PROGRESS REPORT FOR AINGRA07012P

**PROJECT TITLE** Composition of ternary alloys: TCO and MAX phase thin films

**INVESTIGATOR(S)**

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- Dr Daniel Riley (University of Melbourne)

Students:  
- James Stokes  
- Myles Cover  
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ANSTO Investigators:  
- Mihail Ionescu

Specialist Committee:  
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**SCIENTIFIC OBJECTIVES**

We will synthesize technologically important transparent conducting oxides and MAX phase materials as thin films. A range of advanced deposition techniques, in particular a pulsed cathodic arc as well as a high powered pulsed magnetron sputtering system will be used to synthesize the materials of interest. These discharges are unique in allowing fine control of composition due to highly reproducible plasma pulses containing sub-monolayer amounts of depositing ions. The generation of pulses is computerized, allowing unprecedented control of composition for ternary alloys. We will study the composition, microstructure as well as properties and relate them to the fundamental deposition conditions.

**PROGRESS REPORT and RESEARCH OUTCOMES**

Our understanding of the growth mechanisms and properties of thin film MAX phases by PVD processes has been significantly advanced this year. MAX phases have stoichiometry of $M_{n+1}A X_n$ where M is a transition metal, A an A group element and X is either carbon or nitrogen. They have a hexagonal nanolaminate crystal structure with layers of the metal carbide or nitride interleaved with layers of the A group element. We have synthesized these materials as thin films using a high current pulsed cathodic arc and characterized their structure and composition using a combination of techniques available at ANSTO and the University of Sydney.

A major finding was that oxygen is readily incorporated into the hexagonal crystal lattice. Large throughput in composition measurements was achieved by utilizing RBS to obtain the compositions of a range of standard samples, deposited onto 4” silicon wafers using magnetron sputtering. These standards were then used to obtain sensitivity factors for fast turnaround secondary neutral mass spectrometry (SNMS) analyses. Our depth profiling results indicate that the oxygen impurity atoms may be substituting for C in Ti2AlC and that substitution of almost half of the C atoms was tolerated without a phase change to another crystal structure. This surprising result is now being investigated further using both experimental and ab-initio simulation methods. A study focusing on the implications for properties of interest for applications has also commenced.

We found that single crystal MAX phase (Ti2AlC) films with perfect c-axis alignment along the growth direction could be synthesized using an appropriate template at the substrate interface. The best results were obtained using a TiC interlayer template deposited onto sapphire cut normal to the c-axis. Deposition of the Ti2AlC phase directly onto the sapphire resulted in oriented growth with defects and grain boundaries. Deposition onto sapphire cut along other planes showed either no MAX phase formation or the formation of randomly oriented small grained crystallites. In our ab-initio simulations work, we calculated numerical values for all of the independent elastic...
constants, $c_\delta$, for all of the M$_2$AX materials, most of which have not yet been synthesized. These constants were also calculated for a limited range of M$_3$AX$_2$, M$_4$AX$_3$, M$_5$AX$_4$ phases in order to study trends with $n$. We were able to identify a number of unstable phases as well as phases with extreme values of the elastic properties and of the properties that can be deduced from them such as machinability and ductility. The results of statistical correlation analysis showed that the MA bonds had the strongest influence on mechanical properties while MN bonding affected only the in-plane behaviour. The data generated represents the first comprehensive data base of elastic constants for the MAX phase family.

Our work on TCO materials involved the synthesis and characterization of CuAlO and ZnO. CuAlO is of interest because it is a p-type semiconductor. ZnO is increasingly important due to its potential for technological applications. Our work on these materials examined the effects of the deposition conditions on the microstructure and on the properties.

The CuAlO samples and Al doped ZnO samples were synthesized by cathodic arc using alloy targets pressed at ANSTO. The ZnO material was deposited using both cathodic arc and pulsed sputtering methods. The optimum sputtered and arc deposition materials were found to be equivalent.

We compared the electrical behaviour, as measured by the van der Pauw technique, of ZnO samples deposited by cathodic arc at (a) floating potential, (b) with pulsed biased of 5kV and (c) with the substrate heated to 220°C. Conduction mechanisms were found to vary between these samples. RBS analysis performed at ANSTO showed that the films were stoichiometric with equal amount of Zn and O. The presence of hydrogen, a common and problematic impurity in PVD methods was checked with ERDA and was found to be minimal in all of the samples, in most cases, at a level of less than 1%. Transmission electron microscopy studies of the microstructure revealed significant differences in grain size and shape according to the deposition conditions which explained the variations observed in electrical properties.

Ab initio simulations work carried out as part of this project examined co-doping as an approach for effective p-type doping of ZnO. Co-doping involves including a high concentration of stable non-doping complexes consisting of n and a p-type dopants that build a defect band just above the conduction band. P-type dopants with high energy levels, such as nitrogen, can then be used as dopants activated at room temperature. Our work showed that GaN complexes performed better than AlN complexes explaining some new experimental findings in the literature. TiN$_2$ was also found to be a potentially useful complex and will now be investigated experimentally by our group. Four publications on the TCO work are currently under preparation.

**DATA**

RBS was used routinely to determine composition of samples under study and ERDA was employed to determine levels of H incorporation. RBS was also used to characterize standards which were then used to calibrate fast turnaround SNMS measurements employed to tune the pulse ratios used to deposit the multicomponent alloys. Since the effective sticking coefficients of the elements changed with changes in plasma conditions, substrate bias and substrate temperature, the pulse ratios needed adjusting each time deposition conditions were changed. The fast turnaround method (discussed in the previous section) using a combination of RBS and SNMS proved crucial to the synthesis of our films.
Figure 1 shows typical RBS composition analyses for cathodic arc deposited ZnO samples (a) made at floating potential and (b) made with 5kV pulsed bias.
Figure 2 shows some typical ERDA analyses of our ZnO samples. Incorporation of residual hydrogen is low (between 0.1 and 0.8 % ie below 1% in all cases).

Figure 3 shows a depth profile of film composition of a Ti2AlC MAX phase film measured using RBS. The MAX crystal structure was confirmed by XRD analysis. The high levels of oxygen incorporation into the structure are surprising. The inverse relationship between C and O is indicative of substitutional incorporation at the C lattice sites.

<table>
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<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<td>0.36</td>
<td>0.36</td>
<td>0.36</td>
<td>0.39</td>
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Figure 4 shows in tabular form the hydrogen levels in six Cr2AlC MAX phase films as measured by ERDA. Levels of residual hydrogen are well below 1% in all cases.


**PhD STUDENTS**

- Myles Cover – Ab-initio Simulations of the Structure and Elastic Constants of MAX Phases (for submission in July 2011)
- Mathew Guenette – Influence of choice of M and A elements on the properties of MAX Phases (for submission in July 2010)
- Mark Tucker – Deposition mechanisms of MAX Phases (for submission in July 2010)