemical activation of reactive species, and bombardment-enhanced chemical reactions on the surface. The sources of atoms for ionization include chemical vapor precursors, thermal vaporization, sputtering, and arc vaporization. A number of sources have been developed using ancillary systems to provide electrons/plasmas for postvaporization ionization. HIPIMS is a new technology for attaining high ionization of magnetron sputtered species without any ancillary ionization.

This paper will review some of the most important milestones and developments for bringing energetic ion deposition into widespread industrial applications. These applications include coatings for corrosion protection, low friction/wear, tools, hard/wear/decorative, erosion resistant, and optical components. Often these coatings are deposited on temperature sensitive substrates that make other techniques, such as high-temperature chemical vapor deposition (CVD) impractical.

Localization of Ionization in High Power Impulse Magnetron Sputtering

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More-or-less periodic structures of plasmas in high power impulse magnetron sputtering have been observed by groups in Tomsk, Bochum, and Berkeley. Here we recap the observations and report on optical measurements simultaneously using an intensified image camera and a streak camera. Observations were made in end-on and side-on view relative to the target. An example of a periodic structure is shown in the figure below. This structure moves in the ExB direction (here counterclockwise) but with a velocity of only roughly 10% of the ExB drift velocity of electrons. The structure is comprised of ionization zones where electrons are stopped from drifting by strong interaction with the plasma that is already there. Initially, such ionization zones develop from fluctuations, and their mutual effects cause periodicity or self-organization. The mechanism of the evolution will be discussed.

The observed localization of ionization and formation of highly localized dense plasma cause a localized azimuthal electric field, which in turn promotes the escape of trapped electrons from the closed drift. In this sense, the localization of ionization is an important mechanism that enables the HIPIMS discharge to work at high currents. Furthermore, the localization of the ionization is crucial for reaching high power densities and a high degree of ionization of sputtered atoms and background gas, i.e. it is at the heart of motivation for the HIPIMS technology.

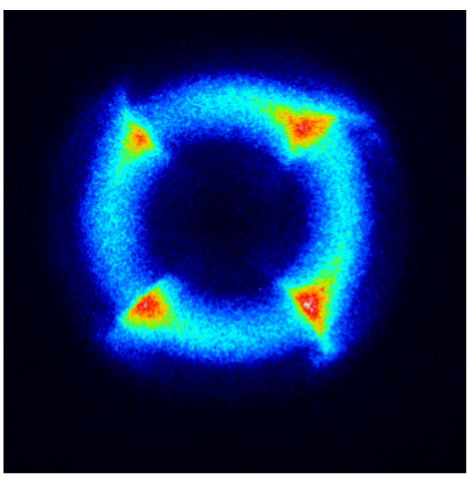

Figure: End-on view on a 76 mm (3") target of Nb in argon. The image has an exposure time of 10 ns and was taken when the discharge current reached 100 A at 42.6 μs after applying a target voltage of 750 V. The false colors represent the intensity of emitted light.

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HIPIMS Discharge Dynamics: Evolution and Origin of Plasma Instabilities

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High power impulse magnetron sputtering (HIPIMS) combines impulse glow discharges at power levels up to the MW range with conventional magnetron cathodes to achieve a highly ionised sputtered flux. If observed with a low time resolution, the optical emission from the HIPIMS discharge may appear to be homogeneous during the pulse. However, we have shown recently that the HIPIMS plasma may develop drift wave type instabilities [1]. They are characterized by well defined regions of high and low plasma emissivity along the racetrack of the magnetron and cause periodic shifts in floating potential. The structures rotate in ExB direction at velocities of ~10 kms^{-1} and frequencies up to 200 kHz.

In this paper a detailed analysis of the temporal evolution of the saturated instabilities using four consequently triggered fast ICCD cameras is presented. The influence of mass of the target material and working gas on the instability properties was investigated using titanium (Ti) and aluminium (Al) targets in either Ar or Kr gases. Furthermore working gas pressure and discharge current variation showed that the shape and the speed of the instability strongly depend on the working gas and target material combination. In order to better understand the mechanism of the instability, different optical interference band pass filters (of metal and gas atom, and ion lines) were used to observe the spatial distribution of each species within the instability. It was found that the optical emission from the instabilities comprises ion emission (both target material and gas ion lines) with strong depletion of the emission lines of the target material atom lines, concluding that instabilities are of generalised ion drift wave type.

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Ion Energy Distribution Measurements in pDC and HIPIMS Discharges

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Retarding field energy analyzers (RFEAs) are commonly used to measure the ion energy distribution function (IEDF) at grounded surfaces and biased substrate holders in plasma reactors. At the grounded surface the RFEA operation is easier to implement due to the absence of large voltages. At the biased substrate holder the RFEA design is more complex. Filtering techniques are required to ensure the entire RFEA floats at the substrate holder bias potential.

When the discharge and/or substrate holder is driven with a pulsed signal the measurement of the time resolved IEDFs through the pulse cycle is extremely desirable. RFEAs and mass spectrometers have been used to make time resolved measurements of the IEDF at grounded surfaces in discharges pulsed in the tens/hundreds of kHz range. Time resolved measurements at a pulsed bias surface are more complicated, mainly because of the need to incorporate high input impedance, low-pass filters to allow the RFEA to float at the bias potential. The use of these filters, which enable the RFEA to float at the bias potential, generally prevents time resolved measurements with adequate time resolution.

Here, we present time averaged and time resolved IEDF measurements in HIPIMS and pDC magnetron sputtering reactors. The RFEA is allowed to float at the substrate holder bias potential, using low pass filters, while a novel technique is implemented to allow time resolution of the IEDF during the bias period. IEDF measurements with up to 100ns time resolution through the period of the substrate holder bias are presented.

In the past, RFEAs have seen limited use in sputtering reactors. The main issue being that the sputtered material contaminates the probe, gradually closing the apertures and mesh orifices. The design presented here incorporates replaceable sensing elements that can be easily changed by the user. This dramatically increases the lifetime of the entire RFEA probe system.

Temporally Resolved Ion Distributions in HIPIMS System with Ti Target

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The high power magnetron sputtering system (HIPIMS) equipped with 2” diameter titanium target has been investigated by means of time-resolved retarding field energy analyser (RFEA) and so called modified-Katsumata probe. Both methods allow determining ions distributions as a function of retarding electric field. However, both methods are not able to resolve the mass of particles. The newly developed modified-Katsumata probe uses a static magnetic field created by Sm-Co permanent magnets to intercept the most of plasma electron and conduct them away to auxiliary electrode. The main stepwise biased electrode collects then plasma ions even above plasma potential. The measurement with ion sensitive probe is similar to measurement with regular Langmuir probe. The commercial apparatus Semion RFEA system has been used. A comparative study of both aforementioned methods has been carried out in pure argon atmosphere at pressure range from 0.3 Pa to 20 Pa and at different distances from the target face. The mean discharge current has been held at 500 mA for all the experiments. The modified-Katsumata probe enables us to obtain ion temperature directly from the probe characteristics because plasma ions are collected directly by discriminating electrode. On the contrary, RFEA can measure ion velocity distribution in direction perpendicular to the analyser only. Both methods revealed significantly enhanced energy tail in ion distributions measured in HIPIMS in contrast to dc magnetron or mid-frequency pulsed-dc magnetron. The variances in the measured ions distribution by both methods at the same plasma conditions are attributed to different principle of operation both methods.

