New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F2-2-ThA

HiPIMS, Pulsed Plasmas and Energetic Deposition II

Moderators: Jon Tomas Gudmundsson, University of Iceland, **Tiberiu Minea**, Université Paris-Sud

2:00pm **F2-2-ThA-3 HiPIMS Deposition of W Thin Films***,* ***Alison Engwall****, S Shin, Y Wang,* Lawrence Livermore National Laboratory, USA

High power impulse magnetron sputtering (HiPIMS) has been shown to deposit W films with desirable physical characteristics including higher strength and uniformity than films deposited with traditional direct current magnetron sputtering (DCMS) under similar processing conditions. In-situ stress measurements paired with ex-situ film characterization and Langmuir probe plasma measurements were used to investigate the fundamental differences between DCMS and HiPIMS film deposition over a range of chamber pressures with and without applied substrate biasing.

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2:20pm **F2-2-ThA-4 Study and Development of Thermochromic VO_2 Thin Films Deposited by HiPIMS***,* ***Jean-Louis Victor****, C Marcel,* CEA Le Ripault, France*; A Rougier,* CNRS, France*; L Sauques,* DGA, France

Vanadium dioxide (VO_2) has attracted a great interest for smart coating applications because of its promising thermochromic properties. Its main characteristic is to transit from a semiconductive state to a metallic state at a phase transition temperature (Tc) of 341 K which is closer to room temperature (300 K) than any other thermochromic material. Nevertheless, the fabrication of high-quality VO_2 films by conventional direct current or radio-frequency Magnetron sputtering (DCMS or RFMS) requires an annealing step over 450°C which limits its compatibility with temperature-sensitive substrates. High power impulse magnetron sputtering (HiPIMS) is a novel sputtering method, developed recently for the deposition of VO_2 films. It is characterized by its high ionization degree of the sputtered species, which allows the control of film microstructure through ion bombardment. Due to this additional energy, the annealing temperature can be reduced for the development of functional VO_2. In this work, we show that HiPIMS supply permits to deposit dense stoichiometric crystalline VO_2 thin films at lower temperature.

2:40pm **F2-2-ThA-5 A Paradigm Shift in Thin Film Growth by Magnetron Sputtering: from Gas-ion to Metal-ion-controlled Irradiation***,* ***Grzegorz Greczynski****,* Department of Physics, Linköping Univ., Sweden*; I Petrov,* University of Illinois, USA, Linköping University, Sweden, USA*; J Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan*; L Hultman,* Department of Physics, Linköping Univ., Sweden **INVITED**

Traditionally, growth of dense refractory thin films by means of dc magnetron sputtering employs gas-ion bombardment to ensure sufficient adatom mobility during deposition at lower temperatures $T_s/T_m < 0.3$ (T_s and T_m: growth and melting temperature in K). This approach often results in significant concentrations of trapped inert gas atoms with accompanying high film stresses leading to cohesive failure and film/substrate delamination. A possible remedy is offered by metal-ion-synchronized bias durings high-power pulsed magnetron sputtering (HIPIMS). The inherent separation of metal- and gas-ion fluxes that stems from gas rarefaction, provides the ability to separate, in both time and energy domains, metal ions and gas ions incident at the substrate. In this approach, a substrate bias potential is synchronized with the metal-ion-rich portion of the HIPIMS pulse. Metal-ions, as opposed to noble-gas ions, are primarily incorporated at lattice sites. This, together with dramatically-reduced concentrations of trapped gas ions, results in lower compressive stresses. Moreover, the metal-ion mass, incident flux, and impact energy can be independently controlled to optimize momentum transfer and provide the recoil density and energy necessary to eliminate film porosity at low deposition temperatures. This novel approach expands the PVD process envelope to allow the use of temperature-sensitive substrates as well as synthesis of supersaturated alloys.

In the first part of the talk, results of time-resolved ion mass spectrometry analyses performed at the substrate plane during HIPIMS sputtering of TM targets in Ar and Ar/N_2 atmospheres are reviewed. Detailed knowledge of the time evolution of metal- and gas-ion fluxes incident at the growing film surface is essential for precise choice of synchronous bias pulse, and, hence, control over the incident metal-ion energy, while minimizing the role of gas-ion irradiation. In the second part of the talk, several examples of metal-ion-synchronized HIPIMS will be discussed including the growth of (i) nanostructured N-doped *bcc*-$CrN_{0.05}$ films possessing atomically-smooth surfaces with unique properties which are characteristic of both metals (*bcc*-Cr crystal structure, electrical resistivity, and toughness) *and* ceramics (high hardness); (ii) fully-dense, hard, and stress-free $Ti_{0.39}Al_{0.61}N$; (iii) single-phase cubic $Ti_{1-x}Si_xN$ with record-high SiN concentrations; (iv) single-phase NaCl-structure $V_{1-x}Al_xN$ layers with unprecedented AlN supersaturation; and (v) dense and hard dilute $Ti_{0.92}Ta_{0.08}N$ alloys deposited with no external heating ($T_s/T_m < 0.15$) .

3:20pm **F2-2-ThA-7 In Vitro and In Vivo Biocompatibility Evaluation of Zr-Ti-Si and Fe-Zr-Nb Thin Film Metallic Glasses***,* ***Ai Ju Chen****, J Wang, Y Yang,* National Taipei University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

Thin film metallic glass (TFMG) has been considered in the biomedical applications due to its better corrosion resistance, which attracts lots of attention from academic and industry. In this study, a co-deposition system consisting of a high power impulse magnetron sputtering (HiPIMS) and a radio frequency (RF) power supply was used to prepare Zr-Ti-Si and Fe-Zr-Nb TFMGs on the surface of 316 L stainless steel specimen.

