A combinatorial comparison of DC and high power impulse magnetron sputtered Cr₂AlC

M. R. Field, Patrick Carlsson, Per Eklund, J. G. Partridge, D. G. McCulloch, D. R. McKenzie
and M. M. M. Bilek

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

M. R. Field, Patrick Carlsson, Per Eklund, J. G. Partridge, D. G. McCulloch, D. R. McKenzie
and M. M. M. Bilek, A combinatorial comparison of DC and high power impulse magnetron
sputtered Cr₂AlC, 2014, Surface & Coatings Technology, (259), 746-750.

<http://dx.doi.org/10.1016/j.surfcoat.2014.09.052>

Copyright: Elsevier

<http://www.elsevier.com/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-114446>

Accepted Manuscript

A combinatorial comparison of DC and high power impulse magnetron sputtered Cr₂AlC

M.R. Field, P. Carlsson, P. Eklund, J.G. Partridge, D.G. McCulloch, D.R. McKenzie, M.M.M. Bilek

PII: S0257-8972(14)00861-5
DOI: doi: [10.1016/j.surfcoat.2014.09.052](https://doi.org/10.1016/j.surfcoat.2014.09.052)
Reference: SCT 19772

To appear in: *Surface & Coatings Technology*

Received date: 1 May 2014
Accepted date: 23 September 2014

Please cite this article as: M.R. Field, P. Carlsson, P. Eklund, J.G. Partridge, D.G. McCulloch, D.R. McKenzie, M.M.M. Bilek, A combinatorial comparison of DC and high power impulse magnetron sputtered Cr₂AlC, *Surface & Coatings Technology* (2014), doi: [10.1016/j.surfcoat.2014.09.052](https://doi.org/10.1016/j.surfcoat.2014.09.052)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A combinatorial comparison of DC and high power impulse magnetron sputtered Cr₂AlC

M R Field^{1*}, P Carlsson², P Eklund², J G Partridge¹, D G McCulloch¹, D R McKenzie³ and M M Bilek³

¹ Physics, School of Applied Sciences, RMIT University, Melbourne, Australia

² Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

³ School of Physics, The University of Sydney, Sydney, Australia

Email: matthew.field@rmit.edu.au

Abstract. Using a combinatorial approach, Cr, Al and C have been deposited onto sapphire wafer substrates by High Power Impulse Magnetron Sputtering (HiPIMS) and DC magnetron sputtering. X-ray photoelectron spectroscopy, X-ray absorption spectroscopy and X-ray diffraction were employed to determine the composition and microstructure of the coatings and confirm the presence of the Cr₂AlC MAX phase within both coatings. One location in both the DCMS and HiPIMS coatings contained only MAX phase Cr₂AlC. The electrical resistivity was also found to be nearly identical at this location and close to that reported from the bulk, indicating that the additional energy in the HiPIMS plasma was not required to form high quality MAX phase Cr₂AlC.

Keywords. HiPIMS; DC magnetron sputtering; MAX phase; Cr₂AlC; NEXAFS

1. Introduction

MAX phase materials have composition of the form $M_{n+1}AX_n$ ($n=1, 2$, or 3) where M is an early transition metal, A is often a group 3A or 4A element from the periodic table and X is either carbon or nitrogen [1-3]. Some of the desirable properties of both ceramics and metals are exhibited by MAX phase materials including machinability, corrosion resistance and high electrical conductivity. These useful properties stem from complex microstructure that includes extremely strong $M-X$ bonds and weaker $M-A$ bonds. Potential applications include protective coatings, low friction surfaces, and high temperature electrical contacts [3].

MAX phase materials are routinely synthesized from hot-pressed powders in bulk form [3] but many applications are better served by thin film coatings. Nickl *et al.* were the first to synthesize a MAX-phase thin film in 1972, using chemical vapour deposition to deposit Ti_3SiC_2 [4]. Ti_3SiC_2 has also been prepared using magnetron sputtering from both a compound target and from three individual elemental targets [5-6]. Numerous other MAX phase materials have been deposited using magnetron sputtering [7-14] including Cr_2AlC [15-23].