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Development of Hard DLC Coatings Using HIPIMS Technology

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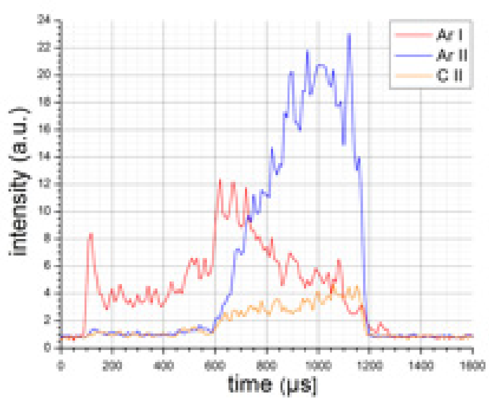
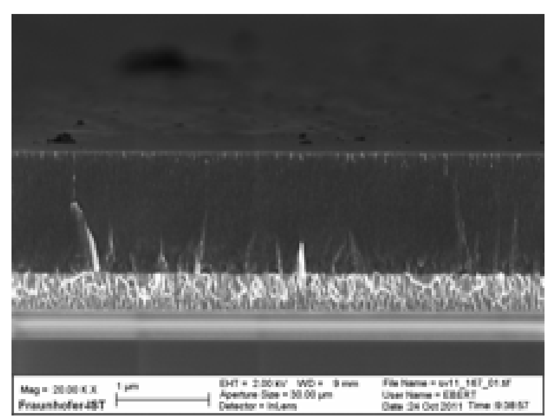
Using high power impulse magnetron sputtering (HIPIMS) for deposition of carbon containing coatings always is discussed to suffer from the low ionization probability of carbon to significantly modify the resulting coating properties compared to state of the art technology. In fact B.M. De Koeven et al. reported in 2003 on an increased density for HIPIMS deposited carbon films of 2.7 g/cm^3, mainly attributed to the Ar ion bombardment connected with a very low hardness of only ~ 7 GPa [1]. First results on carbon prepared by modulated pulse power sputtering (MPP) were published by R. Chistyakov et al. referring to a coating hardness up to 25 GPa [2]. Unpublished results reported from the group of U. Helmersson, Linköping University, Sweden, presented hardness values exceeding 30 GPa for pure carbon. Fundamental studies on energetic deposition of carbon films by mixed mode of triggered cathodic arc and sputtering are reported by M. Lattemann et al. showing light emission spectra including carbon ions [3]. For diamond-like carbon (DLC) coatings prepared reactively no publication data was found.

For reactive C-DLC deposition using HIPIMS technology ionized carbon was found. Especially adding C_2H_2 to HIPIMS of a graphite target resulted in an increase of the CII emission lines using optical emission spectroscopy. The variation of the acetylene content in the process, as well as applying an additional substrate bias voltage led to significant increase of the film hardness. By modification of the deposition parameters DLC films with a plastic hardness of 65 GPa (indentation hardness of 41 GPa) were realized. The deposition rate was well above 1 μm/h.



OES emission intensities in a MPP pulse



SEM cross section; HU_{pl}: 53 GPa

Keywords (optional): HIPIMS; MPP, C-DLC, DLC

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Study of the Coating Properties of Nickel Deposited by Inductively Coupled Impulse Sputtering (ICIS)

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Inductively coupled impulse sputtering (ICIS) removes the need for a magnetron, while delivering equal or higher ion to neutral ratios compared to HIPIMS. This is especially advantageous for the sputtering of magnetic materials, as these would shunt the magnetic field of the magnetron, thus reducing the efficiency of the ionisation process. ICIS produces highly ionised metal dominated plasmas inside a high power pulsed RF coil with a magnet free high voltage pulsed DC powered cathode.

In this new technology the coating properties of magnetic materials are not known. The setup comprises of a 13.56 MHz pulsed RF coil operating at a frequency of 500 Hz and a pulse width of 150 μs, which results in a duty cycle of 7.5 %. A pulsed DC voltage of 1900 V was applied to the cathode to attract Argon ions and initiate sputtering. Nickel (Ni) was deposited with RF powers of 3000 W and 4000 W at pressures of 1.4×10^{-1} mbar and 2.5×10^{-1} mbar.

The deposition rate for Ni is 50 nmh^{-1} for a RF-power of 3000 W and a pressure of 1.4×10^{-1} mbar. The average target power density is 3 Wcm^{-2}.

Measurements of the optical emission from the ICIS plasma show a linear increase of ionisation with increasing RF power and pressure. The relation between ionisation and bottom coverage is discussed. The microstructure of the coatings shows globular growth. Bottom coverage of unbiased vias with width 0.300 μm and aspect ratio of 3.3:1 was 15 % and for an aspect ratio of 1.5:1 was 47.5 %.

Measurements with EDX were used to examine the material composition, especially considering the Cu content in the coating. Also the topography and crystallinity have been examined by AFM and XRD respectively. The current results show that the concept of combining a pulsed RF powered coil with a magnet-free pulsed DC powered cathode can produce dense coatings of hard magnetic material while still having a very good coverage in high aspect ratio structures in a stable plasma.

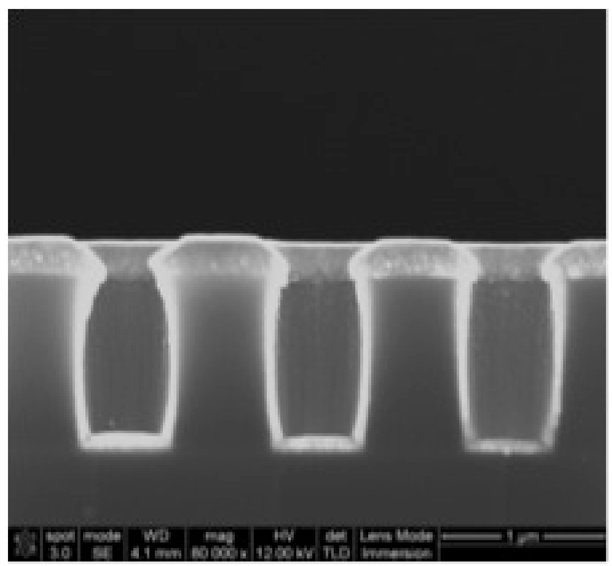

Figure 1: *Crossection of Ni on Si substrate with vias. 200nm top coverage with 15% bottom coverage. Deposited with an RF power of 3000 W*

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Analysis of Ionization Ratio of Nb^+/Nb And Ar^+/Ar on HIPIMS Discharge

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The final aim of this work is to provide the best sputtering configuration to deposit niobium films on copper cavities for particle accelerators. HIPIMS technology has been selected because it gives the possibility, ionizing the atoms of the sputtered material and applying a biasing voltage, to enhance the quality of the film, obtaining a denser and more compact film compared to standard magnetron sputtering, with a well defined growth orientation.

Plasma analysis has been made in Sheffield Hallam University, using an Optical Emission Spectrometer and a Mass Spectrometer, while cavity deposition experiments have been conducted at CERN Laboratories. Measurements of the key neutral and ionized species have been done over a range of current values (from peak current density value of 0.97 Acm^{-2} to 4.33 Acm^{-2}) and different pulse width configurations. The results show that the pulse width doesn't affect too much the ionization ratios, while it seems to increase significantly with the current density. Energy distributions for different ion species are provided. Results provided by the mass spectrometer analysis are presented as well.

Different deposition settings have been tried at CERN based on the above study as a guideline, with and without a bias voltage, comparing deposition rates and film properties (SEM, RRR) with the normal DCMS technique. A 1.3 GHz copper cavity has also been deposited and the prospects for RF measurements will be presented.

The Influence of Inert Gases on the C/N_2/Inert Gas HIPIMS Discharge and Thin Film Growth

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Neon, argon, and krypton were used to map the role of inert gases in sputtering of pure carbon and reactively sputtered carbon-nitride (CN_x) compound thin films for high power pulsed magnetron sputtering (HIPIMS/ HPPMS). The composition of the carbon discharges were investigated using mass spectrometry measurements performed at the substrate position. The measurements were carried out in an industrial deposition system. During the sputter process the ion flux was analyzed with regards to composition and ion energy. The ion energy distribution (IED) was detected for inert and reactive gas ions, C+, C_2+, and C_xN_y+ (x, y ≤ 2) ions. Variations in ion energy and ion flux composition in dependence of the N_2-to-inert gas flow ratio ($f_{N2/inert\ gas}$) at constant process pressure were investigated with time-averaged and time-resolved mass spectrometry. These results are related to the corresponding thin films with regards to their chemical bonding and microstructure measured with X-ray photoelectron spectroscopy and transmission electron microscopy, respectively.

Keeping the average power (and frequency) constant during sputtering, the results show that the peak target current during HIPIMS processing decreases with increasing inert gas mass. For graphite sputtered in pure inert gas, the ion flux increases with increasing inert gas mass. The variation of $f_{N2/inert\ gas}$ gas shows a maximum total ion flux as soon as nitrogen is added to the sputter process ($f_{N2/inert\ gas}$ = 0.16) for all applied inert gases. The sputter process in Ne/N_2 ambient at fN_2/inert gas = 0.16 exhibits a doubled total ion flux compared to that of the Ar/N_2, whereas the sputter process in Kr/N_2, applying the same N_2-to-inert gas flow ratio, yields 20 % increase in the total ion flux. The high energy portion of the IED functions as well as the plasma potential show a dependency on both the nature of the inert gas and $f_{N2/inert\ gas}$. The time evolution of the plasma species were also analyzed and related to the current understanding of C and CN_x - film growth, as the use of different inert gases is mirrored in the microstructure of the a-C and CN_x thin films. An ordering towards fullerene-like films occurs for inert gas masses higher than that of Ne. Carbon and CN_x films deposited in Ne atmosphere are found to be fully amorphous. However, the effect of the inert gas on the microstructure is not as distinct when N_2, as reactive gas, is introduced into the deposition chamber.

