

# Tuesday Afternoon, October 16, 2007

## Advanced Surface Engineering

Room: 617 - Session SE-TuA

### Naturally and Artificially Nanolaminated Coatings

Moderator: D. Gall, Rensselaer Polytechnic Institute

1:40pm **SE-TuA1 Optical Characterization of ZnO/Ag/ZnO Multilayer Films with Ag Layer Deposited by High Power Pulsed Magnetron Sputtering.** *J. Li, S.R. Kirkpatrick, S.L. Rohde*, University of Nebraska-Lincoln

ZnO/Ag/ZnO multilayer films can be used in Low-E glass, solar cells and flat panel displays. Thin silver layers sandwiched between layers ZnO have been deposited by High Power Pulsed Magnetron Sputtering (HPPMS). By varying the deposition conditions during HPPMS, a thin, dense and uniform silver layer with low resistivity, high transmittance in visible light range have been obtained. The optical properties of ZnO/Ag/ZnO multilayer films with silver layer deposited by HPPMS have been studied using spectroscopic ellipsometry and infrared spectroscopic ellipsometry. The results have also been compared with multilayer films with silver layers deposited by conventional DC magnetron sputtering. For ZnO/Ag/ZnO multilayer films, the Ag-HPPMS multilayer films showed lower resistivity, lower IR transmittance than DC magnetron sputtered films. The optical properties of ZnO/Ag/ZnO multilayer films with different silver layer thickness deposited by HPPMS have also been investigated, with respect to their potential in an array of optical applications.

2:00pm **SE-TuA2 Synthesis and Elastic Properties of MAX Phases.** *J.M. Schneider, D. Music*, RWTH Aachen University, Germany **INVITED**

$M_{n+1}AX_n$  phases (space group  $P6_3/mmc$ ), where M is a transition metal, A is mostly IIIA or IVA group element, X is either C or N and  $n = 1-3$ , can be referred to as nanolaminates, where MX layers are interleaved with A layers. We have investigated the valence electron concentration induced changes in the elastic properties of  $M_2AlC$  phases (M = Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) using ab initio calculations.<sup>1,2</sup> In terms of bulk moduli [1], we have suggested that  $M_2AlC$  phases can be classified into two groups based on the coupling between MC and Al layers:  $M_2AlC$  phases with M = VB and VIB are strongly coupled, while  $M_2AlC$  with M = IVB are weakly coupled. In terms of shearing,<sup>2</sup> we have proposed that these phases can also be classified into two groups: one group comprises M = VB and VIB, where the  $C_{44}$  values are independent of the corresponding MC. The other group includes M = IIIB and IVB, where the  $C_{44}$  shows a linear dependency with the corresponding MC. This may be understood based on the electronic structure: shear resistant bands are filled in  $M_2AlC$  phases with M = VB and VIB, while they are not completely filled when M = IIIB and IVB. These classification proposals exhibit identical critical valence electron concentration values for the group boundary. Experimental efforts have been dedicated towards exploring the correlation between the valence electron concentration, constitution, and the elastic properties of  $M_2AlC$  phases (M = Ti, V, Cr).  $Ti_2AlC$  can be deposited onto sapphire substrates at a growth temperature of 800 °C using a compound target and an additional source of Ti.<sup>3</sup>  $V_2AlC$  was grown at a substrate temperature of 850 °C. We report that 450 °C is sufficient to grow crystalline  $Cr_2AlC$  thin films. This is the lowest deposition temperature ever reported for a MAX phase and is significantly lower than the crystallization temperature of an amorphous  $Cr_2AlC$  thin film based on our differential scanning calorimetry data.<sup>4</sup>

<sup>1</sup>D. Music, Z. Sun, R. Ahuja, J.M. Schneider, Phys. Rev. B 73 (2006) 134117.

<sup>2</sup>D. Music, Z. Sun, A.A. Voevodin, J.M. Schneider, Solid State Commun. 139 (2006) 139.

<sup>3</sup>C. Walter, C. Martinez, T. El-Raghy, J.M. Schneider, Steel Research Int. 76 (2005) 225.

<sup>4</sup>C. Walter, D.P. Sigumonrong, T. El-Raghy, J.M. Schneider, Thin Solid Films 515 (2006) 389.

2:40pm **SE-TuA4 Deposition of  $M_{n+1}AX_n$  (n=1-3) Phase Coatings by Magnetron Sputtering from Compound Targets and High Velocity Oxy-Fuel Spraying.** *H. Höglberg*, Linköping University, Sweden **INVITED**

Magnetron sputtering has proven to be a favorable route for synthesis of films of the ternary carbides or nitrides referred to as the  $M_{n+1}AX_n$  (n=1-3) phases. Sputtering from elemental targets has enabled the growth of several materials systems; predominately carbide phases with Ti as the carbide-forming transition metal (M) and with either Al, Si, Ge or Sn as the A-element, but with extensions to other metals as in the V-Ge-C system or to nitride based systems as in the Ti-Al-N system. The majority of the films have been deposited on  $Al_2O_3$  (0001) substrates to promote epitaxial growth at temperatures typically above 700 °C, but for  $V_2GeC$  as low as 450 °C. In addition to deposition of the known phases in each of the studied systems