High Power Impulse Magnetron Sputtering (HiPIMS) provides a more ionized depositing flux [24] when compared with conventional sputtering. This results in both higher average deposition energy and the ability to control the deposition energy using substrate bias. Ion bombardment can then be exploited to improve the properties of the deposited materials. Since deposition energy is known to influence the microstructure of coatings [25], HiPIMS coatings may offer improved performance when compared with conventionally sputtered coatings. The application of the HiPIMS technique to the synthesis of MAX phase materials has thus far been restricted to deposition from composite or MAX-phase compound targets [26-28].

In the present paper, we investigate whether the increased deposition energy available in HiPIMS is beneficial to the synthesis of Cr_xAlC_y thin films including MAX phase Cr_2AlC . Films were prepared under similar conditions using both conventional DC magnetron sputtering (DCMS) and HiPIMS. A combinatorial

approach [29], in which three sputter targets provided flux gradients across the substrate in directions dependent on their location, was used to produce coatings with composition varying as a function of position on the substrate. The composition, chemical bonding, microstructure and electrical resistivity were then measured at selected positions and comparisons were made between the DCMS and HiPIMS coatings.

2. Materials and Methods

A magnetron sputtering system (AJA, Inc.) was used to deposit the coatings onto polished Al_2O_3 (0001)-oriented wafers (diameter 50 mm and thickness 0.5 mm) mounted ~12 cm from the three (three-inch diameter) sputter heads. A substrate temperature of 550 °C was selected. The base pressure of the deposition chamber was less than 0.33 mPa with the sample heated. During deposition, an Ar process pressure was maintained at 0.36 Pa. Cr, Al and C coatings were deposited individually and the film thicknesses and bulk densities were used to calibrate the deposition rates in order to find optimum process conditions to deposit Cr_2AlC . The resulting films were all 400 ± 20 nm in thickness. Al was deposited using a DC power of 70 W, C with a RF power of 577 W and Cr was operated in either HiPIMS or DCMS mode. The HiPIMS Cr deposition was performed using a pulse length of 70 μs at 150 Hz, a voltage of 750 V and a maximum current of 39A and the DCMS Cr deposition was performed with a power of 87 W. The Cr target was operated in HiPIMS mode due to its higher degree of ionization relative to Al and especially C where the use of HiPIMS is expected to have a more limited effect (similar reasoning was employed in [27]).

The coatings were imaged using a Hitachi S-4500 scanning electron microscope operating at 15 keV. Chemical bonding within the coatings was analysed using both x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS). XPS was performed using a Thermo Scientific K-alpha instrument with an Al $K\alpha$ source (1486.7 eV) operating with an x-ray spot size of 400 μm . The compositions of the thin films were determined from XPS depth profiles. These were performed using an Ar ion beam operating at 2 keV. A hot pressed Cr_2AlC magnetron target was used as a standard for XPS (Testbourne Ltd, Chromium-Aluminium Carbide Target Cr_2AlC , 99.5% pure), giving an estimated uncertainties in measured stoichiometries of $\pm 5\%$. XAS was performed using the soft x-ray beamline at the Australian synchrotron, in which the total electron yield (TEY) was collected for analysis. Glancing angle x-ray diffraction (XRD) was

performed using a PANalytical X'pert MRD diffractometer equipped with a 6-axis sample stage. A 5 mm vertical slit was used between the source and the sample. The collection areas of the NEXAFS and XPS measurements were $\sim 0.1 \text{ mm}^2$, while the XRD sampling area was estimated to be 5 mm by 0.5 mm. Four-point probe resistivity measurements were performed using a PC-controlled source meter and a four-probe station.

3. Results and discussion.

The voltage (black) and current waveforms (blue) for the Cr target operating in HiPIMS mode are shown in Figure 1. The pulsed power supply has an output inductance and capacitance that causes the ringing at the start of the voltage pulse and persists whilst there is no load prior to plasma ignition. The delay in the onset of current ($\sim 20 \text{ s}$) is associated with plasma ignition. These characteristics are typical for HiPIMS systems[3]. The fraction of ions in a HiPIMS Cr flux has been reported to be up to $\sim 30\%$ [30]. Under our operating conditions with lower peak power densities, the ion fraction of the HiPIMS Cr flux will be less, but appreciably higher than in the DCMS Cr flux..

Figure 1. The voltage (black) and current (blue) waveforms measured during a single HiPIMS pulse applied to the Cr target.

