Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B4-1-MoM

Properties and Characterization of Hard Coatings and Surfaces I

Moderators: Dr. Naureen Ghafoor, Linköping University, Sweden, **Dr. Marcus Günther**, Robert Bosch GmbH, Germany, **Dr. Fan-Yi Ouyang**, National Tsing Hua University, Taiwan

10:00am **B4-1-MoM-1 Effects of Al and Nd additions and Annealing on Microstructures and Mechanical Properties of CoCrNi Medium Entropy Alloy Films*, YI-LING WU*,** *C. Hsueh,* National Taiwan University, Taiwan

CoCrNi medium entropy alloys have attracted great attention on account of the outstanding strength and ductility. It was reported that the moderate amount of Al addition could enhance the mechanical properties resulting from the solid solution strengthening and the phase change from FCC to BCC. Also, with the negative mixing enthalpies, doping rare earth elements could easily combine with the constituent elements in CoCrNi to form precipitates and result in precipitation hardening. To achieve multiple strengthenings, $(CoCrNi)_{92.7-x}Al_{7.3}Nd_x$ (x = 0, 0.2, 0.5, 1.0, 1.7, 2.6, 3.5) medium entropy alloy films (MEAFs) were fabricated using magnetron co-sputtering deposition by controlling the sputtering power P_{Nd} applied on the Nd target in the present study. With the fixed sputtering deposition time of 40 min, the film thickness was ~1.86 µm for the Nd-free film, and it decreased initially to ~1.65 nm with the increasing P_{Nd} and then increased to ~1.91 nm with the further increase in P_{Nd} which could be explained by the larger atomic radius and atomic weight of Nd. The XRD revealed that the as-deposited MEAFs changed from FCC to a fully amorphous structure with the increasing Nd content. Using nanoindentation, the maximum hardness of 10.15 GPa was obtained at x=0.5, while the minimum hardness of 8.04 GPa was obtained at x=3.5. However, after annealing at 773K for 10 min, both XRD and TEM showed the presence of HCP and L12 phases in the films, and the hardness increased from 10.27 GPa at x=0 to 11.45 GPa at x =3.5. Because of the fast cooling rate during sputtering deposition, precipitates could not readily be formed in the as-deposited Al- and Nd-doped CoCrNi MEAFs which, in turn, would result in limited strengthening. However, post-annealing of the films prompted the formation of dual-phase precipitates to result in multiple strengthenings.

10:20am **B4-1-MoM-2 Microstructures and Mechanical Properties of $(CoCrNi)_{100-x-y}Si_xNd_y$ Medium Entropy Alloy Films*, Hui-Wen Peng*,** *C. Hsueh,* National Taiwan University, Taiwan

A series of $(CoCrNi)_{100-x-y}Si_xNd_y$ medium entropy alloy films (MEAFs) was deposited on p-type (100) silicon substrates by direct current (DC) and radio frequency (RF) magnetron co-sputtering of equiatomic CoCrNi alloy target, $(CoCrNi)_{90}Nd_{10}$ alloy target and Si target. The powers applied on the CoCrNi and Si target were respectively fixed at DC 30 W and RF 20 W, while RF powers from 0 to 450 W were applied on the $(CoCrNi)_{90}Nd_{10}$ target, respectively, to tailor the Nd content. All the films were deposited for 90 min without external substrate bias and heating. The chemical compositions of MEAFs determined by electron probe microanalyzer (EPMA) revealed that the Nd content of the films increased as sputtering power of the $(CoCrNi)_{90}Nd_{10}$ target increased from 0 to 450 W. With the increasing Nd content, a transition from single FCC phase to the coexistence of FCC, HCP CoCrNi and $NdNi_5$ phases was observed in X-ray diffractometer (XRD) and transmission electron microscope (TEM) diffraction patterns. The scanning electron microscope (SEM) and TEM images showed the refined columnar grains due to the Nd addition, and the film thickness increased from 1.09 to 2.60 µm with the increasing Nd content. The hardness (H) and reduced modulus (E_r) were characterized using the nanoindenter. The H showed the initial increase with Nd addition via the solid solution strengthening, reached the maxima at $Si_{0.58}Nd_{5.59}$ film due to the grain refinement and precipitation strengthening. However, the hardness decreased at $Si_{0.58}Nd_{6.06}$ film resulting from the inverse Hall-Petch effect.

10:40am **B4-1-MoM-3 Recent Developments Towards Reliable X-Ray Photoelectron Spectroscopy Analyses of Thin Films*, Grzegorz (Greg) Greczynski*,** *L. Hultman,* Linköping Univ., IFM, Thin Film Physics Div., Sweden **INVITED**

The number of papers in peer-reviewed journals where X-ray photoelectron spectroscopy (XPS) analysis is employed increased by a factor of 40 during last 40 years, to the level of 12000 articles published in 2021 alone. This makes XPS the most common – and for many indispensable - method for characterization of surface chemistry. From a concern within the surface science community that this rapid increase in the number of XPS studies is accompanied by a decrease of work quality,[1] we reviewed efforts towards improving correct use of the technique for reliability of data. Several sources of errors have thus been identified, including an unreliable charge referencing of the binding energy (BE) scale,[2] unrecognized sputter damage,[3] and neglected effects of sample storage.[4] By performing experiments on large sets of thin film samples such as Group IVB-VIB transition metal borides, carbides, nitrides, and oxides, we demonstrated disconcerting failure of the most popular referencing method based on the C 1s peak of adventitious carbon.[2]We appeal that it should no longer be used, with science reproducibility at stake. Furthermore, the extent of spectral changes following Ar^+ etching, commonly applied to remove surface contaminants, was evaluated using reference spectra from *in-situ* capped samples.[3]We showed that changes greatly depend on the type of material system: from very subtle effects in the case of Group IVB TM carbides to a complete modification of spectral appearance for IVB-TM oxides. The effects of sample storage on XPS spectra were evaluated for commonly used storage environments such as office shelf, polypropylene wafer carrier, polystyrene box, cellulose/polyester wipers or sealed polyethylene bag.[4]Results revealed significant differences between the various storage types and provide guidance for planning all sorts of studies including those that employ Ar^+ ion etch prior to analyses. Examples illustrating each of the above issues will be discussed during the talk and several principled practices offered.

