Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B4-3-TuM

Properties and Characterization of Hard Coatings and Surfaces III

Moderators: Naureen Ghafoor, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

8:00am **B4-3-TuM-1 Thermal Stability of Nanotwinned Metallic Thin Films (Virtual Presentation)***, **Fan-Yi Ouyang (fyouyang@ess.nthu.edu.tw)**,* National Tsing Hua University, Taiwan **INVITED**

The vertically integrated systems, three-dimensional integrated circuit (3D-IC), are regarded as a solution to the demand of both the trend of miniaturization for electronic devices and the better performance. Metal-to-metal direct bonding technology has been considered as a promising method to connect different chips in 3D-IC packaging. Twinning structure has been regarded as an important strengthening mechanism because of its special properties, including low electrical resistivity, great thermal stability, high strain rate sensitivity, and increased mechanical strength, which is a good candidate for application in electronic application. In this talk, the key deposition parameters to fabricate nanotwinned structure in FCC metallic Ag and Cu thin films by sputtering system is reviewed and we found the substrate bias and deposition temperature are the most critical one. In addition, their corresponding thermal stability are investigated by annealing at 150 to 500 ℃ under ordinary vacuum environment. The results show that the thermal stabilities of the nanotwinned metallic thin films are significantly affected by interlayer and defects in the films. Highly (111) preferred orientation (over 95% surface area) of metallic thin films can be found and they can maintain a columnar structure with high-density nanotwins with twin spacing around 10 nm after annealing at 450 ℃. However, the (200) anisotropic abnormal grain growth can also be found in the highly (111)-oriented nanotwinned metallic thin film after the annealing process at over 250 ℃, and the columnar structures with high-density nanotwins are consumed. The mechanism of abnormal grain growth in highly (111)-oriented nanotwinned metallic thin films will be discussed. This study successfully established the roadmap on the microstructure and properties of nanotwinned metallic thin films for different industrial applications.

8:40am **B4-3-TuM-3 Phase Stability and Mechanical Characteristics of Sputtering (Mo, Hf)N Coatings***, **Shu-Yu Hsu (stuu96753@gmail.com)**, Y. Chang,* National United University, Taiwan*; F. Wu,* Dept. of Materials Science and Engineering, National United University, Taiwan

This work focused on microstructure and mechanical property evolution of (Mo, Hf)N coatings in terms of input power modulation and annealing temperature. The influence of input power and annealing on composition, phase, hardness, modulus, and tribological behavior was discussed. The MoN,HfN, and (Mo, Hf)N films were fabricated through radio frequency reactive magnetron sputtering at a fixed Ar/N_2 inlet gas ratio of 12/8 sccm/sccm. For MoN and HfN films, the input power on Mo and Hf targets were both set at 150W. As for (Mo, Hf)N coatings, the input power modulation was set as 150W and 25 to 200W. The vacuum annealing was performed at 500 and 650^{o}C for 1 hr, followed by the furnace-cooling to room temperature. The structure of MoN film exhibited B1-MoN, γ-Mo_2N, and MoN_2 phases, while the HfN film existed δ-HfN and c-Hf_3N_4 phases. The Hfcontents in(Mo, Hf)N coatings increased linearly from 0 to 12.8 at.% with input power rose. When Hf was below 5.6 at.%, a polycrystalline microstructure with δ-HfN, B1-MoN, β-Mo_2N, γ-Mo_2N and MoN_2 phases were identified. According to nano-indentation, scratch and wear test results, the best combination in mechanical characteristics of (Mo, Hf)N film were observed when input power ratio of Mo/Hf was set as 150/100W. The coating exhibited a highest hardness of 22.5 GPa and presented a least wear damage. The vacuum annealing effect onmultiphase feature and grain recrystallizing was discussed. The dense structure, excellent adhesion and superior tribological behavior of the nitride films owing to multiphase strengthening and solid-solutioning were anticipated.

Keywords: Microstructure; (Mo, Hf)N; Input power; Annealing; tribological behavior

9:00am **B4-3-TuM-4 Evidencing Different Dislocation Types in Magnetron-sputtered Epitaxial TiN Thin Films on MgO***, **Janella Salamania (janella.salamania@liu.se)**, D. Sangiovanni,* Linköping University, IFM, Sweden*; L. Johnson, I. Schramm, K. Calamba,* Sandvik Coromant, Sweden*; T. Hsu,* Linköping University, IFM, Sweden*; B. Bakhit,* Linköping University, IFM, Thin Film Physics Division, Sweden*; R. Boyd, F. Tasnadi, I. Abrikosov, L. Rogström, M. Odén,* Linköping University, IFM, Sweden

