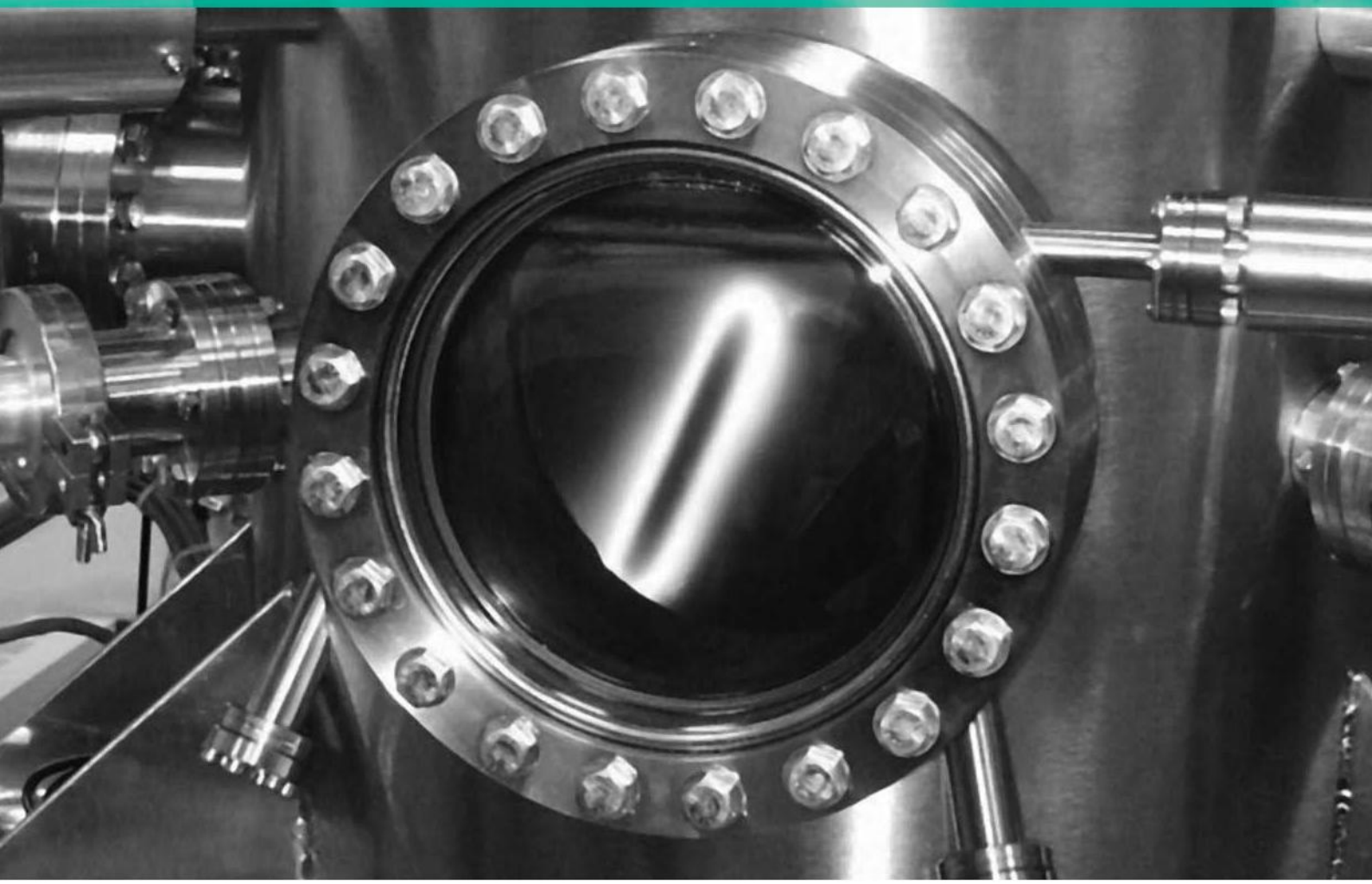
HIPIMS 2010

1ST INTERNATIONAL CONFERENCE ON HIPIMS ABSTRACT BOOK



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MICROSTRUCTURE EVOLUTION DURING HIPIMS GROWTH

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We consider two model cases to study microstructure evolution during HIPIMS sputter deposition. Comparing the microstructure of HIPIMS to DCMS deposited CrN films we find a pronounced effect of energetic species when films are deposited on floating substrates as well as with 60 V substrate bias. During HIPIMS deposition intercolumnar porosity is eliminated which is accompanied by incorporation of intragranular residual damage manifested as darker average contrast in TEM images associated with local strain fields. HIPIMS discharges result in to larger grain size, slightly lower nitrogen incorporation, pronounced 002 preferred orientation, and much smoother films. These effects are well correlated with the greater ionized fraction of the arriving deposition flux and their higher average energy.

We further study the structure of 2.5 μm thick TiAlCN/VCN coatings were deposited by reactive a HIPIMS process carried out in a mixed Ar, N_2, CH_4 atmosphere utilising two opposing TiAl and V targets. Cross section transmission electron microscopy showed a gradual evolution of the structure of the coating with thickness. The initial structure is nanoscale multilayer with sharp interlayer interfaces. This transforms to nanocomposite of TiAlCN and VCN nanocrystalline grains surrounded by C-rich tissue phase and finally changes to an amorphous carbon rich Me-C phase. In contrast, deposition in similar conditions using standard magnetron sputtering produces a well defined nanoscale multilayer structure independent from the coating thickness. Thus we observe a transition from a PVD to a PACVD process during reactive HIPIMS process, which results in dramatic changes in the coating nanostructure.

Application of TEM in the Structural Characterization of CrAlYN/CrN and TiN Coatings

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The coatings were deposited on polycrystalline stainless steel and gamma-TiAl substrates at 400^0C substrate temperature and – 75 V bias voltage. The substrates were treated by HIPIMS in both cases. CrAlN base layers were applied in all experiments.

The lecture will review the structural details of the coatings considering the substrate - base layer interface and the local orientational relations, the texture, the columnar morphology and the defect structure (density) of the films.

It is concluded that the HIPIMS substrate treatment promoted the oriented (epitaxial or axiotaxial) growth of the base layer locally on the individual crystals of the polycrystalline substrates. This is valid both for the crystals of γ-TiAl hexagonal Ll_0 and α_2-Ti_3Al tetragonal DO_{19} phases. These orientational relationships develop also on the surface of the individual substrate crystals of large miscut angles. In films of larger thicknesses (> 1μm) the orientation of crystals (starting with local texture related to the substrate crystal) might change along the thickness. Considering the orientation of the base layer crystals controlled by the substrate crystal this variation of the texture can be related to the competitive growth of crystals controlled by the growth conditions. The density of films related to the defect structure of the grain and column boundaries is improved by applying HIPIMS deposition of CrAlYN/CrN nanoscale multilayer coatings.

TITANIUM ALUMINIUM NITRIDE SPUTTERED BY HIPIMS

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TiAlN was sputtered reactively by HIPIMS in the composition Ti/Al 33/67 and 50/50 in a modified OC Oerlikon Balzers INNOVA coating equipment. The films properties like deposition rate, surface roughness, hardness, Young's modulus, wear and film stress were analyzed as function of the nitrogen gas flow, pressure, target-substrate distance, substrate bias and substrate temperature. Furthermore the films were characterized by X-ray diffraction and secondary electron microscopy of the cross section and the surface appearance. The process characteristics and films properties were compared with pulsed DC sputtering under the same conditions as well as with arc evaporation.

INFLUENCE OF HIPIMS PLASMA IONIZATION ON THE MICROSTRUCTURE OF TIN

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HIPIMS (High Power Impulse Magnetron Sputtering) discharge is a new PVD technology for the deposition of high-quality thin films. In this method, a high power density is applied at the cathode yielding a higher degree of plasma ionization than in conventional magnetron sputtering.

In this study, the operation of HIPIMS in an Ar and N_2 atmosphere with a Ti target was investigated. Plasma was operated at a pressure of 0.24 Pa and an Ar:N_2 partial pressure ratio of 10:1 was used to operate at the metallic-to-poisoned transition point. The peak current was varied from 5 to 30 A with a pulse duration of 200 µs. The frequency was adjusted between 200 and 1000 Hz to maintain a constant average power of 0.4 kW. Time-resolved measurements of the plasma parameters near the substrate were carried out using energy resolved mass-spectrometry and Langmuir probe (LP) at a distance of 170 and 100 mm from the target respectively. The influence of the gas-metal ion ratio, plasma composition and plasma density on film structure was investigated.

Mass spectrometry measurements showed that the reactive HIPIMS discharge produced a deposition flux with a significantly increased content of ionised film-forming species, such as Ti^{1+}, Ti^{2+} and N^{1+}. Increasing the discharge current from I_d = 10 to 30 A resulted in an enhanced activation of the atomic ion N^+. Ti^+ ions with energies up to 50 eV were detected during the pulse with reducing energy in the pulse-off times. Results from LP showed that the peak plasma density generated during the pulse was in the range of $3x10^{16}$ m^{-3} and increased linearly with peak current.

TiN films deposited by HIPIMS were analysed by X-ray diffraction, atomic force microscopy and electron microscopy. At low I_d, the films were highly textured with a strong [111] orientation whereas at high I_d, a [200] texture was dominant. The effects of the significant activation of the deposition flux observed in the HIPIMS discharge on the film microstructure and texture evolution are discussed.

High Power Pulsed Plasmas for Materials Processing: Research Program and Capability at the University of Sydney

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The utilisation of pulsed plasmas in materials synthesis is rapidly growing due to a number of advantages over their continuous mode counterparts. A major operational advantage is that the pulsed mode is much less affected by problems associated with instabilities, surface charging of substrates and cathode or target poisoning and as such typically has wider process windows. The plasmas are typically transient, operating far from equilibrium, at least in the early stages, and showing an evolution of parameters through the pulse. In our diagnostics studies we aim to characterise and understand the transient phenomena and their affects on plasma conditions at the substrate relevant for thin film deposition with the long term aim of utilising the new understanding for improved process control.

