Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-1

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

10:00am **B1-1-1 Tunable Low Energy Ion Bombardment and its Influence on AlN Thin Films Deposited in Confocal DC Magnetron Sputtering**, ***Mathis Trant,*** *M Fischer, K Thorwarth, J Patscheider, H Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Many thin film properties are strongly influenced by ion bombardment during the deposition. Control of the ion flux and the understanding of its influence on the growth mechanism are crucial for tailoring thin film characteristics such as residual stress and growth morphology. In this work the effect of the magnetic configuration on plasma parameters are studied along with the impact on aluminum nitride thin film growth.

An electromagnetic coil is used to generate an additional tunable magnetic field in order to alter the plasma confinement. Electrical and calorimetric probes are used to measure the plasma parameters in the vicinity of the substrate. The setup allows varying the ion-to-neutral ratio by more than one order of magnitude. This holds for the closed field as well as the open field configurations. Because of its symmetric geometry the latter provides roughly double the ion current density when averaged over the entire sample holder.

The effect of varied ion bombardment and substrate temperature are compared for aluminum nitride thin films, taking into account plasma heating. The residual stress was found to depend only on the ion flux density and could be varied from tensile (+0.9GPa) to compressive (- 4 GPa) by increasing this parameter. This goes along with a change from columnar structure towards more dense films. The films showed a preferential (002) orientation for the entire range of parameters covered in this work.

10:20am **B1-1-2 Unprecedented Al Supersaturation in Single-phase Rock Salt Structure VAlN Films by Al^+ Subplantation**, ***Grzegorz Greczynski,*** Linköping University, (IFM), Sweden; *S Mraz, M Hans,* Aachen University, Germany; *D Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden; *J Lu, L Hultman,* Linköping University, (IFM), Sweden; *J Schneider,* Aachen University, Germany

Conventional design approaches for transition metal nitride coatings with improved thermal and chemical stability are based on alloying with Al. The solubility of Al in NaCl-structure transition metal nitrides is, however, limited which presents a great challenge to increase Al concentration substantially, while avoiding precipitation of thermodynamically-favored wurtzite-AlN phase (w-AlN), detrimental to mechanical properties.

Here, we use VAlN as a model system to demonstrate a new concept for the synthesis of a metastable single-phase NaCl-structure thin films with Al content far beyond solubility limits obtained with conventional plasma processes. This is achieved by separating the film-forming species in time and energy domains through synchronization of the pulsed substrate bias with intense periodic fluxes of energetic Al^+ metal ions during reactive hybrid high power impulse magnetron sputtering (HIPIMS) of Al target and direct current magnetron sputtering of V target in Ar/N_2 gas mixture. 70-µs-long bias pulses with an amplitude of -300 V are applied synchronously with the Al^+-rich portion of HIPIMS discharge, to increase implantation depth of ionized Al. At all other times the substrate is floating at -10 V, which suppresses ion mixing due to gas ion bombardment and leads to VN-rich surface even for the case where time-averaged Al flux significantly exceeds that of V. Thus, single-phase cubic VN crystallites dominate the surface and provide a template for subplanted Al^+ metal ions to crystallize in the metastable NaCl structure rather than to nucleate second phase w-AlN. We show that Al subplantation enables an unprecedented 42% increase in metastable Al solubility limit in $V_{1-x}Al_xN$, from x = 0.52 obtained with conventional method to 0.75. High Al-content cubic VAlN films grown by the Al^+-subplantation technique exhibit fully-dense nanostructure and excellent mechanical properties with hardness in the range of 28-30 GPa for Al fractions on the cation lattice as high as 84%. The elastic modulus is with 325±5 GPa in excellent agreement with density functional theory calculations, and approximately 50% larger than for VAlN films grown with dc magnetron sputtering. This substantial improvement with respect to the conventional techniques opens the way for synthesis of supersaturated single-phase alloy thin films combining excellent mechanical properties with high oxidation resistance. Extensions of the presented method to other materials systems are expected to be straightforward.

10:40am **B1-1-3 Ion Beam Designed Thin-film Metasurfaces**, ***Carsten Ronning,*** Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Germany **INVITED**

Metamaterials and metasurfaces enable unprecedented flexibility in manipulating electro-magnetic waves. The optical response of most metamaterials is static, modified only by adjusting the geometric parameters of the constituent building blocks. Many functionalities of metamaterials and metasurfaces may be greatly enhanced by hybridizing these materials with functional matter, like phase-change materials, where the dielectric properties can be controlled in real-time by an external stimulus such as an applied electric field, light, mechanical stress or temperature.