Figure 2(a) shows an image of the Al_2O_3 wafer following coating using DCMS. Also indicated in the image are the positions of the magnetron targets relative to the substrate. The surface shows a variation in colour, with light grey regions separated by darker bands. Visually, the HiPIMS coating (not shown) appeared

identical. XPS maps of the Cr content from both the DCMS and HiPIMS samples were obtained from regions indicated in Figure 2(a) and are shown in Figures 2(b) and 2(c) respectively. These maps indicate that the surface Cr content of both samples is similar and that employing HiPIMS did not greatly alter the surface composition of the coating.

Figure 2. (a) A digital camera image of the DCMS coating, with the positions of the magnetron targets indicated by the yellow arrows. The labels A-D show the locations where compositional, electrical and XRD measurements were performed. XPS maps of the Cr content within the red enclosed square indicated in (a) are shown for the (b) DCMS and (c) HiPIMS coatings. Note that the black regions in (b) and (c) correspond to the location of sample mounting clips during XPS.

In order to investigate the film morphology in more detail, SEM imaging was performed at positions A-D (Figure 2(a)) on both the DCMS and HiPIMS coatings. As shown in Figure 3, the particle size and shape differ at the positions A-D across the surface of the HiPIMS coating, with the finer surface morphology observed at the location closest to the carbon target (position D). This suggests a dependence of the surface morphology on the directionality of the depositing fluxes and composition. SEM images of the DCMS sample (not shown) closely resemble those of the HiPIMS sample.

Figure 3. Scanning electron micrographs of the coating deposited using HiPIMS at positions A-D (see Figure 2).

Table 1 shows the resistivities and atomic percentages (calculated from the XPS depth profiles) measured at positions A-D across the films. All compositions were determined at etch-depths where the constituent elements did not vary with further etching. The abundances of the constituent elements generally reflect the positions of the sputtering targets. For example, position B has a high Al content and a low C content. Excess Cr was found at the majority of the positions on both samples. Positions C and D exhibited compositions closest to the intended Cr_2AlC . Only point D exhibits significant differences in composition between DCMS- and HiPIMS-deposited films. While the C content in both films is similar (20 at. % and 22 at. %), the Cr/Al ratios are 58/22 (DCMS) and 48/36 (HiPIMS). This is an indication that the higher degree of ionization in the HiPIMS-deposited Cr compared with the DCMS-deposited Cr results in depletion nearest to the C target.

Room-temperature electrical resistivity measurements from the coatings ranged from approximately 5×10^{-7} to $5 \times 10^{-6} \Omega \cdot \text{m}$ (Table 1). At positions A and B (with compositions differing most from Cr_2AlC), the difference between the resistivity of the HiPIMS film and the DCMS film is significant with appreciably higher conduction in the HiPIMS film. At position C (with a composition close to Cr_2AlC), both films have approximately equal resistivities. Surface and interface scattering inevitably cause increased resistance in thin films relative to their bulk counterparts but in the DCMS and HiPIMS film, the measured resistivities at point C are both close to the resistivity of bulk Cr_2AlC ($\sim 7 \times 10^{-7} \Omega \cdot \text{m}$ [3]). Comparison between bulk and thin film resistivity in MAX phase materials can be problematic (for the reasons outlined below) but Emmerlich et al. [5] reported that resistivities of 25–30 $\mu\Omega \text{ cm}$ were measured from DCMS Ti_3SiC_2 MAX phase films; only slightly higher than the 22 $\mu\Omega \text{ cm}$ reported for the bulk material.

One of the most important and difficult challenges remaining in MAX phase research is to understand their electrical properties. In order to interpret the conductivity measurements, the microstructure, orientation, composition (including the exact stoichiometry) and phase purity (including phase content and distribution of any secondary phases) of the MAX phase must be known precisely [1]. Determination of the anisotropy in conductivity requires direct measurement of the conductivity along different crystal orientations, only possible with bulk single crystals much larger than the $\sim 15 \text{ nm}$ diameter grains (calculated by Scherrer's analysis) in the DCMS/HiPIMS films grown here.

Table 1. The composition and resistivity of the DCMS and HiPIMS coatings at the locations indicated in Figure 2(a).

