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

Original Publication:

Andrejs Petruhins, Arni Sigurdur Ingason, Martin Dahlgqvist, Aurelija Mockutė, Muhammad Junaid, Jens Birch, Jun Lu, Lars Hultman, Per O A Persson and Johanna Rosén, Phase stability of $\text{Cr}_{n+1}\text{GaC}_n$ MAX phases from first principles and Cr_2GaC thin-film synthesis using magnetron sputtering from elemental targets, 2013, Physica Status Solidi. Rapid Research Letters, (7), 11, 971-974.

<http://dx.doi.org/10.1002/pssr.201308025>

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<http://www.wiley-vch.de/publish/en/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-103307>

Phase stability of $\text{Cr}_{n+1}\text{GaC}_n$ MAX-phases from first principles and Cr_2GaC thin film synthesis using magnetron sputtering from elemental targets

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Keywords MAX phases; *ab-initio*; magnetron sputtering; epitaxial thin films.

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Ab-initio calculations have been used to investigate the phase stability and magnetic state of $\text{Cr}_{n+1}\text{GaC}_n$ MAX phase. Cr_2GaC ($n=1$) was predicted to be stable, with a ground state corresponding to antiferromagnetic spin configuration. Thin film synthesis by magnetron sputtering from elemental targets, including liquid Ga, shows formation of Cr_2GaC , previously only attained from bulk

synthesis methods. Films were deposited at 650 °C on MgO(111) substrates. X-ray diffraction and high resolution transmission electron microscopy show epitaxial growth of (000 ℓ) MAX phase.

1 Introduction MAX phases constitute a class of nanolaminated ternary carbides and nitrides, described by the general formula $M_{n+1}AX_n$ ($n=1-3$), where M is a transition metal, A is an A-group element and X is carbon or nitrogen. Cr_2GaC along with more than 40 other phases have been known as H-phases since 1960s[1]. Nowadays the term MAX phases is used to describe this class of materials, for which the scientific interest was reignited in the 1990s after synthesis of phase pure samples with a unique combination of metallic and ceramic properties; good thermal and electrical conductivity, being easily machinable, and resistant to oxidation and thermal shock[2].

Cr_2GaC is traditionally synthesized from bulk synthesis methods, such as hot isostatic pressing at 1200 °C[3] or from direct reaction between constituting elements[4]. Bulk Cr_2GaC can also be formed from a metallic melt of the elements, generated by an excess Ga, at 1300 °C [5]. MAX phases in general have previously been synthesized as thin films using physical vapour deposition (PVD) methods such as magnetron sputtering[6] and cathodic arc[7], with process temperatures considerably lower than those of bulk synthesis. Although Ga is a very important element for semiconductor applications, thin film synthesis of related compounds is usually performed by chemical vapour depo-

sition (CVD) and molecular beam epitaxy (MBE)[8,9], due to challenges associated with the liquid state of Ga (melting point 30 °C) during commonly employed PVD synthesis conditions. Only a few groups have successfully demonstrated use of liquid Ga sputtering targets for epitaxial growth of GaN[10,11]. This is a route that we have further pursued in this work.

In this letter we perform theoretical analysis based on *ab-initio* calculations to explore the phase stability and magnetic state of $\text{Cr}_{n+1}\text{GaC}_n$. Only Cr_2GaC ($n=1$) is predicted to be stable, and corresponding thin film synthesis of epitaxial Cr_2GaC MAX phase from co-sputtering of Ga, Cr, and C is presented. The results show a new method for thin film synthesis of MAX phases involving liquid targets, which opens a possibility to explore a wide range of Ga based materials that have not previously been made as thin films.

2 Calculation details All *ab-initio* calculations have been performed using the projector augmented-wave (PAW) method[12] as implemented within VASP[13,14]. Exchange and correlation effects were treated in the framework of the Perdew-Burke-Ernzerhof (PBE)[15] generalized gradient approximation (GGA) in its spin-polarized form. The energy cutoff for the plane waves was

400 eV. Sampling of the Brillouin zone was done using the Monkhorst-Pack scheme[16]. The calculated total energy for phases included in this work is converged to within 0.1 meV/atom in terms of k -point sampling and energy cutoff. To find the optimal structure for each phase, optimization of the geometry, atomic coordinates, volume, shape of unit cell, and c/a ratio (when necessary) was performed. Non-magnetic (NM), ferromagnetic (FM), and different antiferromagnetic (AFM) states were tested for each phase, and the configuration with lowest energy was included in the phase stability investigation.