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Textured CrN Thin Coatings Opening Up New Fields of Application

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Subsequent research work aims to investigate the potential of modern PVD coatings, to explore new fields of application. The present study is based on measurements of electrical conductivity, light absorption and thermodynamic nucleate boiling tests of specific textured CrlCrN-coatings with predominant (1 1 1), (3 1 1) or (2 0 0), (2 2 0) crystal lattice orientations. High Power Impulse Magnetron Sputtering (HIPIMS) in combination with Direct Current Magnetron Sputtering (DCMS) was applied to deposit CrN coatings of 3-4 µm thickness. A thin interlayer of pure Cr was used as adhesive interlayer between substrate and CrN coating. To investigate the influence of process parameters on the coatings crystal structure and hence on the technological coating properties variation of HIPIMS pulse length (50, 100, 150, 200 µs) and pulse frequency (100, 300, 500 Hz) at constant bias voltage as well as bias and booster voltages variations at constant duty cycles were performed.

Crystallographic phases and lattice orientations were determined by X-ray diffraction analyses (XRD) in θ/2θ mode and finally texture coefficients were calculated. The morphology of the coatings was investigated by scanning electron microscopy (SEM) in top view and cross section. Specific electrical resistivity, remission and critical heat flow rates were measured in order to determine the electrical conductivity, light absorption and heat transfer properties of the coatings.

The test results show good light absorption as well as enhanced nucleated boiling properties. In combination with a good mechanical resistance and electrical conductivity those coatings may be interesting, for example, in the application area of solar thermal energy. A second possible area of application could be the cooling in high performance electronics. The CrN coatings can be deposited directly on Si-wafer substrate, thus no separate heat sink is required. Results show that an increase in heat flux density by a factor of five, from 20 000 W/m² up to 100 000 W/m, leads to a comparatively small increase of wall heat by only 2°C. This would allow heat transfer in the case of high electrical power fluctuation, without causing strong temperature shifts.

Study of ZrN Synthesised with HIPIMS/UBM and Cathodic Arc Techniques

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It is well known that Cathodic Arc (CA) deposition is rich with metal and gas ions of the depositing species; however the coatings have a drawback of droplet defects. High Power Impulse Magnetron Sputtering (HIPIMS) has gained reputation for being rich with ionised flux which can be tailored to either pre-treat substrates to improve adhesion or to deposit dense defect free coatings (without droplets and under-dense structure). In this study Zirconium nitride (ZrN) coatings were deposited by HIPIMS/UBM denoted as H/U and CA techniques to investigate the effect of ion-bombardment obtained from respective processes on the properties of the coating. Combining HIPIMS technique with UBM (Unbalanced Magnetron Sputtering) in the same deposition process facilitated increased deposition rate and ion bombardment on the depositing species during coating growth which is otherwise depleted in the UBM technology. Prior to coating deposition, substrates were also pre-treated with Zr^{+} rich plasma in both the techniques. Results obtained exhibited that both CA and H/U deposited coatings had a very high scratch adhesion value (L_{C2}) of 100 N. Characterisation results revealed the overall thickness of the coatings in the range of 2.5 μm and hardness of H/U and CA coatings were 38 and 37 GPa respectively. Stress values for H/U coatings were lower to CA coatings (-4.7 GPa and -5.8 GPa respectively). Cross-sectional Transmission Electron Microscopy (TEM) studies exhibited very dense coating for H/U deposition free from defects. For CA technique the structure surrounding droplets is expected to be under-dense and hence with defects. X-Ray Diffraction (XRD), mechanical characterisation as well as corrosion results have shown a direct effect of ion bombardment on the structure and properties of the coatings. Both coatings show near identical E-Corr values however H/U deposited coating exhibits a higher tendency to passivate (reduction in corrosion currents) above 150 mV as compared to CA coatings- a direct indication of droplet defects and surrounding under-dense structures playing a significant role in reducing corrosion resistance of CA coatings. H/U coatings also show a higher wear resistance (Kc =5.33 x10^{-15} $m^3n^{-1}m^{-1}$) as that of CA (Kc = 8 x10^{-15} $m^3n^{-1}m^{-1}$).

Role of Synchronized Pulsed Substrate Bias during $Ti_{1-x}Al_xN$ Film Growth by Hybrid HIPIMS/DCMS Cosputtering

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Metastable cubic-structure $Ti_{1-x}Al_xN$ alloy thin films near the kinetic solubility limit are grown using a combination of high-power pulsed magnetron sputtering (HIPIMS) and dc magnetron sputtering (DCMS) from elemental Ti and Al targets in an industrial coating system. The Ti target is driven in the DCMS mode, while the Al target is powered by HIPIMS. Different modes of substrate biasing are used. The charge state, energy, and mass of species incident at the substrate position are determined using in-situ time-resolved mass spectroscopy. As-deposited films are compositionally analyzed using time-of-flight elastic recoil detection. Large differences in grain size, phase composition and intrinsic stress are detected.

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Structure and Properties of Tantalum Nitride Coatings Deposited by Modulated Pulsed Power Magnetron Sputtering (MPP)

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Tantalum nitride coatings have been deposited on AISI 304 stainless steel and silicon wafers by modulated pulsed power magnetron sputtering. MPP technique has shown the capability of achieving a high degree of ionization of the sputtered material compared to conventional DC magnetron sputtering (DCMS). The ionization degree is proportional to the peak current density, which can be modified by the variation of the MPP pulse shape. The large fraction of ions generated in the discharge can be usefully manipulated trough substrate bias voltage (V_b) to provide an enhancement of ion bombardment on the growing film. The effect of both peak current density and bias voltage on the microstructure and properties of thin films is analyzed in this study. Hence, two different pulses have been used in the deposition of TaN coatings at two different V_b (-50V,-200V).

The microstructural characterization of the coatings is performed using X-ray diffraction and scanning electron microscopy (SEM). GD-OES measurements are realized for the composition analysis of the growing films.

Hardness values are measured by nanoindentation tests. High dependence on the bias voltage is manifested by all samples. Corrosion response of TaN films is analyzed by electrochemical impedance spectroscopy (EIS) and linear polarization curves (LSV). The porosity and density of the films, directly affected by peak current and bias voltage, are key parameters in the evolution of corrosion resistance with time.

Deposition Aluminium Nitride Films by HIPIMS: Correlation Between Time-Resolved Plasma Investigations and Physical Properties

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Using DC reactive magnetron sputtering, good crystalline quality AlN films were deposited on silicon substrate (Rocking curve FWHM around 2°) and even epitaxial growth of AlN on AlGaN [1] and ZnO [2] substrates was achieved. These results were obtained thanks to optimization of ion/neutral ratio and the energy of impinging species [3]. Nevertheless it's not possible to go further in the improvement of the crystalline quality using this deposition technique.

In fact, as the ionisation rate for DC magnetron is very low, the contribution of the fast neutral is very important and detrimental to the crystalline quality of the deposited films. High Power Impulse Magnetron Sputtering (HIPIMS) as an ionized reactive sputtering technique allows reaching an ionization degree up to 80 % which is sufficiently high to ensure a better control of plasma physic and chemistry. Therefore, the deposition process is dominated by ion species rather than neutral ones [4-6]. Until now few nitrides have been deposited by HIPIMS, mainly CrN and TiN [5] wich have a relatively high conductivity but, to our best knowledge, no nitride insulator has been synthesized using this technique. Our purpose is therefore to synthesize AlN insulating films by HIPIMS.