Position	Method	Composition (%) ($\pm 5\%$)			Resistivity ($\Omega \cdot \text{m}$)
		Cr	Al	C	
A	DCMS	59	18	23	2×10^{-6}

	HiPIMS	62	19	19	5×10^{-7}
B	DCMS	61	28	11	2×10^{-6}
	HiPIMS	59	29	12	5×10^{-7}
C	DCMS	57	24	19	8×10^{-7}
	HiPIMS	56	22	22	9×10^{-7}
D	DCMS	58	22	20	5×10^{-6}
	HiPIMS	48	30	22	1×10^{-6}

X-ray diffractograms from selected positions are shown in Figure 4. Diffractograms from the DCMS coating at positions B and C are omitted since they were similar to the corresponding diffractograms from the HiPIMS coating. The peaks are indexed to Cr_2AlC MAX phase material [15] (labelled M), Cr_2Al metallic alloy [15, 30] (labelled A) and Cr_3C_2 chromium carbide [15, 31] (labelled C). The Cr_2AlC MAX phase appears at all the positions across both the DCMS and HiPIMS deposited coatings. The Cr_2Al alloy was most prevalent at positions A and B, closest to the metal magnetron targets (Cr and Al). Similarly, the Cr_3C_2 carbide could be seen in both positions A and D (closest to the Cr and C targets). Position C (equidistant from each of the targets) shows none of the alloy or carbide peaks and has the sharpest MAX phase M(103) peak. In the diffractograms taken from position D, the MAX phase (103) peak is sharper in the HiPIMS coating but the (002) peak is absent. This shows that the energetic deposition has resulted in a change in preferred orientation in the MAX phase..

Figure 4. Glancing angle X-ray diffractograms from the DCMS and HiPIMS combinatorial coatings at the indicated sample positions (see Figure 2(a)).

Figure 5 shows the near-edge absorption fine structure (NEXAFS) of the (a) Cr L-edges and (b) Al K-edges from the HiPIMS and DCMS coatings. In the Cr L-edges, the L3 and L2 peaks are located at approximately 575 and 584 eV. The L3 peak is split into two sub-peaks (a and b) at approximately 575 eV and 576 eV, indicating the presence of two dominant bonding states with the relative intensities varying according to position. Lifetime broadening causes this splitting to be less clear in the L2 peak [32]. The L3 sub-peak (a) at 575 eV could originate from Cr-Cr bonding or Cr-C bonding [33]. Given there is no evidence of Cr metal in these coatings, this sub-peak is likely to originate from either Cr_3C_2 or from the strong M-X (Cr-C) bonds

within MAX phase Cr_2AlC . The second sub-peak (b) at approximately 576 eV is consistent with Cr-O bonding [34] and is likely to originate from a surface oxide.

In the Al K-edge (Figure 5(b)), the peak located at ~1560 eV (peak e) is attributed to Al-Al bonding [35], consistent with the A-A planar bonding within the MAX phase structure. At location A, this feature is less intense in the DCMS coating, suggesting less of the metallic Al-Al bonding is present. This is consistent with the less intense XRD M peaks exhibited by the DCMS coating (Figure 4). The peaks located at ~1562 eV (peak f), ~1566 eV (peak g) and ~1568 eV (peak h) originate from aluminium bonded to oxygen in either a disordered octahedral (peaks f and h) or tetrahedral (peak g) arrangement [36,37]. The peak located at 1571 eV (peak i) is due to multiple scattering events [38]. These peaks are all attributed to surface oxide.

Figure 5. Soft x-ray absorption spectra from sample positions, as indicated (see Fig. 1a). Shown here are the (a) Cr L-edges and the (b) Al K-edges. In each plot, the spectra from the DCMS and HiPIMS coatings are respectively shown as grey and red lines.

The above results show that at location C, the DCMS and HiPIMS films were almost identical in structure, composition and electrical resistivity. In both films, X-ray diffraction from this location consisted of peaks that could only be attributed to MAX phase Cr_2AlC . We therefore believe that the coatings contained mainly MAX phase, an assertion supported by their low electrical resistivity. No benefit due to the energetic HiPIMS plasma was apparent, possibly due to the separation between the Cr target (in HiPIMS mode) and location C being the largest. At position D, XRD suggested that the MAX phase was dominant in the HiPIMS film whilst the DCMS film contained carbide and alloy phases. This was probably due to the different compositions, with the DCMS and HiPIMS films respectively, Cr rich and Al rich. Differential sputtering due to the more energetic HiPIMS plasma may have resulted in the significant compositional changes at this location.