Although the growth and microstructure of titanium nitride coatings have been extensively studied, the presence and atomic structures of different dislocation types in TiN films remains overlooked. Here, a series of highly crystalline heteroepitaxial (001)-oriented TiN (B1) films has been grown on high-purity MgO substrates by DC reactive magnetron-sputtering from pure Ti targets at 800°C in a mixed Ar/N_2 atmosphere. Using a combination of high-resolution aberration-corrected scanning transmission electron microscopy (STEM), fast Fourier transform (FFT) filtering, atomic segmentation and localization, we present evidence of different dislocation types, including partials, in as-deposited TiN films. Besides the perfect edge dislocation types, Shockley partials, Frank partials, and Lomer sessile configurations exist. We support our experimental findings by performing classical molecular dynamics (MD) and density functional theory (DFT) calculations of these defect configurations to gain detailed insights about the dislocation core structures and properties. Our results suggest that a variety of dislocations should be considered when interpreting and evaluating the properties of TiN films.

9:20am **B4-3-TuM-5 TiN/$Zr_{0.34}Al_{0.66}$N Multilayer Films: Growth Temperature Dependence on Structure and Mechanical Properties***, **Marcus Lorentzon (marcus.lorentzon@liu.se)**, N. Ghafoor, J. Birch,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

TiN/ZrAlN multilayer are shown to exhibit high hardness and thermal stability when grown as cubic(c)-TiN and high Al containing $Zr_{0.43}Al_{0.57}$N nanocomposite layers with segregated domains of c-ZrN and wurtzite(w)-AlN [1]. We extend these investigations to tune the phase and resulting interface structure of nanocomposite layer as a function of growth temperature and ZrAlN layer thickness.

1µm thick TiN/$Zr_{0.34}Al_{0.66}$N multilayer films were deposited at RT, 200°C, 350°C, 500°C, 800°C and 900°C with equal layer thicknesses of 2-10nm using ion assisted reactive DC magnetron sputtering from elemental Ti and compound $Zr_{0.5}Al_{0.5}$ targets on single crystal MgO(001) and Si(001) substrates with a substrate bias of -30V.

Preliminary analysis shows strong effect of growth temperature on overall texture of the multilayers, driven by change in the morphology of ZrAlN layers and interface structure. Regardless of texture, all multilayers exhibit sharp interfaces, analyzed from appearance of higher order multilayer reflections in X-ray reflectivity profiles. In agreement with previous study [2], $Zr_{0.34}Al_{0.66}$N layers exhibit nanocomposite formation with segregated domains of thermodynamically stable c-ZrN and w-AlN binary compounds. On the other hand, RT grown $Zr_{0.34}Al_{0.66}$N layers exhibit single cubic phase with the lattice match with TiN layers. XRD shows single common peak from the layered structure indicative of TiN/$Zr_{0.34}Al_{0.66}$N superlattice formation. Large residual stress observed in low temperature grown superlattice films also indicates interface coherency strain generated due to superlattice formation. We will present details of superlattice structure at different temperatures and layer thicknesses, as well as stress generations and nanoindentation response of TiN/$Zr_{0.34}Al_{0.66}$N films analyzed by x-ray diffraction, x-ray reflectivity, elastic recoil detection analysis, Rutherford backscattering spectrometry, nanoindentation, and transmission electron microscopy.

[1] K. Yalamanchili, F. Wang, H. Aboulfadl et. al., "Growth and thermal stability of TiN/ZrAlN: Effect of internal interfaces", Acta Mater 121 (2016) 396-406, https://doi.org/10.1016/j.actamat.2016.07.006

[2] N. Ghafoor, I. Petrov, D. Holec, et. al., "Self-structuring in Zr1-xAlxN films as a function of composition and growth temperature, Sci Rep 8, 16327 (2018). https://doi.org/10.1038/s41598-018-34279-w

9:40am **B4-3-TuM-6 Physicochemical Properties of Single Phased Tantalum Nitride Thin Films***, **Aurélie Achille (aurelie.achille@icmcb.cnrs.fr)**, A. Poulon-Quintin, F. Mauvy, D. Michau, S. Fourcade,* CNRS, Univ. Bordeaux, ICMCB, France*; C. Labrugere,* CNRS, Univ. Bordeaux, PLACAMAT, France*; M. Cavarroc,* SAFRAN Paris-Saclay – SAFRAN Tech, France

Stoichiometric Tantalum Nitrides (TaN) exist as a face-centred cubic phase, which is a metastable high temperature phase and as a stable hexagonal phase. Using reactive RF Magnetron Sputtering and reactive High Power

Impulse Magnetron Sputtering (HiPIMS) both phases are obtained with different microstructures. This talk will be focus on the metastable cubic phase. First, the structural and optical properties are presented. Evolution of the electrical conductivity with the temperature will be presented. Using cyclic voltammetry measurements, the electrochemical properties (corrosion current and potential) will be analysed as a function of the operating temperature up to 120°. All the presented results will be discussed based on the microstructure differences (depending on the sputtering method used).

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