In this work, HIPIMS technique was used for deposition of such insulating Aluminium nitride (AlN) thin films. The process was optimized for working with Aluminium target in reactive atmosphere (Ar-N_2). As the plasma characterisation of the ionized species is necessary in order to better understand such a specific plasma process, time-resolved investigations were carried out using Langmuir probe measurements, Optical Emission Spectroscopy and Mass Spectrometry. Physical and chemical properties of the as deposited films are then characterized. Well crystallised, textured (Rocking curve FWHM around 1°) and thick AlN films were obtained. These results will be presented, discussed and a correlation between the films and plasma properties will be made.

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Stress Generation in Low-Mobility Metal Films Grown by High Power Impulse Magnetron Sputtering

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The high flux of energetic metal ions in high power impulse magnetron sputtering (HIPIMS) is generally seen as the main cause of the higher density compared to films deposited by dc magnetron sputtering (dcMS) [1]. Ion peening is also known to induce compressive stresses by creation of point defects in the film [2]. In this study we investigate the stress development and final stress state in Mo thin films. These films were deposited onto electrically floating Si(100) substrates covered by a native oxide at different pulse powers and working pressures. The film stresses were measured by *in situ* wafer curvature (using an optical multiple beam setup) and *ex situ* by x-ray diffractometry (XRD) using the $\sin^2\psi$ method adapted for textured layers. Time and energy resolved mass spectrometry was performed to study the deposition flux for the different deposition conditions while the film density and surface roughness was measured by x-ray reflectometry (XRR).

It is found that an increase of the pulse power and/or a decrease of the working pressure lead to film densification and a change from a tensile to a compressive stress state in the films. These results are explained in light of the energetic bombardment the growing film experiences at the various deposition conditions and open a route for stress tailoring and deposition of stress-free films by proper selection of deposition parameters. The combination of *in situ* stress measurements and *ex situ* XRD analysis reveals only very small differences between the stress-free film and the bulk lattice constants. The latter is indicative of a low point defect density. Based on this finding, we suggest that, unlike to other energetic film deposition techniques [3], compressive stress generation in HIPIMS is caused by incorporation of atoms in the grain boundaries and not by implantation of energetic Ar^+ ions and generation of self-interstitials.

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Investigations of Very Short Pulse Sequences in HIPIMS Mode Using a Reactive Process of Aluminum

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Alumina coatings are used besides application in cutting tools as insulator for electric and sensor applications. For this application it is most important to produce defect-free films with high field strength. Pulsed processes already provide good results, but require a fast control for stabilizing the process in the transition mode. Already for HIPIMS processes it was shown, that it is possible to drive the process in oxide mode.

This talk focuses on the deposition of aluminum and alumina using a Cyprium power supply. The investigations were carried out on a planar target (470 mm x 130 mm) and results are presented. The Current-voltage characteristics for different pulse sequences and charging voltages are shown as well as the hysteresis loop in dependence of the oxygen flow, partial pressure and deposition rate for different average powers. Moreover first results are shown regarding an active process control. The insulating properties of the films were characterized by their critical leakage field strength.

Keywords: Aluminum, Alumina, arc free, insulator, breakdown voltage, process control

ZrSiN Coatings Deposited by HIPIMS for Hard Coating Corrosion Protection on Aluminum

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The aim of this study is to compare the effect of high power impulse (HiPI) and direct current (DC) power supplies in the deposition via magnetron sputtering (MS) of ZrSiN coatings for hard corrosion resistance application on aluminum 7075 alloy substrate.

ZrSiN films were deposited in an industrial close field apparatus (target size 12"x4.9") by HIPIMS (500Hz, 200µs pulse duration) and by DC from a ZrSi (90/10 at%) target in N_2 reactive atmosphere at room temperature. The target composition was chosen in order to obtain fine crystal grain size with no columnar structure to enhance corrosion resistance. OES and current waveform were used to highlight the different reactive regimes and in the hysteresis. The samples were deposited for DC and HIPIMS at 0V and -60V substrate bias voltage on Si (100) and aluminum alloy substrates. Prior to deposition HIPIMS plasma on Zr target was used for etching and interlayer deposition.

Compositional analysis were carried out by RBS and cross-section SEM investigation was used to highlight coating morphology and the presence of defects. Moreover the differences between the HIPIMS and DC and between the substrate bias values were observed on crystal structure by XRD, on coating resistivity by four point probes measurement and on mechanical properties by nanoindentation and microscratch test.

Electrochemical impedance spectroscopy and salt-spray test were used to evaluate the corrosion resistance of the different coatings.

Key words: HIPIMS, ZrSiN, corrosion protection

Preferred presentation: ORAL

Optical Emission Spectroscopy of AIP-, HIPIMS- and UBMS Deposition of TiAlN

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Different types of nitride coatings including standard TiN and TiAlN were deposited by industrial arc ion plating (AIP), a new nearly droplet free arc technology, DC Magnetron Sputtering and HIPIMS. All coating conditions were analyzed by Optical Emission Spectroscopy (OES) with respect to metal and gas ionization. The results of the OES measurements were then correlated with the resulting coating properties.

TiAlN coatings deposited by the HIPIMS process show strong preferred (111) orientation and a relatively high hardness up to 35 GPa is obtained. On the other hand AIP TiAlN coatings are characterized by a moderate hardness up to 30 GPa and (200) or nearly random orientation at an equivalent substrate bias condition. Cross sectional TEM observations of both coatings revealed that HIPIMS coatings show smaller grain sizes compared to AIP coatings.

In the presentation, a comparison between AIP, nearly droplet-free AIP, DC Magnetron Sputtering and HIPIMS coating by different power supply, arc source and deposition conditions will be made not only from property of the coating but also from industrial perspective such as productivity and tribological performance.

On ECWR Assisted HIPIMS Discharge: Time Resolved Diagnostics During Deposition of Thin Films

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Ionization of sputtered metal particles lead to the growth of smooth and dense films, allows to control the crystallography phase, mechanical and optical properties etc. Further the film properties are strongly influenced by the energy influx towards the growing film. The energy distribution depends on the pressure; there are energy losses at higher pressures due to particle collisions. Because of that reason we have developed hybrid sputtering source which provides high level of metal atoms ionization and works in wide range of pressures down to 0.05 Pa.

Developed system is based on High Power Impulse Magnetron Sputtering (HIPIMS) of an electrode inserted in RF discharge with an additionally superimposed magnetic field. Static dc-magnetic field $\boldsymbol{B}_0$ causes slight plasma anisotropy which allows propagation of electron cyclotron waves through the plasma. The strength of magnetic field $\boldsymbol{B}_0$ varies refractive plasma number $\boldsymbol{n}_R$ to attain the wavelength ($\lambda_{pl} = \lambda_{vacuum}/n_R$) appropriate for resonant plasma excitation. Electron Cyclotron Wave Resonant (ECWR) effect occurs when odd numbers of cyclotron half the wavelength corresponds with the geometrical size of the plasma. ECWR assistance provides pre-ionization effect of HIPIMS discharge which allows: (i) significant reduction of pressure during HIPIMS operation down to p = 0.05 Pa; it is nearly more than one order of magnitude lower than at typical pressure range for HIPIMS, (ii) intensive ionization of metal atoms with substantial amount of double ionized species and (iii) increases HIPIMS power density and other discharge parameters.

Our contribution focuses on time-resolved diagnostic of ECWR-HIPIMS discharge during deposition of TiO_2 thin films. From time-resolved Langmuir probe measurements was estimated mean electron energy, electron density and electron energy probability function (EEPF). The plasma density reached values about 5.10^{18} m^{-3} during HIPIMS pulses at low pressure (0.05 Pa). The time–resolved measurements of Ion Velocity Distribution Functions (IVDFs) and Ion Energy Distribution Functions (IEDFs) were performed. It was found that ion energies during HIPIMS pulses are strongly enhanced (about 20-30 eV). Parameters from Langmuir probe diagnostic serve also as input for calculation of influx contributions of particular species, e.g. neutral particles. The study of plasma transport effects was done by fast optical emission imaging and spectroscopy.