4. Conclusions

Combinatorial deposition was used to prepare Cr_xAlC_y coatings on sapphire wafers using both DCMS and HiPIMS. XRD revealed the presence of MAX phase Cr_2AlC , the intermetallic phase Cr_2Al and the carbide phase Cr_3C_2 in both films. Only the MAX phase Cr_2AlC was observed at all locations in both DCMS and HiPIMS coatings. NEXAFS measurements of the major bonding states confirmed the presence of the M-X and A-A bonding in the MAX phase. According to XRD, compositional- and electrical- measurements, the same location within the DCMS and HiPIMS coatings contained almost pure MAX phase. At this location, the composition, structure and electrical resistivity were almost identical, indicating that the additional energy in the HiPIMS plasma did not significantly alter the properties of the coating.

5. Acknowledgements

The authors acknowledge support from the Australian Research Council (ARC), the soft X-ray beam line at the Australian Synchrotron and the RMIT Microscopy & Microanalysis Facility (RMMF). P. E acknowledges support from the Swedish Foundation for Strategic Research through the Synergy Grant FUNCASE.

7. References

- [1] P. Eklund, M. Beckers, U. Jansson, H. Högberg, L. Hultman, The $M_{n+1}AX_n$ phases: Materials science and thin-film processing, *Thin Solid Films* 518 (2010) 1851-1878.
- [2] Z. M. Sun, Progress in research and development on MAX phases: a family of layered ternary compounds, *Int. Mater. Rev.* 56 (2011) 143-166.
- [3] M. W. Barsoum, *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides*, John Wiley & Sons: New York, 2013.
- [4] J.J. Nickl, K.K. Schweitzer, P. Luxenberg, Gasphasenabscheidung Im System Ti-Si-C, *J. Less-Common MET*, 26 (1972) 335-353.
- [5] J. Emmerlich, H. Hogberg, S. Sasvari, P.O.A. Persson, L. Hultman, J. Palmquist, U. Jansson, J.M. Molina-Aldareguia, Z. Czigany, Growth of Ti_3SiC_2 thin films by elemental target magnetron sputtering, *J. Appl. Phys.* 96 (2004) 4817-4826.
- [6] P. Eklund, M. Beckers, J. Frodelius, H. Hogberg, L. Hultman, Magnetron sputtering of Ti_3SiC_2 thin films from a compound target, *J. Vac. Sci. Technol. A*, 25 (2007) 1381-1388.
- [7] P. Eklund, M. Bugnet, V. Mauchamp, S. Dubois, C. Tromas, J. Jensen, L. Piraux, L. Gence, M. Jaouen, and T. Cabioc'h, Epitaxial growth and electrical transport properties of Cr_2GeC thin films, *Phys. Rev. B* 84 (2011) 075424.
- [8] P. Eklund, M. Dahlqvist, O. Tengstrand, L. Hultman, J. Lu, N. Nedfors, U. Jansson, and J. Rosén, Discovery of the Ternary Nanolaminated Compound Nb_2GeC by a Systematic Theoretical-Experimental Approach, *Phys. Rev. Lett.* 109 (2012) 035502.
- [9] H. Högberg, L. Hultman, J. Emmerlich, T. Joelsson, P. Eklund, J.M. Molina-Aldareguia, J.-P. Palmquist, O. Wilhelmsson, U. Jansson, Growth and characterization of MAX-phase thin films, *Surf. Coat. Technol.*, 193 (2005) 6-10.
- [10] T.H. Scabarozi, J. Roche, A. Rosenfeld, S.H. Lim, L.Salamanca-Riba, G. Yong, I. Takeuchi, M.W. Barsoum, J.D. Hettinger, S.E. Lofland, Synthesis and characterization of Nb_2AlC thin films, *Thin Solid Films*, 517 (2009) 2920-2923.
- [11] T.H. Scabarozi, C. Gennaoui, J. Roche, T. Flemming, K. Wittenberger, P. Hann, B. Adamson, A. Rosenfeld, M.W. Barsoum, J.D. Hettinger, S.E. Lofland, Combinatorial investigation of $(Ti_{1-x}Nb_x)_2AlC$, *Appl. Phys. Lett.* 95 (2009) 101907.

