Live Session
Room Live - Session LI-MoM2
New Horizons in Boron-Containing Coatings Live Session

Moderators: Mr. Marcus Hans, RWTH Aachen University, Germany, Dr. Helmut Riedl, TU Wien, Institute of Materials Science and Technology, Austria

11:00am **LI-MoM2-1 Welcome & Thank You to Sponsors***, **Marcus Hans (hans@mch.rwth-aachen.de)**,* RWTH Aachen University, Germany*; H. Riedl,* TU Wien, Institute of Materials Science and Technology, Austria

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11:15am **LI-MoM2-2 Insights in the Structure, Defects and Stability of Mo_2BC Thin Films by Advanced Characterization Methods***, S. Gleich, R. Soler, B. Breitbach,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; H. Bolvardi, J. Achenbach, J. Schneider,* RWTH Aachen University, Germany*; G. Scheu, **Christina Scheu (scheu@mpie.de)**,* Max-Planck-Institut für Eisenforschung GmbH, Germany **INVITED**

Mo_2BC thin films find application as protection layers for cutting tools due to their high strength and ductility. These properties are governed by the microstructure, which can be controlled by the growth temperature or by post-processing annealing. In the present work, the structure and defects of thin Mo_2BC thin films deposited on (100) Si substrates by bipolar pulsed direct current magnetron sputtering were studied in-depth by various (scanning) transmission electron microscopy (S)TEM techniques. The substrate temperatures T_s ranged from 380 °C to 630 °C [1]. Post-processing experiments were performed on the film deposited at 380 °C, which was heated up to 900 °C [2].

The film grown at 630 °C has a columnar structure and is fully crystalline [1]. The grains with a size of around 10 nm possess several defects such as stacking faults as observed in atomic column resolved STEM images, which are related to the slight deviation from the nominal stoichiometry. A different microstructure was found for the films deposited at lower T_s. They consist of an amorphous matrix in which ~1,9 to 1.2 nm sized nanocrystals are embedded [1]. The amount of amorphous matrix is increasing with decreasing T_s while the size of the nanocrystals is decreasing. STEM imaging together with electron energy-loss spectroscopy revealed that all films contain Ar-rich clusters originating from the deposition process. The size of the clusters is similar for all films but their volume content is strongly increasing with decreasing T_s. The observed difference in microstructure can explain the mechanical properties with the highest hardness and Young's modulus value found for the coating deposited at 630 °C.

The microstructural changes of the film deposited at 380 °C induced by annealing were studied by ex-situ and in-situ X-ray diffraction and TEM experiments. The as-deposited, mainly amorphous film transformed to a fully crystalline one. Elongated crystals with a lengths of up to 1 µm were found at elevated temperatures [2]. Furthermore, at temperatures above 840 °C delamination from the Si substrate took place. Nevertheless, the results revealed that an annealing treatment below this temperature is a possible approach to improve the crystallinity and thus the mechanical properties [2].

[1] Gleich, S.; Soler, R.; Fager, H.; Bolvardi, H.; Achenbach, J.-O.; Hans, M.; Primetzhofer, D.; Schneider, J. M.; Dehm, G.; Scheu, C.: Materials and Design 142, 203 - 211 (2018).

[2] Gleich, S.; Breitbach, B.; Peter, N. J.; Soler, R.; Fager, H.; Bolvardi, H.; Schneider, J. M.; Dehm, G.; Scheu, C.: Surface and Coatings Technology 349, 378-383 (2018).

11:45am **LI-MoM2-4 Metal Diborides Everywhere: Conformal Coating, Infilling, and Alloying by Low Temperature CVD***, **John R. Abelson (abelson@illinois.edu)**,* University of Illinois at Urbana-Champaign, USA **INVITED**

Using low-temperature (< 300°C) CVD, it is possible to deposit refractory metal diborides in an extremely conformal fashion on complex and re-entrant substrate shapes. Kinetically, this is due to the properties of CVD precursor molecules based on borohydride ligands; for example, $Hf(BH_4)_4$ has a (huge) vapor pressure of 15 *Torr* at room temperature and decomposes above 150°C. Under these conditions, growth involves a competition on the film surface: the rate of precursor adsorption is large with respect to the rate of desorption of precursor or products, hence, the surface is dynamically covered with reaction intermediates. The reactivity to impinging precursor is then very low, while in parallel, the adsorbed intermediates react continuously to afford metal diboride film. The result is the growth of extremely conformal layers at useful rates [1] on complex morphologies [2].

We demonstrate the growth of HfB_2 films with > 90 % conformality on deep trenches for microelectronics and on carbon nanotube (CNT) forests 400 µm tall. The HfB_2-coated CNT is a new refractory hybrid material in which the density, modulus, and failure strength can be controllably varied over orders of magnitude via the HfB_2 film thickness.

The metal diboride growth kinetics can be further modified by adding an *inhibitor* molecule that adsorbs on the growth surface, but which does not decompose and ultimately desorbs from the surface without incorporation. We demonstrate three unique results using different inhibitors. First, an inhibitor can be used to convert a 'non-conformal' precursor such as $Ti(BH_4)_3$dme into one that affords conformal coatings [3]. Second, an inhibitor that sticks differentially to film vs. substrate can be used to alter the dynamics of nucleation; for example, the use of NH_3 as an inhibitor produces an extremely uniform density of HfB_2 nuclei on SiO_2, such that the fully coalesced film has a roughness < 1 nm [4]. Third, a highly reactive inhibitor such as atomic H, generated by a remote H_2 plasma, can be used to reduce the growth rate near to the opening of a deep feature but not at depth; the result is superconformal growth (faster at the bottom) by CrB_2.

Finally, we describe the use of alloying elements, such as N, C, or Al, to afford CVD coatings that have various combinations of low-friction and wear [5], or oxidation resistance at temperatures > 800°C.

References:

1. Yang, Y., Chemistry of Materials 18, 5088 (2006)

2. Yanguas-Gil, A. JVST A <u>27</u>, 1235 (2009)

3. Kumar, N., JACS <u>130</u>, 17660 (2008)

4. Babar, S. JVST A <u>32</u>, 060601(2014)

5. Mohimi, E., TSF <u>592</u>, 182 (2015)

12:15pm **LI-MoM2-6 A Progress Report on Bulk MAB Phases***, **Michel Barsoum (barsoumw@drexel.edu)**,* Drexel University, USA*; S. Kota,* Drexel University, USA **INVITED**

The MAB phases are atomically layered, ternary or quaternary transition metal (M) borides

(TMBs), with the general formula $(MB)_{2z}A_x(MB_2)_y$(**z** = 1–2; **x** = 1–2; **y** = 0–2), whose structures

are composed of a transition M-B sublattices interleaved by A-atom (A = Al,Zn) mono- or bilayers. Most of the MAB phases were discovered prior to the year 2000, but recent discoveries of intriguing magnetocaloric properties and high-temperature oxidation resistance has led to their **'**re-discovery**'**. Herein, bulk MAB phase synthesis is reviewed and their magnetic, electronic, thermal, oxidation and mechanical properties will be overviewed with an eye on applications. Because the M-B layers in the MAB phases are identical to their corresponding binaries of the same M:B stoichiometry, the effects of the A-layers on properties are discussed. Fruitful avenues for future research are proposed; potential limitations are also considered.

12:45pm **LI-MoM2-8 Closing Remarks and Sponsor Thank You!***, **Helmut Riedl (helmut.riedl@tuwien.ac.at)**,* TU Wien, Institute of Materials Science and Technology, Austria*; M. Hans ,* RWTH Aachen University, Germany

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Author Index

Bold page numbers indicate presenter