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High-Rate Reactive Deposition of Multifunctional Ta-O-N Films Using High Power Impulse Magnetron Sputtering

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High power impulse magnetron sputtering of a planar tantalum target (diameter of 100 mm) in various argon-oxygen-nitrogen gas mixtures was investigated at a fixed average target power density of 50 Wcm^{-2} in a period. A strongly unbalanced magnetron was driven by a pulsed dc power supply (HMP 2/1, Huettinger Elektronik) operating at the repetition frequency of 500 Hz and the average target power density of up to 2.4 $kWcm^{-2}$ in a pulse with a fixed 50 µs duration. The nitrogen fractions in the reactive gas flow were in the range from 0 to 100% at the argon partial pressure of 1.5 Pa and the total pressure of the argon-oxygen-nitrogen gas mixture around 2 Pa. The Si (100) and glass substrates were at a floating potential, and the substrate temperature was less than 250°C. The target-to-substrate distance was 100 mm. An effective reactive gas flow control made it possible to produce high-quality Ta-O-N films of various elemental compositions with high deposition rates (97 to 190 nm/min). Their compositions (in at. %) were varied from $Ta_{27}O_{72}$ with a low content (less than 1%) of hydrogen to $Ta_{38}O_4N_{55}$ with 3% of hydrogen. The former films were nanocrystalline with high optical transparency (extinction coefficient less than 10^{-4} at 550 nm), refractive index of 2.12, band gap of 4.0 eV, very low electrical conductivity (resistivity of $7.7x10^9$ Ωcm) and hardness of 7 GPa. The latter films exhibited a more pronounced crystallinity, they were opaque with relatively high electrical conductivity (resistivity of $4.2x10^{-2}$ Ωcm) and hardness of 19 GPa. The $Ta_{27}O_{40}N_{31}$ films with 2% content of hydrogen, produced at the 50% nitrogen fraction in the reactive gas flow with the highest deposition rate of 190 nm/min achieved, were nanocrystalline with the band gap of 2.4 eV, electrical resistivity of $5.5x10^6$ Ωcm and hardness of 8 GPa. Such films seem to be suitable candidates for visible-light responsive photocatalysts.

Details of the deposition process and measured properties of the films will be presented.

Process-Property Relations in Photocatalytic Ta-O-N Films Deposited by High-Ionization Magnetron Sputtering

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Global demand for clean air and water is escalating and is a major challenge faced by contemporary society. Photocatalysis is a phenomenon that has great potential to address this challenge since it allows for conversion of photon energy into chemical energy. The most widely used photocatalytic material is titanium dioxide (TiO_2); however, it is limited to functioning exclusively in the ultra-violet range of the electromagnetic spectrum. In order to utilize solar radiation and increase the efficiency of photocatalytic devices, materials that exhibit photocalytic activity in the visible spectra range are a prerequisite. One candidate for such a usage is tantalum-oxynitride (Ta-O-N) when synthesized with certain attributes, i.e. chemical composition and crystal structure [ref 1].

High power impulse magnetron sputtering (HIPIMS) is a thin film deposition technique that provides a large flux of energetic film forming species and allows for a stable reactive deposition process. The dynamics of HIPIMS have been shown to facilitate efficient control of composition and structure in reactively grown metal oxide and oxynitride films [ref 2].

The present work aims at identifying the HIPIMS process conditions under which Ta-O-N films with photocatalytic activity in the visible spectral range are synthesized. Emphasis is given on the effect of the pulsing characteristics and the magnetic field configurations on the crystalline formation and the properties of Ta-O-N. The atomic composition and the crystal structure (i.e. attributes) of the Ta-O-N films employing reactive HIPIMS (in an Ar-O_2-N_2 atmosphere) are tuned for a wide range of deposition conditions with respect to the gas composition and the HIPIMS parameter space (e.g. pulsing frequency and pulse duration) and the relations between the above mentioned attributes and the photocatalytic behavior of the films are elucidated.

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Enhanced Photocatalytic Activities Under Visible Light of C-doped TiO_2 Thin Films Deposited by HIPIMS-PLD

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Photo-catalysis using anion doping semiconductors is potentially a feasible way to take advantage of solar energy activating the water splitting reaction to produce hydrogen and oxygen. The main interest of them is the decrease of the band gap energy, making them sensitive to visible light range, which intensity is dominant on the Earth [1].

A new doping method, which consists in combining High Power Impulse Magnetron Sputtering process with Pulsed Laser Deposition process, is proposed in order to obtain C-doped TiO_2 thin films with high photocatalytic activity in visible light. Reactive HIPIMS is used for TiO_2 thin film deposition (Ar and O atmosphere and Ti target) and the plasma produced by laser ablation of an additional C target placed in the same deposition chamber is used as C doping atoms source. The proposed solution has the advantage of better control of C atoms doping due to the independence of the two atoms sources (magnetron plasma and PLD plasma). Doping control and stoechiometry was achieved by choosing the adequate laser power, the laser fluency and repetition frequency, PLD and magnetron targets - substrate distance and magnetron plasma parameters (pulse length, frequency, working gas pressure, reactive gas partial pressure, target voltage). The C-doped TiO_2 thin films was characterized using perform chemical spectroscopic analysis (XPS, Raman microscopy), structural investigation (XRD, AFM, SEM), standard optical measurements (UV-Vis spectroscopy), and finally, the photocatalytic activity was tested using contact angle and fluorescence technique. It was investigate the influence of the C atoms concentration in deposited films on the photocatalytic activity.

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Pulsed HIPIMS Deposition of Iron Oxide Thin Films

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Fe_2O_3 thin films were deposited by low temperature pulsed plasma systems. Various configurations of pulsed HIPIMS magnetrons and pulsed modulated RF magnetron systems were used for these purposes. The pulsed HIPIMS magnetron used a pure iron target specially designed for the loop magnetron type which is capable to sputter ferromagnetic materials. This target was reactively sputtered in $Ar+O_2$. The pulsed modulated RF magnetron system used the ceramic Fe_2O_3 target reactively sputtered in $Ar+O_2$. The low frequency voltage with different duty cycle was applied to the cathode for the pulsed HIPIMS discharge plasma excitation. Fe_2O_3 thin films deposited with these techniques were analyzed by XRD, AFM, XPS in order to study presence of hematite phase, concentration of impurities, surface roughness and chemical composition. Optical properties of these films were measured by UVVIS absorption spectroscopy. Photochemical properties of Fe_2O_3 films were measured by the photoelectrochemical cell. The magnetron pulsed plasma was characterized during the deposition process by a time resolved Langmuir probe system. Time evolution of ion and electron density, plasma potential and mean electron energy was measured by this method. A retarding field analyzer Semion was used for diagnostics of ion velocity distribution function (IVDF) at the position of the substrate. This devise was capable to measure time resolved IVDF at different deposition conditions in all the investigated pulsed plasma sources.

Gyrokinetic Axisymmetric Modeling of a HPPMS Planar Magnetron Discharge - a Valid Approach?

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High Power Pulsed Magnetron Sputtering (HPPMS) is a novel Ionized Physical Vapor Deposition (IPVD) technique, able to achieve an ultra dense plasma with a high ionization degree among the sputtered atoms. This is accomplished by applying a large bias voltage to the target in short pulses with low duty cycle.

In most HPPMS configurations the following ordering of spatial quantities holds: $\lambda_D \ll s_t \ll r_L \ll L$, where D is the Debye length, s_t is the sheath thickness, r_L is the Larmor radius, L is the system characteristic length.
As concerns time scales, the ordering is: $w_{pe} \gg w_{ce} \gg v_{ce}$, where w_{pe} is the electron plasma frequency, w_{ce} is the electron cyclotron frequency and v_{ce} is the electron collision frequency. In the plasma bulk, the gyro-motion of the electrons around a magnetic field line provides the system smallest time and spatial scale. Therefore, it seems reasonable to describe the electron dynamics with gyro-averaged equations of motion.

Moreover, given the axial symmetry of the set-up, one is induced to neglect the angular dependence, reducing the number of independent variables.

Here, we individuate and discuss two reasons why this simplified approach may not apply or should be improved. Several authors have recently reported the presence of rotating structures during a HPPMS discharge. According to the experimental observations, these emission peaks rotate with constant angular velocity, when the discharge parameters are held constant. This phenomenon clearly breaks the axial symmetry mentioned. We present here a simplified phenomenological model for these structures, based on the solution of a system of 1D Advection-Diusion-Reaction equations to be solved analytically for the electron $n_e(\theta,t)$ and neutral $n_n(\theta,t)$ densities. We look for the existence and the stability of a set of solutions in a frame rotating with speed Ω.