Over the last few years we have developed a multi sourced high current centre triggered cathodic arc system operating in a high power pulsed mode [1,2]. A suite of plasma diagnostics were developed and employed to study the discharge as a function of time in the pulse. The centre triggered design allowed us to correlate changes in the charge states produced, detected with time resolved optical emission spectroscopy, with the numbers of cathode spots present and there separations on the cathode surface, as measured by fast framing photography. The results indicate that elevated charge states can be produced in the early stages of the pulse due to short range coupling between cathode spots. Time resolved Fizeau interferometry was also developed and utilised to detect ions travelling both towards and away from the cathode. The system has been used for the deposition of nanostructured materials such as MAX phases [3], nanoscale multilayers [4] and phase separated nanostructured coatings [5].

Recently we have commissioned a multi-source sputtering system which can be driven by a pulsed power supply capable of operating in two modes: fixed voltage and pulse shaping according to an arbitrary wave input. We have now commenced time resolved diagnostic studies on this system. In this paper we will present our first results and compare them with phenomena observed earlier in our arc source.

Statistical and Formative Time Lags in High Power Impulse Magnetron Sputtering

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It is well known, and usually well disregarded, that the discharge current pulse lags a rather long time behind the voltage pulse. This time lag has been very pronounced in the seminal paper by Kouznetsov and coworkers [1] and many other reports that followed. The time lag is generally not a problem because it is exceptionally well reproducible and can therefore be taken into account when designing a process recipe. In this contribution, though, the focus is on the underlying physics of the time lag, which is composed of two contributions, generally labeled as statistical and formative time lag. The statistical time lag is associated with the absence or presence of initial electrons that can serve as the 'seeds' for ionization avalanches in the Townsend process. A Townsend process is the formation of ionization avalanches by electron impact ionization (α process) and emission of secondary electrons (γ process).

Experimental data presented here show that the statistical time lag can be as little as 0.5% of the delay of the apparent current onset, and hence is negligible. Consequently the remainder of the work focuses on the formative time lag which describes the evolution of the initially very small current caused by the 'electron seed' to measurable discharge currents, which may be as much as 10 orders of magnitude larger. The work includes an experimental study of the time lag using several different target materials and process gases, as well as a range of pulse parameters in terms of applied voltage, pulse repetition rate, and pulse length. The theoretical part expands on the classical treatment of the formative time lag by Schade [2] by considering the low pressures and presence of a permanent magnetic field which impedes the motion of electrons to the anode. In the generalized treatment, both inertia of ions and the non-zero time for ionization by secondary electrons is taken into account. However, even in the expanded treatment, the inverse of the time lag is shown to be proportional to the applied voltage. This is well confirmed by the experimental data. In summary, the rather large time lag is caused by the finite time of ion motion to the target, where secondary electron emission occurs, and the finite time secondary electrons need to generate new electron-ion pairs by electron impact ionization. The time lag may be much reduced by providing a much more significant electron 'seed' – for example by using higher pulse repetition rates or by using a low current 'keeper discharge' between pulses.

This work was supported by the U.S. Department of Energy.

[1] V. Kouznetsov, K. Macak, J. M. Schneider, U. Helmersson, and I. Petrov, "A novel pulsed magnetron sputter technique utilizing very high target power densities," *Surf. Coat. Technol.,* vol. 122, pp. 290-293, 1999.

[2] R. Schade, "Über die Aufbauzeit einer Glimmentladung," Zeitschrift für Physik, vol. 104, pp. 487-510, 1937.

The Deposition Rate of Copper in HiPIMS is Reduced by the Presence of Sputter Gas

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By using low duty cycle, high power density pulses in a magnetron discharge, high plasma density is attainable and a large fraction of the sputtered atoms are ionized. This facilitates substrate etching and interface tailoring, control of density and texture as well as stress and provides means to affect surface roughness. Unfortunately, most reports on HiPIMS deposition rates agree on a substantial reduction compared to the DC sputtering rate. Explanations of this phenomenon brought forward include the increased return of metal ions to the sputter target, the linear increase in dissipated power with voltage in contrast to the approximate square root dependence on the voltage for the sputter yield as well as 'sputtering wind' and rarefaction effects of the sputtering gas.

A recent development is 'gasless sputtering', where the plasma from a short arc discharge is used to initiate a magnetron copper discharge, even in the absence of any sputtering gas. This allows the comparison of the magnetron discharge with and without the gas, and can therefore provide information on the effects of the gas.

The amount of deposited copper in such processes was measured by a quartz crystal microbalance for a range of pressures and pulse lengths. It was found that for relatively long pulses (in excess of several hundred microseconds), the rate of deposition is not severely affected by the presence of gas. However, at shorter pulse-lengths the reduction is severe. For example, at a pulse-length of 100 microseconds in 2 Pa of argon the deposited amount of copper is only 1/3 compared to gasless sputtering. It was found that shorter pulses and higher gas pressure reduced the deposition efficiency of copper.

These results will be discussed in terms of discharge characteristics, particle transport in sputtering and related to power efficiency.

The gasless sputtering process allows deposition of pure copper using very high ion currents, even higher than the discharge current itself.

The ion-to-neutral ratio is controlled by the magnetron voltage and by adding gas, different mixtures of neutral and ionic species can be created. This may be a valuable tool for further experiments on condensation from the plasma phase. The higher deposition rate and the tunable ionization fraction offered by the gasless process could be of interest to industry.

Charged Particle Transport in HiPIMS and its Effects on Thin Film Deposition

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HiPIMS is one of the most promising improvements of common IPVD techniques and is already making its way to industrial applications. The HiPIMS plasma generates large quantities of ions of the sputtered material due to a high plasma density, but also acceleration of the ions increasing the bombardment of the growing film without using a substrate bias voltage. Also observed is a lower deposition rate for HiPIMS than that obtained for conventional DC sputtering, using the same average power. In order to optimize the process, controlling ion acceleration and increasing deposition rate, it is necessary to spatially as well as temporally resolve what transport mechanism is operating in the HiPIMS discharge. In this study the total current densities J_φ (azimuthal direction) and J_D (axial direction) have therefore been measured above a cylindrical magnetron using Rogowski coils, which, unlike electrical probes, require no further information regarding the plasma characteristics when determining the current density. The new data shows that there are spatial and temporal variations of the key transport parameter J_φ / J_D, governing the cross-**B** resistivity and also the energy of the charged particles. During the ignition phase the discharge is characterized by an anomalously low azimuthal-to-discharge current density ratio, J_φ / J_D < 4, as earlier reported by several authors, and only a weak dependence on the magnetic field variation with distance from target. As the peak of the current pulse is reached, the transport changes towards a classical scaling proportional to the magnetic field strength, but still below the Bohm-regime (J_φ / J_D < 16). Moreover, a strong second peak of the internal currents is detected well after the discharge current peak. The transient to this stage is again characterized by a low current density ratio indicating faster-than-Bohm diffusion, but is gradually increasing when approaching the second peak. These results on transport are essential input when modeling the axial electric field, governing the back-attraction of ionized sputtered material, and might furthermore provide a link between the different resistivities reported in HiPIMS, pulsed-DC, and DC magnetron discharges.

Two Types of Pulsed Magnetron Systems – Characterization and Application

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High-power pulsed magnetron sputtering of zirconium was investigated at a high average target power density in a period, being approximately 100 Wcm^{-2}. The depositions were performed using an unbalanced circular magnetron with a directly water-cooled planar zirconium target of 100 mm diameter. The repetition frequency was 500 Hz at duty cycles ranging from 4 to 10% and an argon pressure of 1Pa. High fractions (21 - 32%) of doubly charged zirconium ions at rapidly decreasing fractions (from 23 to 3%) of singly charged zirconium ions, and hence the total fractions (from 44 to 29%) of the zirconium ions, were found in total ion fluxes onto the substrate (located d = 100 mm from the target), when the average target power density in a pulse increased from 0.97 to 2.22 $kWcm^{-2}$. The enlarged target power densities during shortened voltage pulses resulted in a decrease of the deposition rate of films from 590 to 440 nm/min at a weakly decreasing ionized fraction (from 55 to 49%) of sputtered zirconium atoms in the flux onto the substrate. For d = 200 mm, the doubly charged zirconium ions have become strongly predominant (up to 63%) in the total ion flux onto the substrate.

Hard (22 – 24 GPa) amorphous Si-B-C-N coatings with high thermal stability and oxidation resistance (even above 1500°C) were deposited on various substrates by pulsed dc magnetron sputtering using a single B_4C-Si (25:75%) target in an Ar-N_2 (50:50%) gas mixture. The substrate temperature of 350°C and the total pressure of 0.5 Pa were held constant during the depositions on the substrates at a floating potential or an rf induced bias of -100 V. A planar rectangular (127 x 254 mm^2) unbalanced magnetron was driven by a pulsed dc power supply operating at the repetition frequency of 10 kHz and the average target power over a period of about 500 W with 50% and 85% duty cycles. Laser confocal scanning microscopy showed a very smooth surface morphology of the as-deposited coatings with an average roughness R_a = 6 nm determined over the surface area of 120 µm x 120 µm. Prior to deposition, a modification of the substrate surfaces was performed by pulsed magnetron sputtering of the B_4C-Si target in Ar gas at the same pressure, the duty cycle of 20% and the average target power over a period of about 250 W, the substrate temperature from 350°C to 480°C and the rf substrate bias of -1300 V for 12 min to enhance adhesion of the deposited Si-B-C-N coatings to various substrates. A substantial increase in the critical load (from 16 to 75 N for the WC-Co substrate) caused by the substrate surface modification was proved.

Characterization of HiPIMS Discharges with Tailored Constant Current Phase

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While typical HIPIMS processes show a triangular current shape the ionization degree changes with the current. Basing on a new principle for HIPIMS generation the plasma is initially kicked to a certain current level within 20 µs and then kept constant for 100 µs. The idea of creating a constant current discharge over defined period of time is to adjust and keep a constant ion to neutral ratio resulting in improved film quality. While typical HIPIMS plasmas with pulse on tine below 200 µs typically integrate over several states of ion to neutral ratios an extended constant current phase at defined current level is expected to improve the resulting film properties.

