

# Monday Afternoon, October 31, 2005

## Advanced Surface Engineering Room 201 - Session SE-MoA

### MAX Phases: Nanolaminates and Nanomechanical Measurements

Moderator: D. Gall, Rensselaer Polytechnic Institute

#### 2:00pm SE-MoA1 The MAX Phases: Ductile, Machinable Ternary Carbides and Nitrides, *M.W. Barsoum*, Drexel University **INVITED**

With over 100 refereed publications and 8 patents in the past 8 years we have made tremendous progress in understanding the properties of a class of layered, hexagonal ternary carbides and nitrides with the general formula:  $M_{n+1}AX_n$  (MAX), where  $n = 1$  to 3, M is an early transition metal, A is an A-group element and X is C or N. The MAX phases combine some of the best attributes of metals and ceramics. Like metals, they are electrically and thermally conductive, readily machinable, not susceptible to thermal shock, plastic at high temperatures, and exceptionally damage tolerant. Like ceramics, some are elastically rigid, lightweight, and maintain their strength at high temperatures.  $Ti_3SiC_2$  is also creep, fatigue and oxidation resistant. Furthermore, basal planes of  $Ti_3SiC_2$  possess very low friction coefficients ( $3 \times 10^{-2}$ ) that are quite robust vis-a-vis exposure to the atmosphere. Two characteristics distinguish these phases from other layered solids: i) the metallic-like nature of the bonding, and ii) they deform by a unique combination of kink and shear band formation resulting from the glide of basal-plane dislocations. Polycrystalline  $Ti_3SiC_2$  cylinders can be repeatedly compressed at room temperature, up to 1 GPa. The stress-strain curves outline fully reversible, reproducible closed loops whose size and shape depend on grain size, but not strain rate. The energy dissipated per cycle is of the order of 1 MJ/m<sup>3</sup>. At the grain level we have shown that it is possible to nanoindent grains of  $Ti_3SiC_2$  with up to 10 GPa, dissipate roughly 25 % of the mechanical energy and not be able to find any trace of the indentation. Both phenomena are attributed to the formation and annihilation of incipient kink bands. The technological implications of having these naturally nanolayered materials will be discussed.

#### 2:40pm SE-MoA3 Alternating Covalent-Ionic and Metallic Bonding in Nanolaminated Cubic Perovskites, *D. Music, J.M. Schneider*, RWTH Aachen, Germany

Using ab initio calculations, we have studied 35 cubic perovskites of  $RM_3X$  stoichiometry, where R and M are metals and X is a 2p nonmetal. In this structure (space group Pm-3m, prototype  $CaTiO_3$ ), R atoms fill primitive cubic sites, M atoms are located at face centered cubic positions, and X is placed at body centered cubic Bravais nodes. We show that the coupling between M-R and M-X layers in  $RM_3X$  can be switched from predominantly covalent-ionic to metallic in character by varying the population of the M and R d-shells. As the X 2p population increases, the bulk modulus decreases, which can be understood by changes in bonding character from more covalent to more ionic due to splitting in density of states. We will also discuss transport properties obtained from phonon calculations. Based on the electron density distribution resemblance to the so-called MAX phases, it is reasonable to assume that alternating covalent-ionic and metallic bonding in these compounds may give rise to similar properties as observed for MAX phases.

#### 3:00pm SE-MoA4 Observation of the Growth and Microstructural Development of MAX Phase $Ti_2AlN$ Thin Films during Magnetron Sputtering using Synchrotron Radiation, *N. Schell, M. Beckers, R.M.S. Martins, A. Mücklich, W. Möller*, Forschungszentrum Rossendorf, Germany

The heteroepitaxial growth of MAX phase  $Ti_2AlN$  ( $M_{n+1}AX_n$  with  $M = Ti$ ,  $A = Al$ ,  $X = N$  and  $n = 1$ ) on single crystal substrates  $MgO(001)$  and  $MgO(111)$ , deposited by reactive magnetron co-sputtering from Ti and Al targets in an  $Ar/N_2$  atmosphere at a temperature of 690°C, has been studied in situ. Using real-time specular x-ray reflectivity, layer-by-layer growth first of an approximately 10 nm thick epitaxial B1-cubic  $Ti_0.63Al_0.37N$  seed layer, then, after changing the deposition parameters, of the MAX phase itself was observed, with an increased surface-roughening on  $MgO(001)$  substrate. Using off-plane Bragg-Brentano x-ray scattering, the heteroepitaxial growth of  $Ti_2AlN$  to the underlying seed-layer as well as  $MgO$  was established with lattice parameters of  $c = 1.3463$  nm and  $a = 0.2976$  nm. From ex-situ pole figures at a laboratory source the epitaxial relationship between film and substrate lattice was determined to be  $MgO\{111\} //$

$Ti_2AlN\{1012\} \parallel [11\bar{2}0]$  regardless of choice of substrate orientation during deposition, e.g. a non-basal plane epitaxial growth of the  $Ti_2AlN$  thin films along  $MgO$  directions, leading to a threefold grain orientation as also seen in cross-sectional transmission electron microscopy. In temperature dependent four-probe measurements at room temperature a specific resistivity of  $37 \mu\Omega/cm$  has been derived.