On the other hand, we focus on the electron trajectories. Most of the electrons are conned by the magnetic field, but a fraction enters the loss cone region and is reflected inside the thin sheath region or impacts on the target surface. The latter group is very small in number and can thus safely be neglected, since the target is negatively biased during the pulse duration. The electrons that are reflected inside the sheath cannot be described with the gyro-averaged equations of motion, since $r_L \gg s_t$. If these unconfined electrons are statistically relevant and cannot be neglected, they represent a flux at the boundary of the gyro-averaged region, which should be described by appropriate boundary conditions. Moreover, we show that the electrons reflected in the sheath, which we represent as infinitely thin, have an average drift in the plane of the target surface, directed toward the external perimeter. If statistically relevant, this effect can potentially influence the magnetron performance. Therefore, we employ a single particle simulation to address the importance of this electron population indifferent magnetic field configurations.

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Material Flux Optimization in HIPIMS Through the Control of the Magnetic Field

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Various phenomena affecting deposition rate (r_d) in high power impulse magnetron sputtering (HIPIMS) were investigated as a function of the magnetic field (**B**) above a metal target. In this work, the value of **B** of a 50 mm magnetron was controlled by applying paramagnetic spacers with different thicknesses in between the magnetron surface and the Nb target, while using a constant discharge power of 500 W. A weaker **B** (a thicker spacer) led to an increase in r_d by a factor of ~4.5 (from 10.6 to 45.2 nm min^{-1}) compared to the configuration without any spacer. However, this maximum r_d value was still about 30% lower in comparison to the DC magnetron sputtering mode at an identical average power. We demonstrate that the r_d is governed by two processes depending on **B**: (i) attraction of target ions back to the target is the dominant effect leading to reduced r_d for strong fields **B** (i.e., high discharge current and low cathode voltage), while (ii) nonlinear dependence of the sputtering yield on the ion energy is the principal cause of the r_d loss for weak **B** values (i.e., low discharge current and high cathode voltage). In addition, we observed that a variation in the spatial distribution of the sputtered material needs to be considered for a correct interpretation of the experimental data. Maps of the material flux distribution for different **B** will be presented and discussed.

Advancement of Hardware and Process Technology for HIPIMS Coatings for Cutting Tools

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The cutting tool industry is using HIPIMS coatings for about two years when the 2012 conference will take place in Sheffield. This paper gives a review of the state of the art and the current trends for further advancing the HIPIMS technology for hard coatings for cutting tools.

There is a general trend from CVD coatings to PVD coatings for the large volume production of cutting inserts. The PVD technology allows a much wider choice of the coating composition and sputtered films have low compressive stress whereas CVD films tend to have tensional stress. SEM images and other surface characterisation techniques show how the highly ionised species contributed by HIPIMS accelerate this trend by enhanced film properties. Various field tests have been carried out to correlate the film properties with cutting data. The data show that HIPIMS gives a very uniform thickness distribution on rake and flank face of inserts combined with a super smooth surface free of any droplets.

Design and set-up of the HIPIMS hardware is another factor that has a key impact on the industrial use of HIPIMS machines and coatings. The paper will show recent developments and achievements.

The first commercial HIPIMS films were standard $Ti_xAl_{1-x}N$ systems. It is well known that the addition of doping elements to a more complex system influences the performance of a film greatly. Hybrid DCMS/HIPIMS machines are most commonly used for industrial coating production. Depositing a multinary coating in a hybrid system raises the question about the difference of depositing a certain element on either a DCMS or a HIPIMS source. A detailed analysis of the resulting characteristics of the plasma and the film properties will be presented.

Characteristics of a One-Inch HIPIMS Plasma Source

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We have been developing small-sized sputter deposition equipment for a small-scale semiconductor production system called “minimal fab”. For this purpose, we developed a one-inch high power impulse magnetron sputtering (HIPIMS) plasma source. At 2nd HIPIMS conference, we presented a first prototype of the one-inch HIPIMS plasma source, showing that the source generated very high-power density plasma. We modified the source and provide a water-cooled mechanism. The modifications enable us to stably operate the source with over 10 A/cm^2. The one of the most crucial points of HIPIMS plasma sources is to obtain a high target current density. This feature allowed HIPIMS plasma sources to generate ultra dense glow plasma. Our source has an outstanding performance with respect to the feature of HIPIMS.

Fig. 1 one-inch HIPIMS plasma source

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Gas Temperature and Heat Flux to the Substrate in ICP-Assisted Magnetron Sputter-Deposition of Aluminum-Doped ZnO Films

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Transparent conducting oxide (TCO) has been widely used as transparent conducting electrodes of various optoelectronic devices such as solar cells, flat panel displays, etc. Tin-doped Indium oxide (ITO) has been mainly used so far due to its high transmittance in the visible region, high chemical stability and low resistivity. The metal-doped zinc oxide (ZnO) has lower inherent electric conductivity than ITO, but has advantages over ITO in environment resistance and resource cost. To replace ITO with metal-doped ZnO, however, a reproducible and highly-reliable fabrication process of good quality ZnO-based thin films has to be developed. With the view of controllability, economic potential, functionality, flexibility and so forth, we have been focusing on RF superimposed DC magnetron sputter-deposition process. This paper reports the experimental results gas temperature and substrate heat flux measurements in the ICP superimposed DC magnetron sputter-deposition of aluminum-doped ZnO (AZO) thin films[1,2].

A disk target of ZnO: Al_2O_3 (2 wt%) of 60 mm diameter was used as target and glass substrates were set on a earthed substrate holder with a gap length of 80mm. In between these diode electrodes, a single turn coil antenna of 100 mm diameter was installed and used for the production of 13.56MHz ICP. Owing to the presence of high density ICP between the target and substrate, the ICP-assisted sputter-deposition enables the low-voltage and high-current sputtering and the sputtered particles are efficiently ionized. Thus, enhanced ion fluxes onto the substrate with moderate ion energy contribute to the decrease in surface roughness and promote the crystallinity of thin films without intentional substrate heating. In addition, both the target usability and the spatial uniformity of thin film properties are improved. As a result of optimization of target-coil-substrate distances and operating pressures, we have succeeded in depositing high quality AZO thin films with resistivity of about 10^{-3} Ω•cm so far.

To understand the substrate heating mechanism during the ICP assisted sputtering, neutral gas temperature and particles' densities were investigated with absorption spectroscopy, and the heat flux to the substrate was measured with a thermal probe. As a result of optical absorption measurement of Al and Zn atom densities, we found that the increase in the relative ratio of Al to Zn atom density in the gas phase correlated well with the increase in the element ratio of Al to Zn in the deposited films, resulting in the change in film resistivity. As a result of heat flux measurement, we found that the heat flux to the substrate depended predominantly on the ICP power and the most conductive AZO films were obtained at the substrate position where the heat flux took the maximum of about $3000 Wm^{-2}$. The experimental heat flux was in agreement within 20-30% errors with the calculated heat flux which ignored the heating by neutral species and radiation. The results suggested that the substrate was predominantly heated by the kinetic energies of bombarding electrons and ions and by the exothermic reaction due to surface recombination. The average gas temperature which was measured by the extra cavity diode laser absorption spectroscopy (ECDLAS) for metastable Ar at the position 3cm from the substrate was found to increase from 350 to 550K with increasing ICP-RF power from 0 to 300W at a constant magnetron power of 40W. There was a good correlation between the gas temperature and the substrate temperature measured with a thermocouple. Contribution of neutral Ar atoms to the total energy flux was roughly estimated to be a few percent.

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HIPIMS Arc-Free Reactive Sputtering of Non-Conductive Films Using the Endura 200mm Cluster Tool

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Magnetron sputtering technology is widely used for the deposition of thin films in many commercial applications. Thin films can be pure metals, metal nitrides, or metal oxides. Nitride and oxide thin films can be created by magnetron sputtering in a reactive gas environment.

In this case, sputtered metals react with nitrogen or oxygen gas in a vacuum chamber to form metal nitride or oxide films on a substrate. The physical properties of sputtered films (metals, oxides, and nitrides) are strongly influenced by magnetron plasma density during the deposition process. A typical target power density on the magnetron during the deposition process is ~ (5-20) W/cm^2, which gives a low plasma density. The main challenge in reactive sputtering is the ability to generate a stable, arc free discharge at high plasma densities. Arcs occur due to formation of an insulating layer on the target surface caused by the re-deposition effect.