For investigation of the ionization time resolved optical emission spectroscopy measurements were carried out. For the energy distribution a retarding field energy analyzer was used for repetition frequencies of 1 kHz. The influence of the pulse shape on the deposition rate was also investigated. The investigations were carried out with titanium and chromium targets.

VERY-HIGH-RATE REACTIVE DEPOSITION OF THICK, TRANSPARENT SILICON DIOXIDE COATINGS BY PULSED AC DUAL MAGNETRON WITH MOLTEN TARGETS

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This article briefly summarizes the evolution of reactive magnetron sputtering of transparent oxide films and improvements of this process with the aim (1) to eliminate the hysteresis effect, (2) to suppress the arcing at the target and (3) to increase the deposition rate a_D. Main differences between (1) single magnetron and dual magnetron and (2) DC, pulsed DC and pulsed AC reactive process are explained. Special attention is devoted to the target power density used in reactive magnetron sputtering and to differences in this process when cold, hot and molten magnetron target is used. It is shown that the reactive deposition of transparent oxide films from molten target is a combined process in which both the sputtering and the evaporation of the target material participate simultaneously. At high target power densities $W_{ta} \geq 50$ W/cm^2 (this value depends on the target cooling) averaged over pulse period *the ionized evaporation* of the target dominates over the sputtering and the deposition rate a_D of the transparent oxide film is greater than its deposition rate $a_{D\ MM}$ at the end of the metallic mode with cold target, i.e. $a_D >> a_{D\ MM}$. These statements were demonstrated on the very-high-rate (up to 814 nm/min) reactive deposition of thick (up to 8000 nm) transparent silicon dioxide coatings containing low amount (<5 at.%) of Zr on a stationary substrate located at the substrate-to-target distance $d_{s\text{-}t}$=100 mm by the pulsed AC dual magnetron with molten target operated at $W_{ta} \geq 50$ W/cm^2. It is shown that these reactively sputtered transparent Si-Zr-O coatings are very elastic and exhibit excellent resilient properties. Performed experiments indicate that there are no principal reasons which prevent to increase the deposition rate a_D of thick transparent oxide films to several micrometers per minute, maybe several tens of micrometers per minute.

HiPIMS Discharge Analysis by Energy Resolved Mass Spectrometry in a Reactive Atmosphere with Oxygen Content

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HIPIMS (High Power Impulse Magnetron Sputtering) discharge is a PVD technique for the deposition of high-quality thin films. With this method, a high power density is applied at the cathode, yielding a higher degree of plasma ionization than in conventional magnetron sputtering. Due to a low duty cycle, high power density is accumulated into the active part of the pulse. Recently, HIPIMS has been used for deposition of oxides in particular for TiO_2 and TiO_xN_y.

In this study, the operation of HIPIMS in an atmosphere of working gases of Ar and N_2 with 20% O_2 content and a Ti target was investigated. The plasma was operated at a pressure of 1-1.7 Pa and an Ar:Air partial pressure ratio ranging from 45:1 to 45:10 was used to operate at the metallic-to-poisoned point. The peak current was varied from 3 to 10 A with a pulse duration of 200 µs. The frequency was adjusted between 100 and 400 Hz to maintain a constant average power of 0.6 kW. Time-resolved measurements of the plasma parameters near the substrate were carried out using energy resolved mass-spectrometry 170 mm from the target. The main aims of this study were to investigate the influence of the gas metal ion ratio and plasma composition on film structure.

Mass spectrometry measurements showed that the reactive HIPIMS discharge produced a deposition flux with a significantly increased content of ionised film-forming species, such as Ti^{1+}, Ti^{2+}, N^{1+}, O^{1+}, TiO^{1+} and TiO_2^{1+}. Increasing the air content in the discharge resulted in an enhanced activation of the oxide species, TiO^{1+} and TiO_2^{1+}, and a reduction in the atomic ion N^{1+}, Ti^{1+} and Ti^{+2}. Ions with energies up to 80 eV were detected during the pulse with reducing energy in the pulse-off times in the metallic mode. The ion energy decreased considerably when the discharge was operated in the oxide mode

In the mass spectrum of the negative ions only the O^- and O_2^- species were observed .The detailed study of the energy distribution of O^- and O_2^- shows high-energy ions formed at the cathode with energies proportional to the full cathode voltage. The ion energy distribution function shows that in the transition from metallic to the oxide mode there is about 100 V drop of the voltage on the oxide surface layer on the cathode; this corresponds well with the measured cathode voltage.

The effects of the oxygen content in the deposition flux observed in the HIPIMS discharge on the film microstructure are discussed.

Reactive High Impulse Power Magnetron Sputtering: Hysteresis Behaviour and Process Control

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High Power Impulse Magnetron Sputtering (HIPIMS) is a technologically important Physical Vapour Deposition process that is able to provide a highly ionised flux of sputtered species. It is thought to be particularly important for applications where there is a need to coat 3D features (e.g. vias and trenches in semiconductor industry). HIPIMS may have other added benefits, as compared to DC or medium frequency magnetron sputtering, that are related to improved coating structure-property relationship control through self-species ion/plasma assistance. Enhanced structure and properties of thin film materials produced in reactive sputtering are also highly desirable.

Significant progress related to providing control means for reactive HIPIMS processes and ensuring stability has been made recently. This paper reports on the recently developed Plasma Monitoring (PM) based reactive HIPIMS control/monitoring method and its performance as compared to that of conventional PM, Penning-PM and λ-sensor based methods. PM based process control technology is shown to provide precise control and stable operation of reactive HIPIMS discharges anywhere within the hysteresis loop. It also appears to be superior when compared to oxygen partial pressure control based techniques. Since PM provides information on the sputtered flux and target state, important knowledge on the features of reactive HIPIMS processes can be obtained using this technique.

DEPOSITION OF γ-ALUMINA BY HIPIMS IN AN INDUSTRIAL COATING UNIT

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In our presentation we describe the deposition of γ-alumina deposited by reactive High Power Pulsed Magnetron Sputtering (HPPMS/HIPIMS) onto cemented carbide (WC/Co) and steel substrates. We show the potential of HPPMS with respect to the avoidance of both, insulating films on the target surface and hysteresis effects that would require a complex control of oxygen in dependence of the cathode voltage. Film deposition was performed by using Al targets in an Ar/O2 atmosphere at a temperature of 450 - 500°C and a total pressure of 310 mPa. Peak power densities up to 240 kW were applied to the sputtering cathode.

The coating properties were investigated by means of X-ray diffraction, energy dispersive Xray microanalysis (EDS) and nanoindentation. Good coating adhesion on the substrate was determined by applying the Rockwell test. The analysis results clearly show that with HPPMS it is possible to deposit γ-crystalline Al_2O_3 at temperatures below 500°C. By choosing the appropriate pulse parameters back sputtering was suppressed and therefore high deposition rates of more than 2.5 µm/h were obtained.

HOT CORROSION AND SULPHIDATION OF NEW HIPIMS NANOSTRUCTURED AND MICROSTRUCTURED COATINGS ON GAMMA-TIAL

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Molten sulphates and sulphide environments are formed in most of the energy production devices, such as gas turbines. There are different attempts in the use of electrochemical techniques in this environments, but the corrosion of the testing samples do not allow to go more than hours of corrosion testing. Based in this problems, and tanking into account the new development of micro and nano-structured coatings for high temperature applications under INNOVATIAL EU project, a new kind of testing sensors with the micro and nano-structured coatings have been develop to monitor their corrosion process in real time. It will allow to know different corrosion mechanism in real time and the expected behaviour in the steady state. Electrochemical impedance spectroscopy is the base analysis for these systems, and the development of reference equivalent circuits for the interpretation of results will be explained in detail. The results will provide a general overview of the oxidation behaviour of each coating and also a semi-quantitative comparative analysis in real time for different nano-structured coatings on γ-TiAl. Some of the coatings developed in this project have shown an excellent result, comparing with some traditional protective systems. Comparative results will be shown

Ion Mass Spectroscopy Investigations During High Power Pulsed Magnetron Sputtering of Cr in Ar and Ar/N_2 Atmospheres

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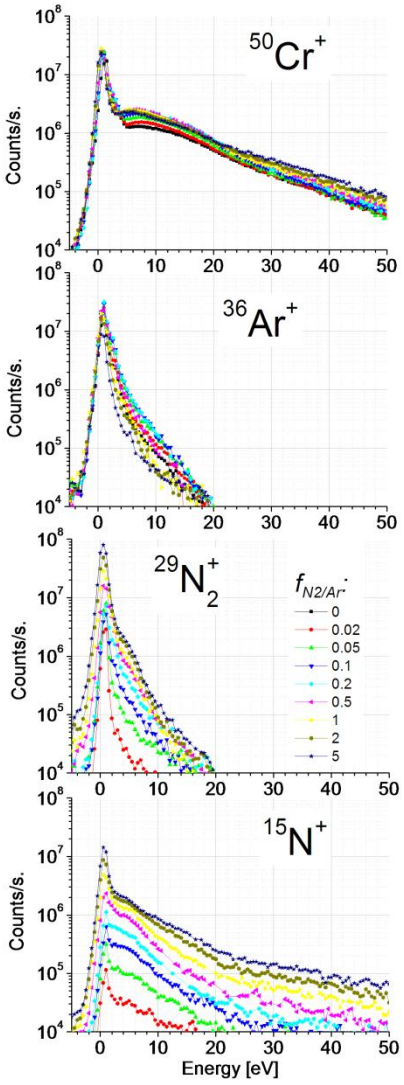