this type of process also enables the growth of new phases such as  $Ti_3SnC_2$  and so-called intergrown structures in the Ti-Si-C and Ti-Ge-C systems. Using sputtering from compound targets of  $Ti_3SiC_2$  and  $Ti_2AlC$  in either Ar or Ar/ $N_2$  plasmas we are currently investigating the growth conditions for the respective phases as well as potentially quaternary Ti-Si-CN and Ti-Al-CN phases. The studies show that sputtering of the compound targets in pure Ar plasmas favors epitaxial growth conditions for  $Ti_3SiC_2$  and  $Ti_2AlC$  when the sources are co-sputtered with Ti. The as-deposited coatings consist predominately of MAX phase, but with intergrown layers of TiC. This behavior is attributed to higher carbon content in the deposited films compared to the target composition. Addition of  $N_2$  during growth of both systems results in films of lower crystalline quality, and with preferential nucleation of TiC or TiCN for higher  $N_2$  flows. XPS shows that up to 30 at. %  $N_2$  is incorporated in the Ti-Al-CN films, and that the content of nitrogen in the deposited films scales with the amount of nitrogen available in the plasma. For deposition of thick (appr. 200  $\mu m$ )  $Ti_2AlC$  coatings, we have applied high velocity oxy-fuel (HVOF) spraying. Characterization shows that dense and well-adherent coatings can be deposited on steel. Structural analysis shows that the HVOF coatings consist of  $Ti_2AlC$  (the powder phase) together with Ti-Al melting phases and residual TiC and  $Ti_3AlC_2$ . Vickers indentation experiments and scanning electron microscopy imaging of the indented area showed a hardness of appr. 6 GPa, with concentric cracks at the indent.

4:00pm **SE-TuA8 Effect of Swift Heavy Ion Irradiation on the Hardness of Chromium Nanorods.** *R. Nagar*, Indian Institute of Technology Delhi, India, *K. Sai, D. Gall*, Rensselaer Polytechnic Institute, *D. Jain*, UGC-DAE, CSR, India, *B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi, India

This presentation discusses the use of ion irradiation to controllably tailor the hardness of Cr columnar thin films. Regular arrays of slanted Cr rods, 2  $\mu m$  long and 250 nm wide, were grown by glancing angle dc magnetron sputter deposition on patterned Si(100) substrates. The patterns consist of 500-nm-diameter polystyrene spheres that self-assemble to form hexagonal close-packed monolayers. The Cr rod arrays were irradiated with 100 MeV  $Ag^{+8}$  ions at three different fluences of  $10^{13}$ ,  $5 \times 10^{13}$  and  $10^{14}$  ions/cm<sup>2</sup>, while maintaining the sample at a constant temperature of 80K. The ion-irradiation induced defect formation is dominated by electronic energy losses, with a very small contribution (approximately 0.5%) from the nuclear energy losses and negligible Ag-implantation. The average nanohardness of pristine Cr rods, as determined using a Berkovich diamond tip attached to an atomic force microscope, was found to be 0.6 GPa. Irradiation of the rods with  $10^{13}$  ions/cm<sup>2</sup> does not lead to a measurable change in the hardness. However, for the fluence of  $10^{14}$  ions/cm<sup>2</sup>, the hardness increases to about 4 GPa, leading to an about eight-fold increase. The fluence-dependent hardness in these Cr rods is attributed to the ion-irradiation induced defect formation that may lead to dislocation pinning which is particularly effective due to the nanoscale dimensions of the Cr rods. These results are very promising as they demonstrate the use of swift heavy ion irradiation to tune the hardness of nanorod coatings.

4:20pm **SE-TuA9 Formation of Surface Relief of As<sub>2</sub>S<sub>3</sub> Films using Glancing Deposition.** *M.V. Sopinsky*, V. Lashkaryov Institute of Semiconductor Physics, Ukraine, *V.I. Min'ko*, V. Lashkaryov Institute of Semiconductor Physics NAS, Ukraine, *I.Z. Indutnyy*, *O.S. Lytvyn*, *P.E. Shepeliavyy*, V. Lashkaryov Institute of Semiconductor Physics, Ukraine

In this report we present the first results on the surface morphology and optical properties of 1-3  $\mu m$  thick  $As_2S_3$  films that were thermally evaporated on the glass and silicon substrates within 70-80° range of the vapor incidence angles. The AFM has revealed the details of the surface relief of glancing-deposited films showing quasi-regular grating-like structure, with the spatial frequency of quasi-gratings being in the 3000-6000  $mm^{-1}$  range, and relief depth of 10-60 nm range. Ordering degree also depends on the substrate. The preliminary deposition of thin Cr film on the glass substrate results in more pronounced surface self-ordering of glancing-deposited  $As_2S_3$  films. Multiangle ellipsometric measurements have been performed to determine the refractive index, and check the anisotropy of the films. It has been found that the refractive index values in these films are lower compared to the values for the films with the normal (perpendicular) deposition. In addition, there is anisotropy of refractive index in the plane of the film. This indicates that the structure of the films is columnar, with the columns tilted relative to the substrate normal. The most probable explanation for the observed effect is the surface stress that plays significant role in the self-organized ordering of nanostructures at the mesoscopic length scales (several nm - hundreds of nm). It is the known fact that the thermally deposited  $As_2S_3$  films are mechanically stressed, especially in the near-surface area. Thus, due to the structural anisotropy of

the obliquely deposited As<sub>2</sub>S<sub>3</sub> films, the stress forces are also anisotropic. The more pronounced columnar structure of these samples provides a lot of free space where the bond breaking and atomic movements are facilitated. Both of these factors result in anisotropic plastic shears in the film' near-surface region. The effect is a cheap and easy way to create quasi-gratings on the surface of amorphous chalcogenide films and could be used for fabrication of nano- and microdevices.

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