Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP2-1-ThM

HiPIMS, Pulsed Plasmas and Energetic Deposition I

Moderators: Martin Rudolph, Leibniz Inst. of Surface Eng. (IOM), Germany, **Tetsuhide Shimizu**, Tokyo Metropolitan University, Japan

9:00am **PP2-1-ThM-4 Metal-Ion Synchronized HiPIMS of AlN and AlScN for Piezoelectric Applications***, J. Patidar,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; S. Bette,* aixACCT systems GmbH, Aachen, Germany*; O. Pshyk,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; R. Kessels,* aixACCT Systems GmbH, Aachen, Germany*; **Sebastian Siol (sebastian.siol@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Ionized physical vapor deposition (PVD) techniques, such as High Power Impulse Magnetron Sputtering (HiPIMS), offer unique opportunities to control the microstructure of thin film materials by accelerating ions onto the growing film using substrate-bias potentials. At moderate acceleration potentials, the increase in ad-atom mobility often leads to improved crystalline quality and texture. This, in turn, enables the deposition of high-quality thin films at low deposition temperatures. However, gas-ion incorporation can limit the feasibility of such synthesis approaches for defect-sensitive materials. In recent years, HiPIMS processes with a synchronized pulsed substrate bias have been developed with the goal to selectively manipulate the kinetic energy and momentum transfer of the film-forming species, particularly the metal ions. These processes hold remarkable potential to significantly reduce the defect concentration and stress in HiPIMS-deposited films, potentially unlocking a host of new applications for the technique.

In this presentation, I will showcase our latest work on the development of reactive metal-ion synchronized HiPIMS processes for the growth of piezoelectric AlN and AlScN thin films. It will be shown how highly textured, c-axis oriented AlN and AlScN films can be grown using reactive metal-ion synchronized HiPIMS. Here, even unconventionally moderate substrate bias potentials of up to only -30 V already lead to significant improvements in the films' properties. Most strikingly, the application of a substrate bias facilitates the deposition at oblique deposition angles and on structured substrates, while also significantly reducing the fraction of undesirable misoriented grains. A detailed characterization of the piezoelectric coefficients of the materials show values comparable to the current state-of-the-art. In addition, for AlScN in particular, the phase formation and stress state can be tailored by applying different biasing schemes and combinations of different sputter modes (i.e., HiPIMS or DCMS, or hybrid). Importantly, it will be shown that the applicability of these types of processes can be significantly extended, even on insulating substrate materials.

The goal of this presentation is to demonstrate the tremendous potential of synchronized HiPIMS processes for the deposition of defect-sensitive materials, especially in applications where tailoring microstructure and texture of the thin film materials is important.

9:40am **PP2-1-ThM-6 Optimization of Deposition Parameters of Titanium Oxide Films by Taguchi Method***, **Shih-Yang Hsu (pupuyang0120@gmail.com)**,* Department of Materials and Mineral Resources Engineering, Institute of Materials Science and Engineering, National Taipei University of Technology, Taipei, Taiwan*; B. Lou,* Chemistry Division, Center for General Education, Chang Gung University, Taoyuan, Taiwan*; J. Lee,* Department of Materials Engineering, Ming Chi University of Technology, New Taipei, Taiwan*; Y. Yang,* Department of Materials and Mineral Resources Engineering, Institute of Materials Science and Engineering, National Taipei University of Technology, Taipei, Taiwan

Titanium dioxide thin film exhibits excellent photocatalyst effect, antibacterial ability, and optical performance, which makes it widely studied and applied in related applications. Due to its antibacterial and transparent performance, the TiO_2 film can be deposited on touch screens and touch panels to prevent the infection of microorganisms. This work used a superimposed high power impulse magnetron sputtering and mid-frequency (HiPIMS-MF) sputtering system to deposit TiO_2 films on 304 and 420 stainless steel, silicon wafers, and glass slide substrates. Through the Taguchi method, nine batches of TiO_2 thin films were grown under different deposition processing parameters, including the HiPIMS frequency, HiPIMS duty cycle, working pressure, and substrate bias. The cross-sectional morphology of the film was observed with a field emission scanning electron microscope. the phase structure of the film was analyzed with an X-ray diffraction analyzer, and the hardness and adhesion of thin films were measured with a nanoindentation instrument and a scratch tester. The antibacterial and transmittance properties of TiO_2 thin films were examined. The Taguchi method was employed to investigate the optimal deposition conditions using signal-to-noise ratio and analysis of variance (ANOVA), discussing and optimizing the impact of process parameters on the antibacterial and transmittance properties of TiO_2 thin films.