Mass spectroscopy was used to analyze the energy and composition of the ion flux during high power pulsed magnetron sputtering (HIPIMS/HPPMS) of a Cr target in an industrial deposition system. The ion energy distribution functions were recorded in the time-averaged and time-resolved mode for Ar^+, Ar^{2+}, Cr^+, Cr^{2+}, N_2^+, N^+, and CrN^+ ions. In the metallic mode the dependence on pulse energy (equivalent of peak target current) was studied. In the case of reactive sputtering in an Ar/N_2 atmosphere, variations in ion flux composition were investigated for varying N_2-to-Ar flow ratio, $f_{N2/Ar}$, at constant pressure and HIPIMS power settings. We find that the composition (and energy) of the ion flux can be significantly altered by varying the pulse energy. With increasing pulse energy from 3 J to 30 J (while keeping the pulse width and pulsing frequency unchanged) the number of doubly charged Cr ions shows a linear increase, while the amount of detected Ar^+ ions remains constant. Low-energy N_2^+ molecular ions and high-energy N^+ ions are present during sputtering in reactive mode. The N^+ ions constitute the primary source of nitrogen ions detected and are for $f_{N2/Ar} \geq 0.3$ the second highest contribution to the total energy flux. This is in contrast to the reactive DC sputtering where N_2^+ ions dominate over N^+. The time evolution of ion flux composition is analyzed in detail and related to the film growth process. The ionization of working gas mixture is hampered during the most energetic phase of the discharge by a high flux of sputter-ejected species entering the plasma, causing both gas rarefaction and quenching of the electron energy distribution function. It is suggested that the properties (composition and energy) of the ion flux incident on the substrate can be intentionally adjusted not only by varying the pulse energy (discharge peak current), but also by taking advantage of the observed time-variations in the flux composition [G. Greczynski and L. Hultman *Time And Energy Resolved Ion Mass Spectroscopy Studies Of The Ion Flux During High Power Pulsed Magnetron Sputtering Of Cr In Ar And Ar/N_2 Atmospheres*, Vacuum (2010), in press].

New Type HiPIMS Reactive Deposition of Superhard Nanocomposite nc-TiN/a(nc)-SiN coatings

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Thick 6 µm÷12 µm nanocomposite nc-TiN/a(nc)-SiN coatings (with at least partly nanocrystalline SiN phase) have been deposited onto 1" diam. Vanadis 23 HS steel and two types of indexable inserts CNMA and CNMG (mode 12-04-12) devoted to high speed machining of 15-3-3-3-1 type titanium alloy. The specimens were fixed to a heater, which was rotating during deposition and the temperature of the specimens during deposition was ~800 K. The coatings have been deposited in a vacuum chamber with use of four rectangular magnetrons forming a closed unbalanced magnetic field. Three of the four targets were sintered from high purity Ti and Si powders at relative fraction 1:11 of Si to Ti atoms and one target was made of pure grade 1 plate 9 mm thick. The magnetron targets were powered with four newly developed medium frequency 150 kHz with synchronized high power 15 kW sinusoidal current generators with extremal voltage -1600 V modulated with an acoustic frequency (10 Hz ÷ 4 kHz), whereas the magnetrons' power was modulated with use of non-electronic pulses at an infrasound frequency ~1 Hz. The mean power density released during a single pulse on the active surface of a magnetron target was approximately 0.3 $kW \cdot cm^{-2}$ and a mean value of pressure of the reactive atmosphere N_2+Ar during deposition was ~0.1 Pa. Before deposition of the nc-TiN/a(nc)-SiN coating at first a thin 50 nm TiN interlayer has been deposited for better adhesion. After deposition the coatings have been submitted to a number of investigations, as, f.ex.: X-Ray phase analysis, EDS chemical composition verification, SEM morphology, TEM and HRTEM observations, SAED diffraction identification, Raman shifts' spectrometry, MTS M-200 nanoindentation and others. After 1 hour deposition the nanocrystallites (diam. 4 nm ÷ 10 nm) of the TiN phase were well developed (with FWHM peak widths as low as Δè~0.2 deg) and corresponded well to ICDD 38-1420 TiN Osbornite phase, the hardness was changing between 40 GPa and 80 GPa and the nitrogen content between 13 at.% and 35 at.% (depending on the pulsing parameters and partial pressures of Ar and N_2 components of the reactive atmosphere). The adhesion values of different coatings to the Vanadis 23 HS steel were approximately limited to 50 N ÷ 70 N (from the scratch tests). The plots in Fig. 1 represent the differences in the intensities of the magnetron discharge between different stages of a single impulse.

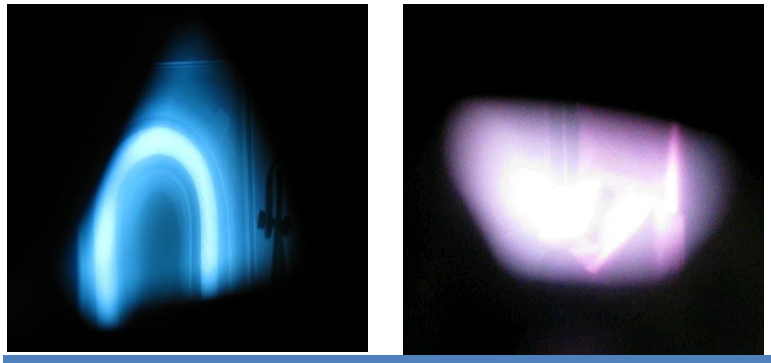

Fig. 1. Differences in the intensities of the magnetron discharge between diffe-rent stages of a single impulse during re-active HIPIMS deposition of a nano-composite nc-TiN/a(nc)-SiN coating.

Comparison of the Properties of TiN and CrN Coatings Synthesized by Reactive Arc Evaporation and HIgh Power Impulse Magnetron Sputtering

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The developments of physical vapour deposition processes can be an alternative to enhance thin films properties. Some years ago, several researchers showed a great interest in the use of highly ionised plasmas provided by cathodic arc evaporation, which is now extensively developed at industrial level. More recently, HIgh Power Impulse Magnetron Sputtering (HIPIMS) should be an alternative between arc evaporation and conventional DC sputtering. This new technology of power supplies also allows enhanced plasma densities with a high degree of ionisation of the sputtered particles. This allows the possibility to control the ion bombardment on the surface of the substrates. Then, film density and adhesion should be enhanced by applying a negative bias voltage to the substrates.

In this paper we propose to compare arc evaporation and HIPIMS processes by developing and characterising well known coatings such as TiN and CrN. In all cases, thin films are synthesised from pure metallic target in an Ar-N_2 atmosphere. The influence of the process used and of the substrate bias voltage is investigated in relation to the chemical, structural, morphological and mechanical features of the layers.

Effect of Substrate Bias Voltage on the Structure and Properties of ZrN Coating Deposited by HIPIMS Technology

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Monolayer ZrN coatings were deposited solely by the novel High Power Impulse Magnetron Sputtering (HIPIMS) technology in an industrial scale PVD machine (HTC-1000-4 target system). Coatings were deposited on 1 micron polished M2 High speed steel (HSS), 304 L Stainless steel (SS) specimens and on Si (100) specimens. Prior to deposition, HIPIMS plasma sustained on a Zirconium (Zr) target was utilised to pretreat the specimens.

Coatings were deposited at 400°C in a mixed N_2 and Ar atmosphere using 2 magnetrons with pure HIPIMS technology, at three different bias voltages keeping all other process parameters constant. The thicknesses of the coatings measured by the ball cratering technique were in the range of 1.84 µm, 1.96 µm to 2.13 µm at bias voltages of -95 V, -75 V and -65 volts respectively where the difference in thickness can be attributed to the re-sputtering effect. X-ray diffraction experiments on SS specimens revealed a dominating 111 texture for all three coatings irrespective of the bias voltage. Cross-sectional scanning electron microscopy revealed extremely dense coating structures at all bias voltages, similar to the transition zone structure (Zone T) reported by Thornton. The coatings appeared extremely smooth on the top and with no dome shaped structures often associated with low ion bombardment during deposition. HIPIMS pretreatment lead to high adhesion (L_C) of the coatings to the substrate. A continuous ductile perforation of the coating was observed at progressive loads greater than 65 N however no spallation of the coating was observed up to loads of 100 N. High values of hardness (40.4 GPa), Young's Modulus (424 GPa) and compressive stress (10 GPa) were recorded for coatings deposited at -95 bias voltage. The hardness and internal stress of the coating was found increasing with more negative bias voltages. All the coatings exhibited high dry sliding wear resistance (K_C) in the range of 6×10^{-15} $m^3N^{-1}m^{-1}$. Cross-sectional Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) analysis has been used to study the effect of ion bombardment obtained from HIPIMS on the structure of the coatings.

Synthesis of Boron Nitride by Reactive High Power Impulse and RF Magnetron Sputtering – Linking Discharge and Film Properties

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Boron nitride, especially in his cubic phase (c-BN), is a significantly interesting material for various technological applications thanks to its thermal, electrical, mechanical and optical properties. Reports on the formation of c-BN by means of PVD, PACVD or even CVD methods indicate ion bombardment of growing film as an essential condition[1]. Nevertheless, this high level of ion bombardment has some drawbacks: high level of stress, bad adhesion which inhibits the deposition of thick films.

This study deals with attempts to overcome these drawbacks by the use of two methods for c-BN films deposition:

- Conventional reactive r.f. magnetron sputtering
- Novel technique of high power impulse magnetron sputtering using a fast pulsed-magnetron discharge operating in a preionization regime[2].

The purpose was, first, to find out the plasma conditions for obtaining BN thin films and even the cubic phase by HIPIMS method and, second, to perform a comparison between these two methods considering both plasma parameters and films properties.

Mass spectroscopy measurements were performed in order to define the energies and the fluxes of the species impinging the substrate for well chosen discharge parameters. The plasma properties will then be linked to the synthesized films' characteristics determined by a large set of techniques as SEM, EPMA, AFM, XPS, FTIR and HRTEM.