In order to theoretically investigate the phase stability of a specific MAX phase, we use the approach introduced by Dahlqvist et al.[17,18]. A linear optimization procedure based on the simplex method is applied, in which all known competing phases as well as hypothetical competing phases based on neighbouring and similar systems are included for comparison. The stability of $\text{Cr}_{n+1}\text{GaC}_n$ ($n=1-3$) relative to the identified most stable combination of competing phases (cp) is then expressed in terms of formation enthalpy ΔH_{cp} , according to

$$\Delta H_{\text{cp}}(\text{Cr}_{n+1}\text{GaC}_n) = E(\text{Cr}_{n+1}\text{GaC}_n) - \sum_i x_i E_i \quad (1)$$

where E is the energy of the respective MAX phase, which is compared to the sum of energies E_i that should be minimized subject to the constraints of different amount x_i of compound i , altogether corresponding to MAX phase stoichiometry. Hence, a negative value of ΔH_{cp} indicates a stable MAX phase.

This approach has previously been used to verify the existence of a large set of well-known carbide and nitride MAX phases, with 100% consistency for existing phases, see, for example, Ref. [18]. The approach has also been used for predictions of new stable combinations of M , A , and X elements, which subsequently have been realized experimentally, e.g., Nb_2GeC [19], $(\text{Cr,Mn})_2\text{AlC}$ [20,21] and $(\text{Cr,Mn})_2\text{GeC}$ [22].

In the present work we have considered several collinear magnetic configurations of Cr_2GaC . In a ferromagnetic (FM) configuration all M atoms have the same spin orientation. For an antiferromagnetic (AFM) states, the set of possible configurations are many, although in practice limited to configurations which maximize the number of anti-parallel moments on a few nearest neighbour shells. We have considered 5 different collinear AFM configurations in addition to the FM and the non-magnetic (NM) state. For further details see Ref. [23]. It is worth noting that for some AFM configurations, the original unit cell ($1 \times 1 \times 1$) with 8 atoms is insufficient, and needs to be expanded into an in-plane supercell of at least $2 \times 1 \times 1$ in order to have opposite spins for M atoms within the same layer. This motivates the here used notation of in-AFM1 as the identified lowest energy magnetic state.

3 Experimental details DC magnetron sputtering from elemental targets was performed in an ultra-high vacuum chamber at a pressure of 0.6 Pa Ar, with a base pressure of 10^{-7} Pa. Cr_2GaC thin films were grown epitaxially on $10 \times 10 \times 0.5 \text{ mm}$ $\text{MgO}(111)$ substrates (MTI Corp.) at 650°C . Sputtering targets were operated in constant power mode using 50 W, 10 W and 125 W power for Cr, Ga and C, respectively. 3 inch Cr and C sputtering targets were used, positioned confocally at an angle of 35° from the substrate normal. For Ga, a 2 inch concave shaped stainless steel crucible was constructed, into which Ga pellets were melted, creating a flat target surface. The Ga was then cooled down with liquid nitrogen to solidify the material prior to inserting it into the vacuum chamber directly below the substrate. During pre-sputtering the Ga target melted, and thus subsequent sputtering during deposition was performed from a liquid. The $\text{MgO}(111)$ substrates were ultrasonically cleaned in acetone, ethanol and isopropanol, for 10 min each and heated in the vacuum chamber at 750°C for 1 h prior to deposition.

The structural properties of the films were investigated through X-ray diffraction (XRD), using standard θ - 2θ geometry and pole figure measurements in a Panalytical Empyrean MRD with Cu $K\alpha$ radiation ($\lambda=1.54 \text{ \AA}$). Cross-sectional high resolution scanning transmission electron microscopy (HR(S)TEM) imaging was performed using the doubly corrected Linköping Titan.

4 Results and discussion The results from the stability calculations can be found in Table 1. Only Cr_2GaC is predicted to be stable with an identified set of most competing phases being Cr_3C_2 , CrGa_4 and Cr_7C_3 , resulting in a formation enthalpy of $\Delta H_{\text{cp}}=-19 \text{ meV/atom}$. ΔH_{cp} for Cr_3GaC_2 and Cr_4GaC_3 is well above zero, hence indicating that these phases are unstable or at best metastable. These results are consistent with previous bulk synthesis experiments for $\text{Cr}_{n+1}\text{GaC}_n$. Exploring different magnetic configurations of Cr_2GaC , the so called in-AFM1, see Figure 1, was found to have the lowest energy. Similarly, in-AFM1 is also the lowest energy configuration for the Cr_2AlC MAX-phase. The NM, FM, and four additional AFM configurations, explained in Ref. [23] all have energies within +4 meV/atom relative to in-AFM1. The magnetic state of Cr_2AlC as well as Cr_2GaC remains to be experimentally investigated. Synthesized samples are commonly not single crystalline and phase pure, which makes analysis of the magnetic properties of specifically the MAX phase challenging.

Figure 1 shows a schematic of the in-AFM1 spin configuration in the supercell, together with calculated data for cell parameters and magnetic moment. The total magnetic moment per formula unit (f.u.) of the structure is 0, as expected for an AFM configuration. However the Cr atoms have a local magnetic moment of $\pm 0.75 \mu_B$.

Table 1 Identified set of the most competing phases (cp) for $\text{Cr}_{n+1}\text{GaC}_n$ phases ($n=1-3$) with corresponding calculated formation enthalpy ΔH_{cp} . Negative value of ΔH_{cp} indicates a stable phase with respect to decomposition into its competing phases.