10:20am **PP2-1-ThM-8 Phase Transformation of Boron Carbon Nitride Coatings Deposited by High-Power Impulse Magnetron Sputtering***, H. Nagakura, H. Komiya,* Tokyo Metropolitan University, Japan*; Y. Touta,* Tokyo Metropolitan Industrial Technology Research Institute, Japan*; I. Fernandez,* Nano4Energy, Spain*; R. Boyd, U. Helmersson, D. Lundin,* Linköping University, Sweden*; **Tetsuhide Shimizu (simizu-tetuhide@tmu.ac.jp)**,* Tokyo Metropolitan University, Japan

To realize the growth of cubic boron nitride (c-BN) towards a full-scale industrial application of this coating materials, this work has been aimed to understand the discharge physics and growth kinetics in reactive high-power impulse magnetron sputtering (HiPIMS) of B_4C target in Ar/N_2 gas mixtures. One of the most significant challenges to industrialize the c-BN coating is the significant degradation of film adhesion due to the high residual stresses during the cubic phase formation. While the key to nucleate c-BN phase is a formation of “nano-arches” by ion bombardment on turbostratic BN phase (t-BN), the bombardment by the gas ions, such as Ar^+ ions, leads the entrapment of the gas atoms into the crystal lattice, causing the increase in residual stress. On the other hand, time-transient discharge of HiPIMS makes the time separation of ion arrivals to the substrate and it enables the tuning of incident ions and the independent control of its kinetic energy by the use of synchronized pulsed substrate biasing technology. This would realize the selective ion bombardment of film forming species, expecting to result in efficient momentum transfer without introducing film stresses through the rare gas incorporation. In addition, this great feature of HiPIMS discharge allows us to systematically isolate the influencing factors and will dramatically advance the understanding of nucleation physics of c-BN. In this study, the impact of ion acceleration schemes, including DC bias, synchronized pulsed bias and bipolar pulse configurations and its process parameters, such as the pulse duration, delay time and the substrate bias potential are thoroughly investigated, based on the mass-spectroscopy study of reactive HiPIMS discharge of B_4C target in Ar/N_2 gas mixture. In addition to the great importance of bias potential, the obtained results clearly show the effect of the synchronized pulse duration and the time delay on the chemical bonding states of B-C-N films and its mechanical properties, owing to the time domain of accelerated ions during film growth. By focusing on the average momentum transfer per deposited atoms at each biasing conditions, role of mass and flux of incident ions on the formation of c-BN bonding state are discussed.

10:40am **PP2-1-ThM-9 Thick and Smooth Nanostructured Cr Coatings with Enhanced HiPIMS Ionization***, **Ricardo Serra (ricardo.serra@dem.uc.pt)**,* University of Coimbra, Portugal*; S. Adebayo,* University of Coimbra, Nigeria*; J. Oliveira,* university of coimbra, Portugal

In sputtering deposition processes the atomic shadowing effect, originated from the preferential deposition of obliquely incident atoms on higher surface points of any substrate, drives the formation of open columnar anisotropic microstructures, with columns interspersed with voids or underdense regions. The effect increases the surface roughness as the film thickness increases and undermine their performance, also limiting the maximum achievable thickness of films. Energetic ion bombardment during film growth counteracts the atomic shadowing effect by increasing the ad-atoms mobility, promoting subplantation of the impinging species and triggering re-deposition processes. However, film surface bombardment with highly energetic particles forms higher density of defects, disrupting the crystalline structure of the films and adding compressive internal stress.

In a previous work was shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing mechanism is mostly controlled by the ionization degree of the sputtered material. Thus, at high ionization degree, dense and compact films can be deposited without the need of high energy particles bombardment.

Thick chromium films were prepared by DOMS, with different levels of ionization to test and study the influence on the film growth conditions and respective coating properties, like structure and surface morphology. An electrostatic flat probe mounted at the substrate location was used to characterize the saturated current density of positive charges bombarding the substrate during film growth, evaluating the flux of positive ions bombarding the growing film. Film hardness decreases with increase of thickness, however, Young's Modulus values remain close to Cr bulk value. The films have [110] preferential orientation depending on the bombarding conditions.