[1] I. Bello,T, C.Y. Chan, W.J. Zhang, Y.M. Chong, K.M. Leung, S.T. Lee, Y. Lifshitz, Diamond & Related Materials 14 (2005) 1154

[2] M.Ganciu et al, "Deposition by magnetron cathodic pulverization in a pulsed mode with preionization", European Patent Appl., 4447072.2, Mars 22, 2004, WO 2005/090632

High Resolution Studies of Multilayer Coating Structure and Changes Through High Temperature Exposure

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Nanoscale multilayer coatings deposited by advanced PVD techniques are now recognised as the leading coatings for high temperature wear and oxidation resistant applications, a classic example being the TiAlYN/CrN system. Because of the nanoscale structure and the significant residual strain often found in the coating, characterisation of the true coating structure remains a challenge. Over the last few years there has been literally a revolution in the ability to probe atomic structure; a 50 year old dream has just been fulfilled: R. Feynman, Nobel Laureate, predicted the need in 1959 with the words: *"It would be very easy to make an analysis of any complicated substance; all one would have to do would be to look at it and see where the atoms are. … I put this out as a challenge: Is there no way to make the electron microscope more powerful? From his lecture:" There's Plenty of Room at the Bottom".* This question has, at last, been answered with a resounding yes. This talk will look at the application of these new techniques to understand the structure of multilayer coatings, particularly those deposited using HIPIMS pre-treatment and deposition. Particular attention will be paid to the latest coating developed by the Nanotechnology Centre for PVD Research at Sheffield Hallam University, CrAlYN/CrN which is believed to be able to operate at higher temperatures than any other composition. We report the use of aberration corrected TEM to characterise the as-deposited structure, also with a CrAlYON/CrON topcoat, both deposited onto γ-TiAl. Furthermore, we present a detailed examination of the changes in microstructure with high temperature exposure. In addition, we report on the structure of a C/CrC multilayer coating, which comprised a nanocomposite structure with amorphous carbon embedded in a metastable fcc CrC matrix, both as-deposited and after high temperature exposure.

Development of YSZ Thin Films by Reactive High Power Impulse Magnetron Sputtering

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Yttria-stabilized Zirconia is a conventional material to use for electrolyte manufacturing in the SOFC. Due to its good ionic conductivity, chemical stability and low cost it is of high interest for thin film fuel cells development for operating at low temperatures. In order to meet the requirements needed for high performance of the cell, the electrolyte has to satisfy certain constraints. Dense and crystalline structures are expected to be obtained.

YSZ thin films have been prepared by HIPIMS reactive sputtering from a metal compound target on Si(100) substrates. The deposition conditions were varied in order to better understand the influence of the process parameters on the film properties. The substrate temperature, substrate bias, working pressure, oxygen flow rate and repetition frequency were tuned during the sputtering.

The ionic conductance of the films depends on the crystalline structure and chemical composition. Material analysis was carried out to investigate films properties. Scanning electron microscopy was used for morphology analysis. X-ray diffraction at grazing incidence was used for structural studies. RBS measurements were performed for chemical composition verification. TEM was employed for grain size evaluation.

Interesting features of the crystalline structure development were observed. Phase transformations occurred when varying pressure, bias and temperature were applied during the deposition process.

Although more studies must be carried out, the results presented in this work show that HIPIMS can be used for deposition of oxides with high crystalline properties.

Oxidation Behaviour of Intermetallic Ti-Al-Cr-Y and Ti-Al-Cr-Zr Coatings Deposited on γ-TiAl by UBM and HiPIMS Techniques

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Intermetallic alloys based on γ-TiAl are considered as promising candidates for high temperature applications in automotive and gas turbine engines. However, their oxidation resistance is insufficient at temperature above 800°C. To increase the service temperature the use of protective coatings is a suitable method to improve the oxidation resistance of γ-TiAl components. Metallic and ceramic overlay coatings have been investigated. In the present work, the oxidation protection capability of intermetallic Ti-Al-Cr-based coatings was studied.

Intermetallic Ti-Al-Cr-Y and Ti-Al-Cr-Zr layers were deposited on γ-TiAl specimens using magnetron sputtering techniques. The former coating was manufactured by unbalanced magnetron sputtering (UBM); the latter was produced using a combined technique of high power impulse magnetron sputtering (HIPIMS) and UBM operating simultaneously. Before being coated, the interfaces of the samples were etched in argon plasma or pre-treated in highly ionized Ar^+ and Cr^+ plasma generated by HIPIMS.

The oxidation behaviour of the different coatings was determined at 950 and 1000°C performing cyclic oxidation tests in laboratory air. Mass change data were measured during exposure up to 1000 1-h cycles. Post-oxidation analysis of the coating systems was carried out using scanning electron microscopy and energy-dispersive X-ray spectroscopy. Based on mass gain data and microstructural analyses the protection capability of the different coatings was evaluated and failure mechanisms were discussed. The Ti-Al-Cr-Y coatings provided oxidation protection to the γ-TiAl alloy Ti-45Al-8Nb at 950°C, whereas they failed by oxide spallation when exposed at 1000°C. The HIPIMS Ti-Al-Cr-Zr coatings exhibited excellent oxidation behaviour at 1000°C associated with the formation of a protective alumina for dwell times exceeding 1000 hrs.

Raman Spectroscopy Investigation of Worn Surface Produced at Ambient and Elevated Temperatures on TiAlCN/VCN Nanostructured Multilayer Coating Deposited by HIPIMS/(HIPIMS+UBM) Technique.

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Nanostructured multilayer coating of TiAlCN/VCN was deposited by the novel HIPIMS/HIPIMS+UBM technology, where HIPIMS was utilized during both the surface pretreatment and deposition step of the process. The coating has shown high adhesion critical load values of Lc=52 N and reduced friction coefficient value to μ=0.47 at 650˚C from μ=0.68 measured at ambient condition, as determined by pin-on-disc experiment conducted at respective temperatures of ambient, 200, 450 and 650˚C. The Raman spectra were collected from inside and surrounding regions of as-generated wear track after each sliding test, in order to study the oxide phase composition formed due to the combined action of isothermal and tribo-oxidation process. For the tests up to 450˚C, broad spectral bands in 150-400 cm^{-1} and 400-750 cm^{-1} range were acquired, which significantly associate with TiAlCN and VCN phases. These bands appeared due to the transition taking place in acoustic and optic modes of phonon vibration of Ti, Al, V, C and N atoms and clearly demonstrate the stability and availability of the original coating material up to 450˚C in dry sliding conditions. In this temperature range, signals from various oxides namely V_2O_5 and TiO_2 formed due to tribo-oxidation process were also identified. At 650˚C however, the bands for TiAlCN and VCN were replaced with individual oxide peaks from the coating material as well as from the substrate thus demonstrating the synergy of both isothermal and tribo-oxidation processes. Using Raman spectroscopy the presence of various Magneli phase structured oxides such as V_2O_5, VO_2, TiO_2, $AlVO_4$ was identified. The role of the Magneli phase oxides in stabilising the wear mechanism thus resulting in low friction coefficient is well documented. Additionally the spectra have also marked the presence of the D and G bands in 1200-1600 cm^{-1} range associated with the presence of carbon base phase in the wear debris at all experimental temperatures, which is believed to further stabilise the friction and the wear behaviour of the TiAlCN/VCN.

First Decade of HIPIMS: Status and Outlook from the Industrial Perspective.

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2010 marks the first decade of HIPIMS, making it interesting to have a look at this technology from the perspective of the industrial users and see how the migration from the labs into the commercial world takes place. HIPIMS technology offers a range of important advantages as compared with the conventional PVD methods. At the root of these advantages lies the inherent ability of the HIPIMS, or high-power impulse sputtering to generate high density plasma with elevated metal ions content. Generating metal plasma is a challenging task and HIPIMS is one of few methods that can manage it without having 'side effects'. Ease of metal ion management during PVD processing dramatically improves coating adhesion, hardness and other properties. Moreover, the HIPIMS technology allows producing films with unique properties, which are difficult or impossible to produce using conventional deposition methods. Experience of Systec , the first company that offered commercial equipment and technology for HIPIMS processing , in the field of practical applications will be reviewed. Known industrial applications of HIPIMS will be also discussed, as well as hopes and challenges that HIPIMS may face on the way ahead.

HIPIMS Power Supply Equipment – Extremely Reduced Arc Energy

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HIPIMS (High Power Impulse Magnetron Sputtering) is a modern technique for PVD (Physical Vapor Deposition). This method has been successfully used in many applications in aerospace, tool coating, medical, microelectronics, optical, photovoltaic and many other industries. One of the biggest challenges for a HIPIMS power supply is the need for arc energy reduction, which improves quality of process parameters and expands possible HIPIMS applications.

Arc discharges and uncontrolled energy related to them are undesirable but unavoidable phenomena in plasma vacuum processes. The energy is stored in power supplies output circuitries as well as in the inductance of the cable connecting the power supply and a chamber. It is essential not only to inhibit as fast as possible the energy flowing from the power supply's output, but also to decrease the amount of energy delivered to the arc from the cable inductance. This energy, in case of target currents in a range of thousands of amperes is significant and can affect the target life and produce unwanted droplets, which can spoil the quality of the coating. The HIPIMS-related bias currents are lower (hundreds of amperes), but are directly connected to the treated surface, so the reduction of arc energy in this case is equally important.

Arc quenching circuits available on the market are usually designed to minimize the arc energy related to the power supply only. It was a huge engineering challenge to develop HIPIMS power supply equipped with special compensating circuitry, which is able to reduce arc energy by retracting 80 - 90% of the energy stored in the lead inductance, depending on cable length and chamber parameters. Huettinger's HIPIMS generator is able to switch off 4kA target current during an arc occurrence in a few tens of microseconds. Substrate (bias) arcs are quenched even faster. This is provided by a patented electronic design of the HIPIMS biasing unit, which combines fast arc quenching with superb substrate voltage stability. As a result strong adhesion of coating to substrate is obtained.