One current method of generating an arc free discharge is to use the commercially available Pinnacle® Plus + Pulsed DC plasma generator manufactured by Advanced Energy Inc. This plasma generator uses a positive voltage reversal pulse between negative pulses to attract electrons and discharge the target surface, thus preventing arc formation. However, this method can only generate low density plasma and therefore cannot allow full control of film properties. Also, after a long run ~ (1-3) hours, depends on the duty cycle the stability of the reactive process is reduced due to increased probability of arc formation.

Between 1995 and 1999, a new way of magnetron sputtering called HIPIMS (high power impulse magnetron sputtering) was developed. The main idea of this approach is to apply short ~ (50-100) μs high power pulses with a target power densities during the pulse between ~ (1-3) kW/cm^2. These high power pulses generate high-density magnetron plasma discharge that can significantly improve and control film properties.
From the beginning, HIPIMS method has been used in reactive sputtering processes for deposition of conductive and nonconductive films. However, commercially available HIPIMS plasma generators have not been able to create a stable, arc-free discharge in most reactive magnetron sputtering processes. Until now there has been no HIPIMS data presented on reactive sputtering in cluster tools for semiconductors and MEMs applications. In this presentation, a new method of generating an arc free discharge for reactive HIPIMS using the new Cyprium™ plasma generator from Zpulser LLC will be introduced. Data (or evidence) will be presented showing that arc formation in reactive HIPIMS can be controlled without applying a positive reversal voltage pulse between high power pulses. Arc-free reactive HIPIMS processes for sputtering AlN, TiO_2, TiN and Si_3N_4 using the Applied Materials ENDURA 200 mm cluster tool will be presented. A direct comparison of the properties of films sputtered with the Advanced Energy Pinnacle® Plus + plasma generator and the Zpulser Cyprium™ plasma generator will be presented.

On the Energy Deposition in Magnetron Discharges, From dcMS to IPVD and HIPIMS

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A great deal of attention has been devoted to the development of new concepts of magnetron discharges used for deposition of thin films particularly for more recent devices such as IPVD and HIPIMS in order to increase the ionization degree of the sputtered vapour.

The physics of this type of discharge is still not well understood. Efforts have been devoted to simultaneously use local diagnostic techniques such as electrical probes which permit to determine plasma parameters and recently Tunable Diode Laser Induced Fluorescence allowing the determination of metal atom velocity distribution within the discharge [1].

In parallel, a number of different numerical techniques have been developed to capture the main physical effects which control the behaviour of these discharges.

Monte-Carlo simulations give access to particle space exploration but not to plasma parameters. Moreover, the accuracy of their predictions strongly depends on the electric field which is initially assumed to accelerate the charged particles.

Fluid models based on modified transport parameters provide a description of the mean plasma parameters but still require more theoretical developments to improve the magnetized electron transport description in the crossed-field region. Moreover, the accuracy of the fluid model predictions is limited due to the maxwellian assumption for electron energy distribution function (eedf), which has been inferred as being largely non maxwellian [2].

PIC-MCC simulations allow to self-consistently determine realistic spatial distributions of charged particles, eedf as well as voltage and electric field maps. They usually consider the main collisional processes occurring in the plasma. But, accounting for detailed plasma chemical kinetics and especially for metastable atom contributions, PIC-MCC simulations deal with limited sets of collisional processes mainly due to the significant increase of the computational time.

One of the key issues still pending for the understanding of the magnetron process is the energy balance in the discharge. The microscopic Boltzmann approach is able to realistically solve this energy deposition problem by accounting for collisions either with neutral particles or with charged ones. This piece of information is essential for the accurate prediction of ionization in the discharge, consequently for the realistic ion current to the cathode and, therefore for the flux of sputtered particles and further their ionization. The Boltzmann equation for electrons can be coupled to collisional radiative model completely relaxing the Maxwellian character of the eedf, which is usually assumed. The main drawback is the lack of space dependency of charged and excited species (electrons, ions, excited states).

This approach will be illustrated by significant results for IPVD and HIPIMS discharges.

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Optimized Wire Treatment with HIPIMS Due to Effective Anode-To-Cathode Configuration

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It was reported that the ion density in the discharge volume can be limited by a number of effects attributed to HIPIMS, such as the depletion of species in front of the target (rarefaction), self-sputtering, loss of electron magnetic confinement, etc. For sufficiently short pulses, when the discharge current does not reach saturation value, the discharge impedance becomes very important and its magnitude has significant consequences on the properties of obtained coatings. Due to control over ionization process in dual cathode HIPIMS system, consisting of four planar magnetrons, it became possible to establish strong dependence of the film growth mechanism on the plasma main characteristics.

3D Thickness and Property Distribution of TiC Films Deposited by DC Magnetron Sputtering and HIPIMS

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High power impulse magnetron sputtering (HIPIMS) is known for ionising a reasonable amount of the deposition particles emitted from a magnetron sputtering source. Beside of improved density and mechanical properties of the deposited films also a higher thickness uniformity in 3-dimensional structures has been reported as a benefit of this technology. In this work TiC thin films were deposited from a 50 mm diameter TiC-target in Ar atmosphere using DC-Magnetron sputtering (DC-MS) and HIPIMS with a peak power density of 2,3 kW/cm^2. A special 3-dimensional structure with three different drilled blind holes (10, 4 and 2 mm diameter) was used as the substrate. Polished high speed steel samples were positioned as parts of a) the wall and b) the bottom of each hole in a way that the coating thickness could be detected afterwards by tactile measurements at several locations. It turned out that in most cases HIPIMS did not show any improvement in the homogeneity of the film thickness. In fact mostly the DC-MS deposited films exhibited the highest thickness homogeneity. However, the differences between DC and HIPIMS kept rather limited at an Ar-pressure of 0.4 Pa, whereas at 1 Pa they have been much more significant. Applying a bias of -50 V again nearly did not show any impact. On the other hand the film properties partially changed dramatically. The hardness of the HIPIMS deposited TiC-films at the hole walls was up to 4 times higher than that of the DC-MS deposited ones (both without bias). The face-to-face deposited samples showed very high hardness values (>HV2500) which were nearly independent of the deposition method. Examinations of the samples in scanning electron microscope revealed distinct differences in the film structure as an obvious reason for the severe drop of the hardness of DC-MS films at the hole walls.

A detailed overview and discussion of the data will be provided, together with ionisation data obtained by optical emission spectroscopy.

Structure and Optical and Electrical Properties of Amorphous Zinc-Iridium Oxide Thin Films

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Thin films of Zinc oxide with different additives are widely investigated as a potential substitute to ITO. Depending on the additive, the films may exhibit either n- or p- type conductivity. This report focuses on Zinc-Iridium oxide as a candidate for p-type electrical conductor.

The amorphous films have been deposited by reactive sputtering from metallic mosaic targets made of Zn and Ir pieces, with Zn 92-96%, Ir=4-8% surface area. The substrate was glass kept at ≈310°C temperature, the sputtering was conducted at 3 mTorr working pressure and 100W sputtering power. The process was controlled by plasma optical emission spectroscopy, based on Zinc emission line at 480.05 nm and Iridium emission line at 390.2 nm.

The amorphous films of Zinc-Iridium oxide are compared to the crystalline films of pure Zinc oxide and Zinc-Aluminium oxide. Apart from electrical resistance and optical transmittance measurements, the surface morphology of the films is characterized by AFM, the amorphous structure by XRD, and the local structure by EXAFS, respectively. The Zinc-Iridium oxide thin films have a homogeneous amorphous structure, as is detected by grazing incident XRD method, while Zinc oxide and Zinc-Aluminium oxide films have micro or nanocrystalline structure.

A Simple Mathematical Model of a Glow Discharge

AE Ross, DR McKenzie, MMM Bilek

We present a simple mathematical model of a time-dependent plasma glow discharge. The model is based on a simple electric circuit, shown in Figure 1. The script, written in MATLAB, inputs a given voltage-time trace which is applied to the plasma, and calculates the resultant current, comprising both the ion current from glow to cathode and the secondary electron current from cathode to the glow. The model takes into account the resistance R from the plasma itself, as well as an additional resistance R′, inherent in an experimental system.