- [12] D.P. Sigumonrong, J. Zhang, Y. Zhou, D. Music, J. Emmerlich, J. Mayer, and J. M. Schneider, Interfacial structure of V_2AlC thin films deposited on View the (1120) source-sapphire, *Scripta Mater.* 64 (2011) 347-350.
- [13] Q. M. Wang, W. Garkas, A. Flores Renteria, C. Leyens, H. W. Lee, and K. H. Kim, Oxidation behaviour of Ti–Al–C films composed mainly of a Ti_2AlC phase, *Corros. Sci.* 53 (2011) 2948.
- [14] Z. Zheng, Y. Nie, L. Shen, J. Chai, J. Pan, L. M. Wong, M. B. Sullivan, H. Jin, and S. J. Wang, Charge Distribution in the Single Crystalline Ti_2AlN Thin Films Grown on $MgO(111)$ Substrates, *The J. Phys. Chem. C* 117 (2013) 11656.
- [15] R. Mertens, Z. Sun, D. Music, J.M. Schneider, Effect of the Composition on the Structure of Cr–Al–C Investigated by Combinatorial Thin Film Synthesis and ab Initio Calculations, *Advanced Engineering Materials* 6 (2004) 903-907.
- [16] R. Grieseler, B. Hähnlein, M. Stubenrauch, T. Kups, M. Wilke, M. Hopfeld, J. Pezoldt, and P. Schaaf, Nanostructured plasma etched, magnetron sputtered nanolaminar Cr_2AlC MAX phase thin films, *Appl. Surf. Sci.* 292 (2014) 997-1001.
- [17] V. Vishnyakov, O. Crisan, P. Dobrosz, and J. S. Colligon, Ion sputter-deposition and in-air crystallisation of Cr_2AlC films, *Vacuum* 100 (2014) 61-65.
- [18] J.J. Li, Y.H. Qian, D. Niu, M.M. Zhang, Z.M. Liu, M.S. Li, Phase formation and microstructure evolution of arc ion deposited Cr_2AlC coating after heat treatment, *Appl. Surf. Sci.* 263 (2012) 457-464.
- [19] M. Baben, L. Shang, J. Emmerlich, J.M. Schneider, Oxygen incorporation in M_2AlC ($M = Ti, V, Cr$), *Acta Mater.* 60 (2012) 4810-4818.
- [20] A. Abdulkadhim, T. Takahashi, V. Schnabel, M. Hans, C. Polzer, P. Polcik, and J.M. Schneider, Crystallization kinetics of amorphous Cr_2AlC thin films, *Surf. Coat. Technol.* 206 (2011) 599-603.
- [21] J. J. Li, M. S. Li, H. M. Xiang, X. P. Lu, and Y. C. Zhou, Short-term oxidation resistance and degradation of Cr_2AlC coating on M38G superalloy at 900–1100 °C, *Corros. Sci.* 53 (2011) 3813-3820.
- [22] J. J. Li, L. F. Hu, F. Z. Li, M. S. Li, and Y. C. Zhou, Variation of microstructure and composition of the Cr_2AlC coating prepared by sputtering at 370 and 500 °C, *Surf. Coat. Technol.* 204 (2010) 3838-3845.
- [23] C. Walter, D.P. Sigumonrong, T. El-Raghy, J.M. Schneider, Towards large area deposition of Cr_2AlC on steel, *Thin Solid Films*, 515 (2006) 389-393.