Time-Resolved Investigation of Dual High Power Impulse Magnetron Sputtering System with Closed Magnetic Field During Deposition of Ti-Cu Thin Films

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The ionization degree of magnetron plasma and ion flux to the substrate with deposited film is relatively low at conventional dc magnetron sputtering systems. High Power Impulsed Magnetron Sputtering is a method how to increase ionization degree of sputtered particles and ion flux towards the substrate. These plasma parameters can be beneficial for preparation of some alloys with specific physical, chemical and biological properties. Hence, modified configurations of efficient HiPIMS system have been realized in our laboratories. Dual HiPIMS system with closed magnetic field working in a wide range of frequencies, have been optimized for the deposition of Ti-Cu alloy thin films. Planar magnetrons with opposite magnetic field configuration are employed as sputtering sources. Parallel placed sputtering cathodes are equipped by a Ti and Cu targets and driven at different instant current in pulse to get required film stoichiometry of the films. Low (f = 100 Hz) as well as high (f = 4.65 kHz) repetition frequency with pulse widths Ta = 100 µs were applied. The aim of our work is to produce materials for artificial bone implants, which combine good cellular adhesion of osteoblasts at the surface with distinguished antimicrobial effects. Our actual approach is based on the deposition of Ti-Cu thin films. Titanium is a material with very good natural surface biocompatibility and excellent mechanical strength. Copper serves as a metal with known antimicrobial effects. The release of Cu species from Ti-Cu surface during the post-operative time can provide antibacterial effects and increase adoption of the implant by living tissue.

The main aim of the contribution is a comparative study of different types of magnetron systems. The in-situ diagnostic was done in (i) dc mode, (ii) medium frequency dual pulsed and (iii) dual high power impulse magnetron sputtering systems during the deposition of thin Ti-Cu films. Time-resolved diagnostic of ion flux and measurement of ion energy distribution function is combined with measurement of total energy flux (calorimetric probe). Obtained results are employed together with time-resolved Langmuir probe diagnostic as input parameters for calculation of ion flux contributions of particular species, e.g. neutral particles. The active agents in the discharge are observed by time-resolved optical emission spectroscopy. Thin film properties were investigated, too. Crystallographic phases of deposited thin films are diagnosed by grazing incidence x-ray diffractometry (XRD), chemical composition is measured by x-ray photoelectron spectroscopy (XPS). The combination of these diagnostic methods enables an extensive characterization of the films and also agents responsible for their formation. The work is partially supplemented by overview of bio-expertises (copper release, microbial and cell adhesion) in content with deposited sputtering methods.

Dynamics of HIPIMS Discharges Studied by Time- and Species-Resolved Plasma Imaging and Emission Spectroscopy

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Time-resolved imaging using custom-made optical interference filters was performed to investigate plasma-phase processes in HIPIMS discharges operated with a Cr cathode in Ar and N_2/Ar (1:1) reactive mixtures at pressures ranging from 0.7 to 4 Pa. This allowed us to visualize the transport of sputtered material between the target and the substrate. In addition, time- and space-resolved high-resolution optical emission spectroscopy (OES) was used to characterize the propagation of individual excited species (Cr^0, Cr^{1+}, Ar^0, Ar^{1+}, N_2^0, N_2^{1+}) within the deposition chamber. Dense metal plasma created next to the target expanded towards the chamber in the form of an ion-acoustic solitary wave travelling at speeds ranging from 0.7 to 3.5 km·s^{-1}, depending on the working gas composition and the pressure; It increased with higher N_2 concentrations and with lower pressures. Excited working gas region accompanying the advancing metal plasma wavefront indicated the existence of the working gas shock wave. This study improved our understanding of the discharge dynamics and allows us to estimate the energy impact onto the exposed substrate surface.

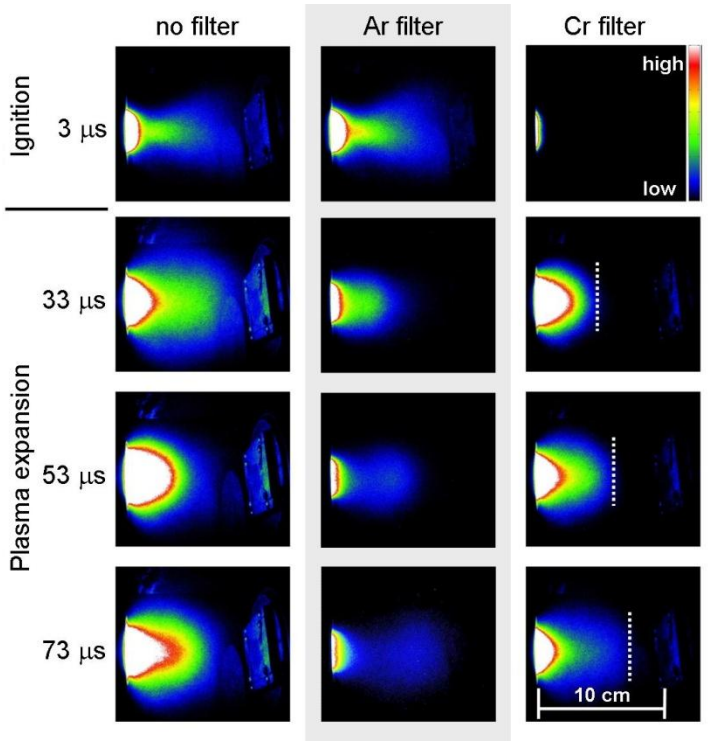

Figure 1: Images taken during 200-μs HIPIMS discharge pulses in pure Ar at 4 Pa with no filter on the camera objective (left column), and with an optical band-pass filter specific for emission from neutral Ar (middle column), and from neutral Cr (right column).

MECHANICAL AND STRUCTURAL PROPERTIES OF HIPIMS$^+$ SPUTTERED TIN FILMS

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TiN films prepared by arc evaporation or DC magnetron sputtering are still widely used in industry as a tool and decorative coatings offering both good adhesion to different substrates, high hardness and a golden-like decorative finish. In addition to that, TiN films have potential as corrosion protective coatings.

The HIPIMS (HIgh Power Impulse Magnetron Sputtering) technology has been known as a process with significantly higher ionization of the sputtered particles in comparison to the conventional DC or pulsed DC sputtering that results in improved film characteristics, such as film structure, surface roughness, mechanical properties and corrosion resistance.

In the present work, TiN films are deposited in an industrial batch coater with closed magnetic field configuration (Hauzer Flexicoat 1000). The deposition is done by two cathodes operated in HIPIMS$^+$ mode. The influence of the pulse shape, deposition temperature and peak plasma current upon the film properties is investigated. Film microstructure and its mechanical properties (hardness, stress, roughness) are studied by means of micro indentation, SEM and XRD. The corrosion resistance of the films is tested in NSS test (neutral salt spray test). The results are compared to those of TiN films deposited by arc evaporation and DC sputtering.

HIGH POWER PULSE MAGNETRON SPUTTERING FOR DIRECTIONAL SPUTTERING APPLICATIONS.

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High power pulse magnetron sputtering is a fairly new technology that was developed in early 1990s. One of the important features of high power pulse magnetron sputtering is the ability to ionize sputtered material atoms in the most simple and cost effective way. Significant effort in terms of hardware (high power pulse plasma generators) design, plasma research of pulsed magnetron discharge and pulsed thin film deposition was exerted during the last 20 years in order to bring this technology to a commercial level. The biggest applications of pulsed I-PVD technology could be directional sputtering processes to deposit metal into different sized high aspect ratio features (trenches, vias and etc.) for integrated circuit fabrication. Recently Through Silicon Vias (TSVs) has emerged as the process of choice of interconnecting stacked and thinned 2-D circuits. Applications for TSV include image sensors, flash, DRAM, processors, FPGA, and power amplifiers. These particular vias have high aspect ratios in the range of 8:1 to 12:1.

In this presentation the experimental data such as the cross-sectional SEM micrographs, voltage pulse shapes, pulse target power densities for directional sputtering of Al, Ti, Si, Cu, Cr in different sizes and aspect ratios trenches and vias will be presented. The experiments were performed with Zpulser SOLO pulse plasma generator that can deliver up to 340 kW during the pulse. Tests were conducted with 10 cm diameter magnetrons, as well as 17cm diameter magnetrons with stationary magnetic arrays. These magnetrons were positioned in an experimental sputtering system. The TSVs process was performed on Axcella ™ series PVD systems manufactured by Tango Systems Inc. The substrates during all these experiments either had floating potential or were connected to the substrate bias power supply. DC power supply or RF power supply were used as a bias power supply. Typical duty cycle of the high power pulse plasma generator (Zpulser SOLO) was in the range of 10% and target power density in the range of approximately 0.5-1 kW/cm^2. The typical RF power level was in the range of 2000-3000 W and substrate voltage bias – 70-100 V. The typical pulse duration was in the range of 1000-3000 µs. The RF bias is an important feature for the directional sputtering process. Since the plasma impedance is different during the pulse and between the pulses the RF power supply was synchronized in the way that RF substrate power was on only during the pulse. The DC bias and RF voltage as a function of RF power at different level of peak power will be presented, as well as the experimental data about field, side and bottom coverage for trenches and vias.

Advanced Control and Monitoring Circuits Create New Possibilities for the HiPIMS Technology

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The developing stage of the new HIPIMS technology is calling for:

- control and monitoring equipment, which offers a good on-line view of the power-supply-related plasma conditions
- power supplies, which can react appropriately to the dynamically changing situation inside the chamber.

Huettinger incorporated powerful DSP, FPGA and fast data acquisition devices into the control circuits of power supplies dedicated for the HIPIMS technology. This opened new opportunities for HIPIMS research as well as industrial HIPIMS applications. It will be now possible to:

- Observe the current and voltage waveforms of the HIPIMS sputtering supply as well as the HIPIMS-dedicated bias supply straight on the same PC computer, which is used to control the device.
- Adjust the impedance matching circuit to get optimal current waveform shape without an oscilloscope and expensive current probes
- Establish application-specific arc detection criteria based on a wide choice of parameters – also the dynamic behavior of voltage and current
- Synchronize the arc detection response of the HIPIMS sputtering supply with that of the bias supply and vice-versa.

Fully digital control and monitoring, together with a fast data acquisition system, will also bring more flexibility into programming the power supply's behaviour and help realize new ideas of the User.