#### 3:20pm SE-MoA5 The Materials Science of MAX Phase Thin Films, *L. Hultman*, Linköping University, Sweden **INVITED**

This presentation is a review of the materials research on  $M_n$  phase thin films. We have deposited epitaxial films from the Ti-Si-C, Ti-Ge-C, and Ti-Sn-C as well as Ti-Al-N systems on  $Al_2O_3$  or  $MgO(111)$  substrates at temperatures of 700-1000°C employing DC magnetron sputtering. This was done using mainly growth from elemental sources, but also demonstrating single source deposition from compound targets. We report single-crystal growth of the previously known phases  $Ti_3SiC_2$ ,  $Ti_3GeC_2$ ,  $Ti_3SnC_2$ , and the discoveries of two phases  $Ti_4SiC_3$  and  $Ti_4GeC_3$  as well as intergrown structures of stoichiometries  $Ti_5Al_2C_3$  and  $Ti_7Al_2C_5$  in the Si and Ge systems. Characterization studies will be reported using XRD, TEM, four-point (resistivity) probe, and nanoindentation. Comparison will also be made with the phase composition in nanocomposite M-A-X films forming during deposition at reduced temperature.

#### 4:00pm SE-MoA7 The Promise of High Power Pulsed Magnetron Sputtering (HPPMS), *W.D. Sproul*, Reactive Sputtering Consulting **INVITED**

High power pulsed magnetron sputtering (HPPMS) applies a very large power pulse to the target in a short period of time. Typical power densities are on the order of 1,000 to 3,000 W/cm<sup>2</sup> with pulse durations of 100-150 μsec. This power density is about 100 times the typical power densities used in conventional sputtering. Depending on the size of the sputtering target, the peak power can reach the megawatt range. The very interesting feature of HPPMS is that there is a high degree of ionization of the sputtered species due to electron impact ionization, and most of the ionized species are singularly ionized although there are reports of small amounts of multiply ionized species of the target material. These ionized species can be used to improve the structure and properties of the deposited film, and the ionized species will follow field lines to a biased substrate producing a dense film in side wall features as has been demonstrated by Alami et al. In many respects HPPMS is very much like the cathodic arc process where there is a very high degree of ionization of the evaporant, but unlike the arc process there are few if no droplets produced in the process. HPPMS has been used for reactive sputtering of conducting materials such as chromium nitride, and it has also been used for the reactive sputter deposition of the oxides of Al, Ta, and Ti. The one disadvantage of the HPPMS process that has come to light so far is that its deposition rate is only 25-30% of the rate for an equivalent amount of power used during conventional DC sputtering. A model by Christie has been developed to explain this loss of rate for the HPPMS process, and the model provides insights that hopefully will bring a solution to this loss of rate issue. In this talk, the current state of the art for HPPMS will be reviewed with an eye toward the future to see where HPPMS can be used to benefit the thin film community.

#### 4:40pm SE-MoA9 Towards Large Area Deposition of $Cr_2AlC$ on Steel, *C. Walter, D.P. Sigumonrong*, RWTH Aachen, Germany; *T. El-Raghy*, 3-One-2 LLC; *J.M. Schneider*, RWTH Aachen, Germany

$Cr_2AlC$  belongs to the MAX phases, which are promising materials for protective coatings on steel due to their unique combination of properties like corrosion and oxidation resistance and damage tolerance. Here the deposition by magnetron sputtering of a Cr-Al-C compound target was investigated varying the substrate temperature and the substrate bias potential. It was found that the MAX phase structure is stable in a substrate temperature range between 850 and 450 °C. At lower substrate temperatures the structure of the film is X-ray amorphous. Varying the DC substrate bias potential between floating potential and 310 V, no significant influence on the film composition and structure was observed. A phase purity of more than 90 % MAX phase in the films was reached and the equilibrium volume measured by X-ray diffraction is in excellent

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agreement with our own ab initio calculations. The method discussed here may provide a pathway towards large area MAX phase deposition on steel.

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