- [24] U. Helmersson, M. Lattemann, J. Bohlmark, A.P. Ehasarian, J.T. Gudmundsson, Ionized physical vapor deposition (IPVD): A review of technology and applications, *Thin Solid Films* 513 (2006) 1-24.
- [25] A. Anders, A structure zone diagram including plasma-based deposition and ion etching, *Thin Solid Films* 518 (2010) 4087-4090.
- [26] Y. Jiang, S. Mráz, J.M. Schneider, Growth of V–Al–C thin films by direct current and high power impulse magnetron sputtering from a powder metallurgical composite target, *Thin Solid Films* 538 (2013) 1-6.
- [27] J. Alami, P. Eklund, J. Emmerlich, O. Wilhelmsson, U. Jansson, H. Högberg, L. Hultman, U. Helmersson, High-power impulse magnetron sputtering of Ti–Si–C thin films from a Ti_3SiC_2 compound target, *Thin Solid Films* 515 (2006) 1731-1736.
- [28] T.F. Zhang, Q. M. Wang, J. Lee, P. Ke, R. Nowak, K.H. Kim, Nanocrystalline thin films synthesized from a Ti_2AlN compound target by high power impulse magnetron sputtering technique, *Surf. Coat. Technol.* 212 (2012) 199-206.
- [29] T. Gebhardt, D. Music, T. Takahashi, J.M. Schneider, Combinatorial thin film materials science: From alloy discovery and optimization to alloy design, *Thin Solid Films* 520 (2012) 5491-5499.
- [30] A.P. Ehasarian, R. New, W.-D. Munz, L. Hultman, U. Helmersson and V. Kouznetsov, Influence of high power densities on the composition of pulsed magnetron plasmas, *Vacuum* 65 (2002) 147-154.
- [31] The International Centre for Diffraction Data (ICDD) Card 00-029-0016, AlCr_2 , <http://www.icdd.com/index.htm>.
- [32] The International Centre for Diffraction Data (ICDD) Card 00-035-0804, Cr_3C_2 (Tongbaite), <http://www.icdd.com/index.htm>.
- [33] S.O. Kucheyev, T. van Buuren, T.F. Baumann, J.H. Satcher, Jr., T.M. Willey, R.W. Meulenberg, T.E. Felter, J.F. Poco, S.A. Gammon, L.J. Terminello, Electronic structure of titania aerogels from soft x-ray absorption spectroscopy, *Phys. Rev. B* 69 (2004) 245102.
- [34] R.D. Leapman, L.A. Grunes, P.L. Fejes, Study of the $L_{2,3}$ edges in the 3d transition metals and their oxides by electron-energy-loss spectroscopy with comparison to theory, *Phys. Rev. B* 26 (1982) 614-635.
- [35] T.L. Daulton, B.J. Little, K. Lowe, J. Jones-Meehan, In Situ Environmental Cell–Transmission Electron Microscopy Study of Microbial Reduction of Chromium(VI) Using Electron Energy Loss Spectroscopy, *Microsc. Microanal.* 7 (2001) 470-485.

- [36] A.N. Buckley, A.J. Hartmann, R.N. Lamb, A.P.J. Stampfl, J.W. Freeland, I. Coulthard, Threshold Al KLL Auger spectra of oxidized aluminium foils, *Surf. Interface Anal.* 35 (2003) 922-931.
- [37] J.A. van Bokhoven, H. Sambe, D.E. Ramaker, D.C. Koningsberger, Al K-Edge Near-Edge X-ray Absorption Fine Structure (NEXAFS) Study on the Coordination Structure of Aluminum in Minerals and Y Zeolites, *J. Phys. Chem. B* 103 (1999) 7557-7564.
- [38] Y. Kato, K.-i. Shimizu, N. Matsushita, T. Yoshida, H. Yoshida, A. Satsuma, T. Hattori, Quantification of aluminium coordinations in alumina and silica–alumina by Al K-edge XANES, *Phys. Chem. Chem. Phys.* 3 (2001) 1925-1929.
- [39] K. Shimizu, Y. Kato, H. Yoshida, A. Satsuma, T. Hattori, T. Yoshida, Al K-edge XANES study for the quantification of aluminium coordinations in Alumina, *Chem. Commun.* (1999) 1681-1682.

Highlights

- $\text{Cr}_x\text{Al}_y\text{C}$ coatings on sapphire wafers were combinatorially deposited using both DCMS and HiPIMS.
- X-ray diffraction revealed the presence of intermetallic, carbide and MAX phases on the coatings.
- A region of the HiPIMS coating contained almost pure MAX phase.
- X-ray absorption spectroscopy confirmed the presence of the M-X and A-A bonding in the MAX phase.
- The HiPIMS coating generally exhibited lower resistivities than the DCMS coating.