FLEXIBLE CONTROL FOR REACTIVE PULSED MAGNETRON SPUTTER PROCESSES

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In recent times HIPIMS processes find more and more successful application in industrial manufacturing of thin films. As the better film properties are achieved on cost of lower deposition rates, especially for reactive processes which use metallic targets, methods of process control are necessary to run the targets in transition mode, as it is known from MF or DC reactive sputtering. For several years oxygen gas probe sensors have been successfully evaluated as a sensor for driving a PID regulator, which can be used to change the pulse pattern for set point stabilization.

In the present paper a combined method is proposed, which uses optical and electrical signals to stabilize pulsed reactive sputter processes developed within the projects KRONOS and TAYLOR. The corresponding hardware is capable to drive two magnetrons in transition mode by feeding its digital pulse outputs to pulsed power sources. Mixed thin films with predefined contents of different materials can be deposited in transition mode. The proposed control unit contains up to two optical channels of high resolution CCD spectrometers, one for each target, combined with an analogue oxygen probe input, which are connected with up to three PI regulators and a number of pulse pattern generators: for pure HIPIMS, for MF, and for mixed HIPIMS/MF patterns. In the present application the oxygen probe input is used to control the off time, while each of the optical channels are used to control the on time for the correspondent target.

For proper operation the system generates a number of internal sync pulses, which can be used to synchronize each of the optical channels with the HIPIMS pulse of the correspondent target. Data read out of optical data is performed within a few milliseconds with simultaneous data pre-processing. So a total response time of the system of down to 100 milliseconds and even less can be observed.

The proposed method is characterized by very fast signal response and shows a high flexibility for configuration of pulse patterns and of signal flow.

Optical Emission and Mass Spectroscopy Analysis of Aluminium Nitride HiPIMS Discharge

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Plasma parameters of physical vapour deposition techniques greatly influence the growth mechanisms of thin films and their structural and physical properties. Over the past decade, magnetron sputtering technique has been developed to provide a high ionization degree of the sputtered vapour. High power impulse magnetron sputtering (HiPIMS) is such a technique. In HiPIMS, high voltage pulses of 1 kV applied to the cathode with a pulse width from 5 µs to 50 µs and at a repetition rate of 1-2 kHz result in dense and highly ionized plasma. The aim of this work is to better understand the discharge parameters on the plasma properties and to link them to the quality of the coatings. Aluminium target was sputtered in pure argon or in a reactive Ar+N_2 environment to study the versatility of HiPIMS for the growth of AlN films. Mass spectrometry was used to identify the energy distribution of the species during the impulse and in the off-time thanks to time-resolved measurements. These experiments coupled to optical spectroscopy of the plasma allow us to identify the relevant parameters of the discharge.

Production of High-Density Capacitive-Discharge Plasma with Ring-Shaped hollow Cathode for Thin Film Preparation

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In the microelectronic industry, the parallel-plate radio frequency (RF) plasma source operating at 13.56 MHz is widely used [1]. This is because its geometry is very simple. In especial, capacitively coupled plasma (CCP) source is frequently utilized for dry etching, plasma enhanced chemical vapor deposition and sputtering processes. However, there are the following problems; (1) density and energy of ions can be independently not controlled by external parameters such as power for the dry etching and sputtering process and (2) plasma density is less than $10^{9}cm^{-3}$ so that the rates of etching and deposition are very low. This is main problem for RF capacitively coupled plasma. In this work, high-density plasma operated by radio-frequency capacitive discharge has been developed by the combination of hollow cathode discharge using a ring-shaped hollow trench electrode for thin film preparation. A maximum plasma density with a magnitude of $10^{11}cm^{-3}$ was attained at Ar gas pressures of 100- 350 mTorr and a lower input power density of 0.64 W/cm^{2}. As shown in Fig.1, in the case of the hollow electrode, the ring-shaped high-intensity emission is observed, whereas for the case of flat electrode the conventional uniform glow-plasma is viewed at the whole electrode. In order to satisfy the hollow cathode discharge, it was clarified that a trench-width was two times longer than the sheath thickness formed in the trench experimentally. It became clear that the wider trench-width produced easily the hollow cathode discharge under lower pressure conditions. It was found that the plasma density radiated from the hollow trench depended strongly on the hollow trench size and/or the electron-neutral mean free path. In the conference, experimental data on radial profile of plasma density will be introduced in detail.

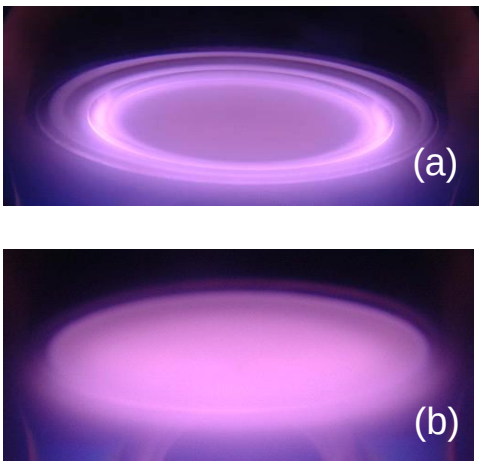

Fig.1 (a) Typical images of plasma structure for (a) the hollow and (b) the flat electrode.

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Investigations on Tailoring the Deposition Conditions in HiPIMS by Varying the Pulse Durations and the Argon Partial Pressure

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In most cases HIPIMS is used to gain the highest possible ionisation of the deposition particles, which is realised by pulse durations with short on- and very long off-times. These conditions are combined with a more or less pronounced decrease in deposition rate.

In this work the pulse durations were varied. A three dimensional matrix of parameters was spanned, made of 3 on- and 3 off-times at 4 argon partial pressures. The average power was kept constant and the data gained were additionally compared to DC-Magnetron sputtering.

The experiments were carried out using 50 mm diameter targets made of Ti and a MELEC SPIK1000A pulser unit. The deposition rate was measured by quartz microbalance in two different positions in front of the target. Peak current density, target voltage and substrate current were recorded and time averaged optical emission spectroscopy (OES) measurements provided information about the ionisation conditions in the plasma.

The results of the data evaluation provide a coherent overview of the impact of the HIPIMS parameters as well as of their complex interrelations.

Time-Resolved Diagnostics of High Power Impulse Magnetron Sputtering System During Deposition of Titania Thin Films

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The deposition of TiOx thin films by sputtering systems are of a great interest in the last decades. During the last ten years the High Power Impulse Magnetron Sputtering (HiPIMS) systems have been widely used for preparation of metallic and dielectric thin films. Due to high ionization degree of sputtered particles the HiPIMS is able to produce thin films with better adhesion, density and structure.

In this work, we focused our research on characterization of plasma parameters during deposition of titania thin films. Namely, the time resolved Langmuir probe technique has been used to measure the plasma parameters such as electron mean energy, plasma density, plasma and 'floating' potential. Further, we have used time resolved optical emission spectroscopy to observe temporal behavior of selected emission lines of titanium and titania neutrals, ions and argon atoms as well. The time resolved ion flux on the substrate has been investigated by means of planar ion flux probe with applied 50 kHz pulsed dc bias of different magnitudes. All the experiments have been carried out in the HiPIMS device equipped with 2” in diameter titanium target operated in balanced mode. The measurements have been done for different working gas pressures in range from 2 mTorr to 150 mTorr. The ratio of Ar/O2 mixture was kept at 4:1 and influence of working gas pressure and mean discharge current has been investigated. The repetition frequency of cathode voltage modulation was always 50 Hz and length of active part of the modulation cycle was 100 µs. The peak discharge current reached 90 A. The influence of measured plasma parameters on the total ion flux at substrate and mutual comparison of measured temporally resolved plasma parameters with time resolved emission lines and time resolved ion flux at substrate will be discussed. Furthermore, possible correlation between titania thin film properties and plasma parameters will be discussed.

Investigation of HiPIMS Sputtering Systems Used for the Deposition of TiO_2 and TiO_2:N Thin Films

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Modified Pulsed planar magnetron system working in the low frequency HIPIMS mode and simultaneously with auxiliary MF frequency power was used as a plasma source for the deposition of TiO_2 and TiO_2:N thin films on different types of substrates. The diameter of the titanium target was 50 mm. Ar, O_2 and N_2 were used as working gas mixture. A glass coated by ITO or ZnO:Al were used as substrates for the deposition experiments. The low frequency HIPIMS mode used repetition frequency 50 Hz and the active part of the modulation cycle has 100 μs. Maximum current in the pulse was 50 A. MF frequency bipolar pulsed power with frequency 300 kHz was applied on the magnetron cathode in parallel with high power pulsed source. In this modified sputtering system, ion flux and heating flux on the substrate were measured. For this reason, AC voltage with the magnitude in the range from several tens of volts up to 150 V with frequency in the range from 50kHz up to 1 MHz was applied on the substrate. In addition, the measurement by time resolved Langmuir probe at the position of the substrate was used as well. Emission spectroscopy was used in order to investigate relative amount of sputtered Ti and Ti^+ atoms in the system. Deposited films were analyzed by XRD in order to get information about crystalline structure. Chemical composition was measured by XPS. Surface morphology was investigated by AFM. Photoelectrochemical properties were measured in electrochemical cell in order to get information about induced photocurrent efficiency of the deposited films

Influence of Plasma Conditions on Self-Assembling of Carbon Nanotubes at Plasma Enhanced Chemical Vapour Deposition of DLC films

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Developing of technology to produce a new composite material comprising carbon nanotubes (CNT) self-assembled in a diamond-like carbon (DLC) matrix is in great interest, since some obstacles delay wide-scale application of CNTs. The opportunity to synthesize a composite material incorporating CNTs or other nano particles may be at the heart of overcoming the mentioned obstacles. Correct technological conditions facilitated the incorporation of CNTs within a DLC film matrix, which takes place spontaneously at the plasma chemical deposition process. We propose an approach whereby CNT and other nanostructures may be formed using a relatively simple and cost-effective technique of plasma-chemical deposition. The approach has a great potential as it enhances the conventional magnetron sputtering technology with an additional ion source, which offers a high flexibility in materials microstructure design. The equipment has a fully computerized control for supplying additional agents (dopants) within the plasma thus allowing high experimental precision, which is crucial for nanostructures formation.