[1] G.H. Major, et al. *J.Vac. Sci. Technol. A* 38, 061204 (2020)

[2] G. Greczynski and L. Hultman, *Angew. Chem.Int. Ed.* 59 (2020) 5002

[3] G. Greczynski and L. Hultman, *Applied Surface Science* 542 (2021)148599

[4] G. Greczynski and L. Hultman, Vacuum 205 (2022) 111463

11:20am **B4-1-MoM-5 Effect of Nitrogen Flow Rate on the Microstructure and Mechanical Properties of (V,Mo)N Thin Films*, Yiqun Feng*,** National Tsing Hua University, Taiwan*; T. Chung,* National Yang Ming Chiao Tung University, Taiwan*; J. Huang,* National Tsing Hua University, Taiwan

(V,Mo)N is considered to be a promising coating material for tribological applications, owing to having high hardness and ductility deriving from its extraordinary metal-nitrogen bonding environment [1]; however, the coating is lack of relevant mechanical properties and fracture toughness data. The objective of this study was to investigate the effect of nitrogen flow rate on the microstructure and mechanical properties of (V,Mo)N nanocrystalline thin films. Five compositions of (V,Mo)N thin films were deposited by dc-unbalanced magnetron sputtering with various nitrogen flow rate. The N/Metal ratios increased from 0.47 to 0.85 with increasing nitrogen flow rate from 1.2 to 6.0 sccm. The texture of the thin films changed from (200) to random texture with increasing nitrogen flow rate. (V,Mo)N thin film deposited at the lowest nitrogen flow rate (D12) was found to contain multiple phases by transmission electron microscopy, and single phase (V,Mo)N thin films were obtained as nitrogen flow rate was above 2.5 sccm. Specimen D12 possessed the largest hardness owing to the multiphase structure, where the Mo metal phase may retard the crack propagation, thereby increasing the film hardness. Fracture toughness (G_c) of the thin films was evaluated using internal energy-induced cracking method [2]. The fracture morphology showed that the cracks initiated in the Si substrate and then propagated into the film, implying the high toughness of (V,Mo)N thin films. The resultant G_c of the (V,Mo)N thin films, ranging from 20.9 to 30.1 J/m^2, linearly increased with increasing nitrogen content. The results showed G_c of the (V,Mo)N thin films was more significantly affected by nitrogen content than by texture. The higher G_c for the (V,Mo)N thin films than that of VN and TiN thin films is consistent with the theoretical predictions.

11:40am **B4-1-MoM-6 *In Situ* Stress Evolution in Ti/Pt Multilayers During Magnetron Sputter Deposition***, **Naureen Ghafoor**, M. Lorentzon, S. Bairagi, P. Sandstrom, J. Birch,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Control of stress evolution during film growth is crucial in many coating applications and requires *in situ* analysis. One such product is a micron-thick free standing biocompatible Ti/Pt multilayer film used as diaphragms for implantable inner ear microphones [[1] [#_ftn1]].For a given size and thickness the diaphragm compliance and hence, the deflection can only be maximized if the intrinsic stresses in the thin film structure are zero. In this work, we have measured intrinsic stresses based on dynamic wafer curvature measurement using multiple laser beam deflection optical Stress measurements. The instantaneous stress state at any stage of Ti and Pt layer's growth and the final stress of a micron-thick film allows for direct feedback of the effects of deposition parameters. We investigated the influence of process pressure, target-to-substrate distance, target power, and influence of applied bias to the substrate- while keeping a low temperature- on the residual stress in Ti single-layered and Ti/Pt multi-layered films deposited on double-sided polished 150 mm thick Si(100) wafers using magnetron sputtering technique [[2] [#_ftn2],[3] [#_ftn3]]. The example of stress evolution during the growth of a Ti single layer compared to oscillating stress state during Ti/Pt multilayer is shown in the figure. An excellent finding here is that tuning the layer thickness ratios in Ti/Pt multilayers particularly at the onset of growth up to 100 nm can be used to engineer the final stress state between compressive and tensile. This is attributed to Ti growing as type I (low mobility) generating tensile stress while Pt grows as type II (high mobility) generating compressive stress, at room temperature. The residual stress is also compared with post-deposition XRD wafer curvature measurement technique and differences along with the structural characterization of the films will be presented at the conference.

[[1]] L. Prochazka, ..., F. Pfiffner, Sensors 4487, 19 (2019), https://hearmore.cochlear.com/

[[2]] D. E. Ibrahim, Master Thesis, LiU-IFM/LiTH-EX-A-20/3821-SE, (2020)-

[[3]] Prochazka, L. ***N.Ghaoor***, *et al.* Novel Fabrication Technology for Clamped Micron-Thick Titanium Diaphragms Used for the Packaging of an Implantable MEMS Acoustic Transducer. *Micromachines***13**, 74 (2021).

Author Index

Bold page numbers indicate presenter