The chemical composition, microstructure and surface roughness of Zr-Ti-Si, Fe-Zr-Nb TFMGs were analyzed by a FE-EPMA, FE-SEM and AFM respectively. The nanoindentation, scratch test and HRC-DB adhesion test were employed to evaluate the mechanical and adhesion properties of TFMGs. The corrosion resistance of TFMGs in 3.5 wt. % NaCl aqueous solution was conducted by a potentiodynamic polarization test. The MG-63 cell line (human osteosarcoma) was used to investigate the biocompatibility of coatings. Finally, the animal tests were executed to examine any allergy, poisoning or carcinogenic reaction was brought by the TFMGs to the rats.

Through the in-vitro cell test and in-vivo animal tests, both Zr-Ti-Si and Fe-Zr-Nb TFMGs exhibited better biocompatibility because of their good corrosion resistance, good hydrophilic properties and improved adhesion on the 316L surface. We can conclude that Zr-Ti-Si and Fe-Zr-Nb TFMGs have very excellent potential application in the biomedical field.

3:40pm **F2-2-ThA-8 Microstructural and Tribological Properties of Sputtered AlCrSiWN Films Deposited with Segmented Powder Metallurgic Target Materials***, W Tillmann,* ***Alexander Fehr****, D Stangier,* TU Dortmund University, Germany

When synthesizing magnetron sputtered films with a complex stoichiometry, integrating the desired coating constituents in one target material is favorable to avoid a nanolaminar film depositions and to enable a homogenous film growth. In contrast to alloyed targets, segmented plug targets allow to merge elements with different physical properties in one target material. Two targets, amalgamating 20 and 48 hot-pressed 80Cr5Si15W (wt. %) plugs, respectively, into a monolithic aluminum target were fabricated and employed in a direct current magnetron sputtering process to deposit AlCrSiWN films on high-speed steel (AISI M3:2, 1.3344). Furthermore, an AlCrSiN film, which served as a reference, was deposited using Cr, Si, and AlCr24 targets. The cathode powers for the Al(CrSiW)20 and Al(CrSiW)48 targets were varied between 3 and 7 kW to analyze how differently composed targets and various cathode powers affect the microstructure and tribological properties of the sputtered films.

The results revealed that the chemical composition as well as the thickness of the films are strongly dependent on the target setup. For all AlCrSiWN films, the Cr and Al contents predominated (19–29 at%), while the Si and W contents varied between 2–3 at. %. This indicates that chromium is preferentially sputtered from the alloyed CrSiW plugs. The film, which was deposited by applying 7 kW to the Al(CrSiW)20 and 3 kW to the Al(CrSiW)48 targets had the highest hardness (27.66 ± 1.87 GPa due to a dense coating growth and a finer crystalline structure. All AlCrSiWN films had a preferred (111)–(CrN/WN) orientation, which exhibited a finer crystalline growth with an increasing cathode power. Analyses of the tribological behavior of the AlCrSiWN films further revealed a significantly lower friction coefficient ($\leq 0.4 \pm 0.04 \cdot 10^{-5}$ mm³/Nm) when sliding against Al_2O_3 balls when compared to the AlCrSiN reference system.

4:00pm **F2-2-ThA-9 Linking an Atmospheric-pressured Arc Reactor to a Magnetron Sputter Device to Synthesize Novel Nanostructured Thin Films***, W Tillmann, **David Kokalj**, D Stangier,* TU Dortmund University, Germany*; Q Fu, E Kruis,* University of Duisburg-Essen, Germany

Due to their properties, nanocomposite coatings offer outstanding advantages compared to single-phase coatings. However, the choice of materials to produce such nanocomposite coatings is severely limited. Basically, there are only three mechanisms that lead to the formation of nanocomposite structures. One possibility is the use of two metals which, in certain compositions, reveal a miscibility gap and form mixed crystals with different structures. Alternatively, metals with strongly different nitrogen affinities also form the desired nanocomposite structure. The third mechanism is based on the use of a nitride-forming transition metal, which is nanocrystalline embedded in an amorphous matrix.

To allow an unrestricted combination of materials, the approach in this project is a decentralized production of nanoparticles and the thin film, whereby the films growth of both phases is combined on the substrate material. For this attempt, an atmospheric pressured arc reactor is used to generate the TiN nanoparticles with mean primary particle sizes of 7 nm to 20 nm agglomerated to clusters of about 120 nm. To inject these nanoparticles in-situ into the vacuum PVD process, an aerodynamic lens is utilized. The purpose of the aerodynamic lens is to separate the process gas from the nanoparticles to only introduce the nanoparticles into the PVD process. Thus, depending on the coating materials used, nanostructured thin films of type nc-MeN / nc-MeN or nc-MeN / nc-Me can be produced in addition to already existing systems, such as nc-MeN/a-nitride and nc-MeC/a-C, synthesized by conventional PVD processes. Within this context, the metal (Me) can also be nitrogen-affine in the new approach.

In this project, TiN nanoparticles are employed and embedded into magnetron sputtered CrN thin films. Initially, the influence of selected PVD deposition parameters, such as the temperature, chamber pressure, and bias voltage, is examined on the morphology and crystallite size of the TiN nanoparticles. Additionally, the influence on the particle distribution on the substrate is discussed. The nanoparticles were successfully deposited on silicon wafer and it was found out that the particle distribution is affected more by the deposition parameters than the particle properties mentioned. This enables the production of nanostructured PVD thin films by means of external nanoparticle injection without the particle properties being subsequently influenced by the deposition parameters during the coating process.

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