Investigation of peculiarities of nucleation and growth in self-assembled composite materials will reveal the processes taking place during film-formation. The influence of external technological parameters on the film characteristics to ensure an understanding and appropriate control of the film growth process has been considered. Both the sustained analysis and comparison of various experimental data are crucial for the successful implementation of the technology. It will provide information on density and size of CNTs. Multiplicity of various nanostructures, their possible arrangement, and peculiarities of processes taking place on the nanostructure-matrix interface - all this cumulatively gives opportunities for sequential experimentation having as its object the further development of advanced technology. The real-time computerized control of plasma conditions by means of recording the plasma emission allows flexible adjustment of the plasma conditions and other parameters responsible for a great diversity of coating properties and microstructures. Mentioned technology allows obtaining the DLC matrix with incorporated CNTs served as additional conducting channels without significant deterioration of mechanical and optical properties of coatings.

Studies of TiN Films Deposited by HIPIMS at Different Substrate Temperatures and Substrate Bias

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Titanium nitride films (TiN) are widely used as wear-protective coatings, diffusion barriers and decorative coatings in various applications. The high degree of ionization in the High Power Impulse Magnetron Sputtering (HIPIMS) process makes it possible to vary the energy of the ions bombarding the film by changing the substrate bias. Another way of altering the energy delivered to the film, and subsequently the ad-atom mobility, is to change the substrate temperature. The aim of this work is to study the influence of the delivered excess surface energy (temperature or ion energy)on the film properties and film growth. We will compare film adhesion, roughness and microstructure of TiN coatings deposited by HIPIMS at different substrate temperatures and bias. The substrate temperature T varied between 25ºC < T < 600 ºC and the bias V_b varied between 0 < V_b < -100 V. The influence of these parameters on the measured film properties will be illustrated and discussed.

Retarding Field Analysis of the Time Averaged and Time Resolved Ion Energy Distribution at a Pulsed Surface, Applicable to HiPIMS Research.

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Retarding field energy analyzers (RFEAs) are commonly used to measure the ion energy distribution function (IEDF) at grounded and driven electrodes in plasma reactors. At the grounded surface the RFEA operation is easier to implement due to the absence of large voltages. At the driven electrode the RFEA design is more complex. Filtering techniques are used to ensure the entire RFEA floats at the electrode bias potential. If the discharge, or the substrate electrode, is driven with a pulsed signal the time resolved IEDFs through the pulse cycle are 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 made 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 to enable the RFEA float at the bias potential removes the possibility to make time resolved measurements during the period of the applied bias waveform.

Here, we present time averaged and time resolved IEDF measurements at a pulsed electrode in a plasma discharge. The RFEA body is allowed to float at the bias potential using low pass filters while a novel technique is implemented to allow time resolution of the IEDF during the bias period. Time averaged and time resolved IEDFs are presented for various pulse biased waveforms. We show that the RFEA is capable of measuring electron parameters and plasma potentials and compare the time resolved RFEA measurements to more standard Langmuir probe results.

THERMAL STABILITY AND WEAR OF A C/CRC NANOCOMPOSITE COATING

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Carbon based coatings have attracted considerable interest in a wide range of industries due to their excellent tribological properties. Nanoscale H-free C/Cr coatings have been produced by unbalanced magnetron (UBM) sputtering at PVD centre Sheffield Hallam University [1]. In this work, the rare metastable NaCl f.c.c. structured CrC was identified using X-ray diffraction (XRD) and transmission electron microscopy (TEM) at the deposition condition of Ji/Jn=6 (bias -350V). The coating is a nanocomposite composed of nanoscale C clusters in a CrC crystalline matrix. The nanoscale C clusters segregate to layers, giving the coating a multilayer appearance. In view of the metastable CrC phase, thermal stability of the coating in $Ar+H_2$ atmosphere was assessed using high temperature XRD coupled with detailed cross-section TEM, which shows that the CrC phase survived up to 750°C [2], but decomposed to $Cr_{23}C_6$ at 900°C. Oxidation resistance of the coating is investigated using in-situ Raman spectroscopy by heating up to 600°C. Wear test of the coating against Al_2O_3 ball suggests friction coefficient of 0.1. Worn surfaces have been examined using TEM via focused ion beam to lift out site-specific specimens. The wear mechanisms are therefore discussed.

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TO BETTER UNDERSTAND THE MEASURED HIPIMS TIME DEPENDENCY OF ARGON METASTABLE IN HIPIMS

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High Power Impulse Magnetron Sputtering (HiPIMS) is a recent promising development of magnetron discharges which is characterized by an increased ionisation degree of the metallic vapour and a high ion flux towards the substrate.

The objective of this study is to investigate the neutral gas dynamics during HiPIMS that is known to have a significant effect on the pulse characteristics [1]. The energetic sputtered metal neutrals (Ti) collide with the neutral gas background (Ar) leading to the gas heating. Consequently, its expansion follows (i.e. gas density decrease in front of the target), so called *gas rarefaction*.

Time and space resolved Tunable Diode Laser Absorption Spectroscopy (TD-LAS) [2] measurements of the argon metastable, the triplet state at 93143.76 cm^{-1}, were performed in the dense plasma region (from 1 to 5 cm in front of the target). From the Doppler linewidth (absorption line at 801.506 nm) and from the integrated absorption coefficient, the evolution of the temperature and the density were derived during the pulse as well during the post discharge. Complex temporal (two maxima for some particular plasma conditions) and spatial evolutions of the metastable density were observed.

To better understand the measured HiPIMS time dependency, a kinetic global (zero-dimensional) model was used to characterize the evolution of the species densities in the ionisation region (the dense plasma region). It is based on a set of coupled differential equations for electron density and temperature and for densities of Ar, Ar^+, $Ar^{metastable}$, Ti and Ti^+. The fraction of energy given to the electrons was adjusted such that the calculated ion current (given by Ar^+ and Ti^+ fluxes) on the target was identical with the measured one.

The metastable density evolution measurements will be compared to the model results. The main mechanisms (kinetics and dynamics) involving the metastable during the discharge pulse and postdischarge will be discussed.

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The Influence of Magnetic Field and Pressure on the Shape of HIPIMS Pulse

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The experiments were conducted in laboratory instrument which was equipped by two different magnetic systems with 2” Cr targets driven by HIPIMs Z-pulser power supply. The setup was made in order to find the correlation between magnetic field strength on one side and working pressure range, pulse shape and initialization of the current peak on the other. It was shown that strengthening of the magnetic field of the magnetron substantially widens the working pressure range and at the same time allows achieving higher current densities on the cathode.

Comparative Study of Magnetic Field Effect on HiPIMS, DC and Pulsed DC Magnetron Discharges

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Despite having many advantages High Power Impulse Magnetron Sputtering (HiPIMS) discharges suffer the drawback of having lower deposition rates compared to conventional magnetron sputtering.

The present study is an investigation of dependence of deposition rate on magnetic field strength in HiPIMS, DC and pulsed DC discharges. A deposition rate monitor has been used to measure the deposition rate at three different magnetic field strengths. These three configurations for a variation of magnetic field strength were achieved by moving the permanent magnets of magnetron behind the target. All these measurements were carried out at the typical substrate position (100 mm from the target).

The discharge was operated at an average power of 680 W and an average pressure of 0.54 Pa. For HiPIMS discharge, the pulse width and frequency was 100 µs and 100 Hz respectively and for pulsed DC discharges the frequencies were 100 and 350 kHz with 50% duty factor.

The results show that magnetic field strength plays an important role in determining the deposition rate and have different effect in HiPIMS discharges and DC discharges. In HiPIMS discharge, deposition rate increases with lowering the magnetic field strength (2 times by lowering 33% magnetic field strength at target position), however in DC and pulsed DC discharges, it behaves in opposite way.

These findings together with magnetic field variations will be discussed in this paper.

HiPIMS Deposition of Hf Thin Films with Varying Ar Backpressures

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The highly ionized flux occurring during high power impulse magnetron sputtering, HiPIMS, offers the possibility of manipulating the kinetic energy of incident film material. The target current waveforms have shown a dependence upon the Ar pressure within the deposition chamber. Accordingly, significant changes to hafnium deposition rates have been observed as argon background pressure is changed from 5 to 40 mTorr. Also, SEM images of the thin films have shown changes in crystalline structure over this same range of pressures. Energy resolved mass spectrometer measurements, have been used in conjunction with steady state simulations and optical spectroscopy of the emitting species, to correlate processing parameters to material properties.

Microstructure and Properties of CrN / AlSiN Nanoscale Multilayers Deposited by UBM and HIPIMS

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CrN / AlSiN nanoscale multilayers with [Cr]/([Cr]+[Al]+[Si]) ratio of ~0.5 were deposited in an industrial scale vacuum system using two different PVD techniques: conventional unbalanced dc magnetron sputtering (UBM) and high power impulse magnetron sputtering (HIPIMS). The deposition was done from four cathodes, two consisting of pure Cr and two of Al with 11at.% Si. In the case of HIPIMS deposition, one Cr-cathode and one AlSi-cathode were used in HIPIMS mode. For each deposition technique two sample series were produced which differed in the bi-layer thickness: one was 1.6 nm and the other ~3 nm.

Rockwell indentation tests and scratch tests showed that the surface pre-treatment with HIPIMS prior coating deposition of all deposition series led to excellent adhesion properties. The phase composition of the single layers was investigated by glancing angle X-ray diffraction (GAXRD) and by high resolution transmission electron microscopy (HRTEM). All coatings were characterised by compressive stress as determined from XRD. Nanoindentation revealed a higher hardness of the multilayers deposited by HIPIMS as compared to the multilayers deposited by UBM. The friction behaviour of the coatings was studied by pin on disc tests in the range of 25°C to 650°C. Thermogravimetry tests in air up to 1200°C revealed the good oxidation behaviour of the coatings.