We demonstrate a new type of temperature-tunable metasurfaces based on ultra-thin films of phase change materials [1]. One of the most widely studied phase change materials is vanadium dioxide (VO_2), which exhibits a reversible insulator to metal transition (IMT) as the temperature is increased above a critical temperature TC ~ 68°C. At high temperatures, VO_2 is in a metallic rutile phase, while the low-temperature insulating state is monoclinic. The transition temperature is very sensitive to structural defects and strain. In thin epitaxial VO_2 films the IMT occurs gradually because of the strain distribution imposed from lattice mismatch with the substrate. Therefore, in the vicinity of the IMT, nanoscale islands of the metallic phase start to nucleate surrounded by insulating VO_2, which then grow and connect in a percolation process. Because of this naturally occurring coexistence of sub-wavelength domains of metallic and insulating phase, VO_2 can already be thought of as a natural disordered metamaterial during its phase transition.

In this contribution, I will demonstrate that phase coexistence can also be artificially introduced in VO_2 by patterned local ion beam irradiation with spatial resolution much smaller than the wavelength of light. The presence of a small amount of structural defects caused by ion irradiation significantly decreases the transition temperature – even below room temperature – of the irradiated regions. Thus, the metal and insulating phase of VO_2 coexist in a regular pattern in the temperature range between the IMT of irradiated and intrinsic VO_2. This results in a metasurface with effective optical properties that can be predicted applying an appropriate effective medium theory. These thin film structures are promising for dynamic polarization control, reconfigurable absorbers and emitters, and the tuning of plasmonic and dielectric resonant nanostructures for adaptive optics applications.

[1] J. Rensberg, et al. "Active Optical Metasurfaces Based on Defect-Engineered Phase-Transition Materials" *Nano Letters* 16, 1050 (2016).

11:20am **B1-1-5 Mechanical and Thermal Behavior of Magnetron Sputtered Zr–Cu and Zr–Hf–Cu Metallic Glasses**, ***Michal Zitek,*** *P Zeman, S Zuzjakova, R Čerstvý, S Haviar, M Kotrlova,* University of West Bohemia, Czech Republic

Metallic alloys are commonly fabricated as crystalline materials by a relatively slow-cooling casting of a melt. Magnetron sputter deposition as a non-equilibrium process with high cooling rates (higher than 10^6 K/s) allows us to prepare metallic alloys also as thin-film materials in an amorphous glassy state. A short-range atomic order, based mainly on icosahedral clusters, in these metastable materials gives rise to their exceptional physical and functional properties compared to their crystalline counterparts.

Recently, we have showed that Zr–Cu thin-film alloys can be prepared as metallic glasses in a very wide composition range (30–65 at.% Cu) by non-reactive magnetron co-sputtering. In the present study, we focus on characterization of their mechanical and thermal behavior in more detail. In addition, we investigate the effect of an incorporation of Hf into the Zr–Cu thin-film metallic glasses on a potential improvement of their behavior. The films were deposited using three unbalanced magnetrons equipped with Zr, Hf and Cu targets in pure argon. The magnetron with the Zr and Hf targets were operated in a dc regime while the Cu magnetron in a high-power impulse regime. The Zr, Hf and Cu contents in the films were controlled by adjusting the dc powers and the average target power in a period, respectively. The films were deposited without an external heating onto rotating substrates. The films were analyzed by X-ray diffraction, energy dispersive X-ray spectroscopy, differential scanning calorimetry, micro- and nanoindentation, scanning electron microscopy and atomic force microscopy.

Mechanical properties of the Zr–Cu thin-film metallic glasses are strongly dependent on the elemental composition. A gradual growth of hardness with increasing Cu content up to 70 at.% correlates well with an evolution of the glass transition temperature and the crystallization temperature. This behavior can be explained by an increasing concentration of icosahedral clusters having the highest atomic packing density. The Zr–Cu films prepared with the Cu content higher than 50 at.% or at a moderate substrate bias exhibit a tendency to be more resistant to the formation of shear bands during indentation. An incorporation of Hf into the Zr–Cu thin-film metallic glasses improves the mechanical properties of the films and the thermal stability of their glassy state. Further experiments are still in progress and will be presented as well.

11:40am **B1-1-6 The Development of Ultrathin Zr-Cu-Ni-Al-N Thin Film Metallic Glass as a Diffusion Barrier for Cu-Si Interconnect***, Joseph Lee,* National Tsing Hua University, Taiwan*; Y Chen,* Metal Industries R&D Centre (MIRDC), Taiwan*; J Duh,* National Tsing Hua University, Taiwan

In this study, a Zr-Cu-Ni-Al-N thin film metallic glass (TFMG) has been developed and applied for the diffusion barrier between copper and silicon. The Si/TFMG/Cu stacked structures with various TFMG thickness have been fabricated. Rapid thermal annealing was conducted at 500, 600, 700 and 800 ^{o}C. The X-ray diffraction analysis was applied to identify the formation of Cu_3Si intermetallic compound. The ESCA depth profile was executed to quantitatively evaluate the degree of Cu-Si inter-diffusion. With the aid of HR-TEM, the microstructure of the TFMG and the whole stack could be observed. Finally, the correlation between microstructure, thermal properties, thickness and barrier performance of the TFMG will be revealed and discussed.

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