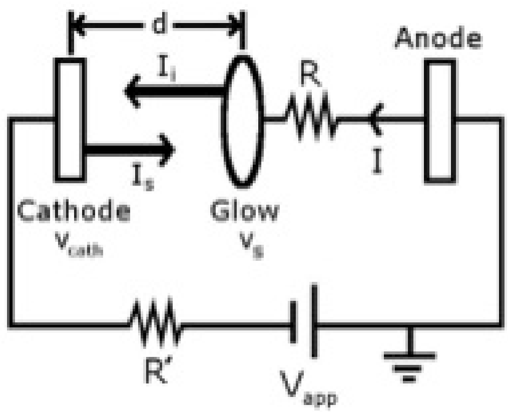

Figure 1: Glow discharge model

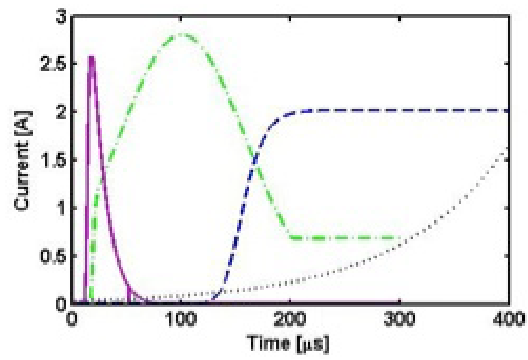

Figure 2: Current traces produced

The script reproduces some common current/voltage characteristics for plasma glow discharges reported in the published literature, an example of which is shown in figure 2. We present an analysis of the effects of various parameters, identifying possible explanations for various experimental results as seen in the literature.

The model is deliberately kept simple, with a number of approximations. Users can adjust many parameters to tailor the model to suit a specific scenario, including the secondary electron emission, ionisation probability, loss factors, and ion mass. It is hoped the model will prove useful to the HIPIMS community, being robust and flexible enough to accurately model the physics of a variety of glow discharges, and providing insight into observed behaviours.

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HIPIMS Power Supply Utilization for Oxide Coating Deposition on Roll Polymeric Substrates

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Oxide coatings deposition in reactive process from metallic targets has particular importance because metallic targets are cheaper in comparison with conductive ceramic targets. Besides use of metallic targets from indium-tin alloy can make utilization factor up to 90%.

In paper utilization of HIPIMS power supply for oxide and metal coating deposition on polymeric substrates is considered.

Key parameters of the power supply for work with thermosensitive polymeric substrates are defined. For oxide coating deposition metal targets ware used and reactive process was spent in a transition mode. Besides the original algorithm of process control for maintenance of the set parameters of a coatings during the long period of time was used.

Dependences of the basic properties of coatings (optical characteristics, electric characteristics, dynamic deposition rate, etc.) from power supply parameters are defined.

Comparison oof DC and HIPIMS Sputtered Molybdenum Films

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In chalcopyrite solar cell such as $Cu(In,Ga)Se_2$ molybdenum is used as metallic back contact. Molybdenum is selected because of its low work function and ability to react with selenium and sulfur. Due to these properties an ohmic contact to the p-type absorber layer can be formed. Usually the direct current magnetron sputtering (DCMS) is used for preparation of the molybdenum back contact. Film properties like conductivity, density and stress depends on the deposition parameters such as base or deposition pressure, power and temperature. Beneficial for adhesion is especially a higher density of the molybdenum. With the use of high power impulse magnetron sputtering (HIPIMS) technology the density of coatings are typically enhanced. Therefore at Fraunhofer IST Molybdenum films have been deposited with DCMS and HIPIMS on glass substrates. Different sputter conditions were used to influence the film properties. Both sputter techniques were compared concerning the mechanical stability, conductivity and morphology.

Keywords: HIPIMS, Molybdenum, CIGS solar cells

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Reactive HIPIMS Deposition of Photocatalytic TiO_2 Coatings Using an Industrial Coating Unit

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TiO_2 coatings have been synthesized by reactive High Power Impulse Magnetron Sputtering (HIPIMS) using an industrial-scale CemeCon CC800/9 deposition unit equipped with two 500 mm × 88 mm HIPIMS cathodes. The aim is to investigate the influence of various deposition parameters such as the HIPIMS discharge peak power, repetition frequency and pulse length on the hysteresis behaviour, deposition rate, phase composition, morphology and photocatalytic activity of the obtained coatings. Moreover, the coatings are deposited on witness samples in a setup mimicking real industrial complex-shaped substrates in order to exploit the coating properties grown in different locations of such geometries. This is motivated by the fact that the photocatalytic activity of TiO_2 depends strongly on phase composition and coating thickness, both parameters being sensitive to the sputtering geometry. HIPIMS has previously been shown to improve coating homogeneity of complex geometries when compared to coatings deposited by e.g. mid-frequency pulsed-DC sputtering. However, TiO_2 phase formation is highly sensitive to bombardment with energetic ions; the rutile phase is favoured by high energy fluxes while the photocatalytic active anatase phase is mostly encountered at low ion energy fluxes.

Preliminary experiments reveal that stoichiometric, crystalline TiO_2 coatings can be deposited at temperatures below 150°C containing the anatase and/or rutile phase. Furthermore, higher HIPIMS discharge peak powers promote the formation of rutile TiO_2. The phase composition is characterized by grazing incidence X-ray diffraction, chemical composition by Rutherford Backscattering, morphology by scanning electron microscopy. Finally, the photocatalytic activity is measured by photocatalytic oxidation of acetone activated by UVA-light exposure of the coatings.

Preferred type of presentation: Poster.

Mechanical and Tribological Properties of TiN/WN Multilayer Coatings Deposited by High Power Impulse Magnetron Sputtering

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Titanium nitride/tungsten nitride (TiN/WN) multilayer coatings were deposited on tungsten carbide substrates by high power impulse magnetron sputtering technique. The TiN/WN multilayer coating was deposited using Ti and W target materials by two facing magnetron cathodes while different powers and impulse durations were applied. The morphology and microstructure of the films were investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and high resolution transmission electron microscopy (HRTEM). The mechanical and tribological properties were evaluated using a nanoindentor and a conventional ball-on-disk tribometer respectively. The multilayer TiN/WN coatings exhibited a low surface roughness between 3 and 13 of Ra value, and a highest hardness of approximately 30 GPa. Wear test results show that the multilayer TiN/WN film has a variable coefficient of friction with values between 0.4 and 0.7, which strongly depends on the deposition conditions of HIPIMS.

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Cleaning of Substrates Prior to Vacuum Coating

Borer Chemie AG of Switzerland is a leading manufacturer of aqueous cleaning detergents and disinfectants for various applications. Especially for applications with high quality requirements the Swiss company has gained a very good reputation. The company develops cleaning processes which are exactly adapted to the customers needs and of course consider the available installation to operate the cleaning process. Borer Chemie AG also supports the customer with the installation of the process and helps to close the gap between the laboratory and the industrial process. Borer Chemie AG has a wide range of equipment for surface analysis or residues and particles on cleaned substrates.

Cleaning prior to a vacuum deposition process is essential and has a big influence on the quality of the coating. It has a very direct relation to the adhesion and the structure of coatings becoming more and more complex, also on the quality of the coating itself. The selection of the cleaning detergents is usually delicate since the temperatures in the sputtering process are lower as compared to a PVD process. This applies before all for optical components but as well to sophisticated mechanical parts. The lecture explains the many variable parameters of a cleaning process and how to establish a process. The possibilities for cleaning and the preconditions required to obtain residual free substrates will be explained. The quality of rinsing water is one of the key factors in cleaning and some explanation will be given hereto also. Cleaning is adding value and helps to reduce drop offs and improves the quality and reliability of the coating process.

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Chromium and Chromium Nitride Thin Films Deposited by HIPIMS Using Short Impulsions

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CrN is an excellent wear and corrosion resistant material. There is much interest in the research community to develop CrN thin films for coating tools for metal and wood machining operations [1,2]. Chromium nitride was widely studied and developed by classical magnetron sputtering [3] and more recently for further improvements by HIPIMS [4, 5].

In this work, we varied different process parameters but we choose to focus on the short durations, typically between 10 and 50*µ*s and to study the influence of peak current on the crystallinity and the morphology of coatings. Deposited films were characterized by classical techniques such as: XRD, AFM, SEM and XPS. Nanoindentation and oxidation tests were also performed. Concerning hadrness measurements, the Jönsson and Hogmark model [8] was applied to separate the contributions of the substrate and the film. Annealing tests were carried out up to 1000K in order to study the thermal stability of Cr and CrN films under different atmospheres.

Keywords
HIPIMS, DC sputtering, Chromium nitride

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HIPIMS 2012

3rd International Conference on HIPIMS

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