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11:00am **PP2-1-ThM-10 Implementation of HiPIMS Technology in Different Industrial Sectors***, IVAN FERNANDEZ (IVAN.FERNANDEZ@NANO4ENERGY.EU),* NANO4ENERGY SL, Spain

After 20 years of continuous development by several research groups and companies it is now clear that real industrial breakthroughs for the high-power impulse magnetron sputtering (HiPIMS) technology are happening. HiPIMS is a state-of-the-art tool for applying high demanding metal and ceramic coatings with superior properties for applications such as: metal fabrication process (machining, stamping, molding or other tools), functional decorative, trench filling in semiconductor industry, or tribological (H-free DLC coatings with reduced friction, high hardness and enhanced thermal stability). Despite the great perspective and the positive forecasts for HiPIMS-technology since its' discovery in 1999, it has taken more than 15 years for the real industrial breakthrough to start. For example, the deposition rate of HiPIMS is still considered to be rather low compared with conventional magnetron sputtering and even more so when compared to cathodic arc-deposition. Another issue is the complexity of use due to the large number of adjustable process parameters. It is not only the HiPIMS power supply, which itself has more controllable parameters than any traditional power supply, what contributes to this great deposition technology. It is also the process regulation (monitoring), the magnetron system (magnetic configurations), the gas flow, the pumping speed, etc.

Apart from the traditional use of HiPIMS which is being currently implemented by the industry, it has been recently demonstrated that the application of a positive voltage reversal pulse adjacent to the negative sputtering pulse (Bipolar HiPIMS) gives rise to the generation of high fluxes of energetic ions. This solution allows unprecedented benefits for the coating industry, such as the energetic deposition onto insulating or grounded substrates, improved coverage on 3D parts or components, or even substrate etching. Also, Dual Magnetron HiPIMS operation is implemented more often in combination with multiple magnetron sources for the large production of high-end decorative coatings. A few examples of implementation of HiPIMS technology in industrial systems as well as the experimental results obtained in different configurations will be presented in this talk.

11:20am **PP2-1-ThM-11 Impact of Energetic Film-Forming Particles in Ion Beam Sputter Deposition of Epitaxial Ga_2O_3 Thin Films***, Dmitry Kalanov (dmitry.kalanov@iom-leipzig.de), Y. Unutulmazsoy, J. Gerlach, A. Lotnyk, J. Bauer, A. Anders, C. Bundesmann,* Leibniz Institute of Surface Engineering (IOM), Germany

Ion beam sputter deposition (IBSD) is an energetic deposition technique, which provides intrinsic heating and kinetic assistance to the growing film by energetic particles arriving at the substrate surface, which affect various thin film properties such as density, microstructure, and forming phase. In IBSD, the kinetic energy distributions of film-forming particles can be controlled by changing process parameters, including the sputtering geometry, the flux, and the energy of primary ions. This is especially important for the growth of epitaxial thin films since it is necessary to find the optimal energetic assistance while minimizing the damage to the crystal lattice.

In this study, reactive IBSD is used for deposition of epitaxial Ga_2O_3 thin films on Al_2O_3(0001) substrates.The influence of process parameters such as substrate temperature, kinetic ion energy, ion beam current, sputtering geometry, oxygen pressure, and deposition time on the properties of the epitaxial films is investigated. The kinetic energy distributions of ions in the film-forming flux are measured by using a combined mass and energy analyzer and the resulting films are characterized regarding growth rate, roughness, crystalline structure, and microstructure. The impact of energetic bombardment by film-forming particles on the thin film structure is analyzed, and a significant change in crystalline quality is observed above the threshold in the average energy of film-forming particles (around 40 eV for the sputtered Ga^+ ions).

11:40am **PP2-1-ThM-12 Quantification of the Negative Oxygen Ion Yield***, Diederik Depla (diederik.depla@ugent.be),* Ghent University, Belgium

Many thin film applications are based on oxides. The optimization of the oxide properties is an on-going process and requires a deep understanding of the deposition process. A typical feature of reactive (magnetron) sputter deposition is the presence of negative oxygen ions. The presence of negative ions in gas discharges was already postulated in the very first paper on sputtering by Grove.

In a magnetron oxygen containing discharge, two groups of ions can be identified based on their energy. Low energy ions are generated in the bulk of the discharge. The high energy ions are emitted from the oxide or oxidized target surface. As these ions are generated at the cathode, they are accelerated by the electrical field towards the growing film. Depending on the discharge voltage and the powering method, their energy is typically several tenths to hundreds electron volt. As such the ions can have a strong impact on the film properties. Nevertheless, despite the many illustrative studies on the impact of negative oxygen ions, quantification is often lacking as the negative ion yield is only known for a few oxides. A compilation of several literature sources permits not only the prediction of the negative ion yield, but also a comparison amongst different oxides.

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