$\text{Cr}_{n+1}\text{GaC}_n$ n	Identified set of the most competing phases (cp)	ΔH_{cp} (meV/atom)
1	Cr_3C_2 , CrGa_4 , Cr_7C_3	-19
2	Cr_2GaC , Cr_3C_2 , C	+74
3	Cr_2GaC , Cr_3C_2 , C	+101

Magnetic order	AFM	
a (Å)	2.88
c (Å)	12.54	
Atoms/unit cell	16	
Total magnetic moment (μ_B / f.u.)	0.00	
Local magnetic moment (μ_B / Cr atom)	± 0.75	

Figure 1 Calculated data for the lowest energy magnetic configuration (in-AFM1) of Cr_2GaC . The schematic unit cell to the right shows the Cr atom spin configuration in red (plus sign) and blue (minus sign), while grey and white denote C and Ga atoms, respectively.

Figure 2 shows an X-ray diffractogram of a thin film deposited for 30 min on a $\text{MgO}(111)$ substrate. Reflections originating from the basal $(000l)$ planes of the MAX phase can be seen, as well as peaks from the substrate and an impurity Cr_3Ga phase. The peak intensity and peak area of Cr_3Ga constitutes up to 4 and 3 %, respectively, of the corresponding summarized values. Hence, the film is predominantly composed of MAX phase. A θ offset was determined and set from the 0006 peak of the Cr_2GaC , hence the MgO peaks are significantly reduced. The inset in Figure 2 presents a pole figure at the $(10\bar{1}3)$ position ($2\theta=42.09^\circ$, $d=2.145$ Å), showing a set of peaks at a tilt angle of $\chi=59.4^\circ$, corresponding to the angle between the $(10\bar{1}3)$ and $(000l)$ planes in the Cr_2GaC unit cell. Obtained values are in very good agreement with the $(10\bar{1}3)$ spacing (2.140 Å) and the angle between $(10\bar{1}3)$ and $(000l)$ planes ($\chi=59.19^\circ$) from the calculated structure. A broadening can be seen for three peaks in the pole figure, corresponding to traces of the three fold symmetric $\text{MgO}(200)$.

The XRD measurements allow an estimation of the lattice parameter c to 12.62 Å, as calculated from the (0006) lattice spacing. Furthermore, in-plane ($\chi \approx 90^\circ$) θ - 2θ measurements show a peak at $2\theta=64.51^\circ$, corresponding to the

Figure 2 XRD θ - 2θ scan of a Cr-Ga-C thin film on a $\text{MgO}(111)$ substrate. The inset shows a pole figure at the Cr_2GaC $(10\bar{1}3)$ peak ($2\theta=42.09^\circ$).

Cr_2GaC $(11\bar{2}0)$ spacing, which in turn gives a direct measure of the lattice parameter $a=2.89$ Å. Another peak at $2\theta=62.49^\circ$ is clearly visible, which corresponds to the $(10\bar{1})$ of the MgO substrate, in turn showing the epitaxial relationship between $\text{MgO}[10\bar{1}]$ and $\text{Cr}_2\text{GaC}[11\bar{2}0]$. The experimentally obtained lattice parameters and theoretically calculated values $a=2.88$ Å and $c=12.54$ Å are in good agreement. Furthermore, both a and c are close to those obtained from bulk Cr_2GaC , $a=2.90$ Å and $c=12.63$ Å, as reported by Etzkorn et. al.[5] The experimentally determined unit cell volume of 91.2 Å³ is only about 1.2% larger than the theoretically predicted 90.1 Å³ and 0.9% smaller than 92.1 Å³ in Ref[5].

Figure 3 HR(S)TEM images of the Cr_2GaC MAX phase presented with increasing magnification from a) to c).

The HR(S)TEM images in Figure 3 reveal the microstructure of a film grown for 10 min on a MgO(111) substrate. At low magnification (Figure 3a) the film exhibits an island-like appearance with surface cusps at the island boundaries. The particles exhibit a high crystal quality and, as can be seen by the medium-magnification image in Figure 3b. At high magnification, the characteristic stacking sequence of the nanolaminated MAX phase is evident, as shown in Figure 3c. In addition, energy dispersive X-ray spectroscopy (EDX) shows presence of Cr, Ga and C with Cr:Ga ratio of 2:1, consistent with the chemical formula of the Cr_2GaC MAX phase. A few grains of Cr_3Ga could be identified with HR(S)TEM (not shown here), which is in line with the XRD presented in Figure 3. It should be noted that Cr_3Ga was included as a competing phase in the stability calculations, though not identified one of the most competing phases subject to the constraint of an elemental film composition corresponding to the MAX phase stoichiometry. It is therefore likely that the formation of Cr_3Ga is due to excess Cr or deficiency in C. To avoid this impurity phase, further optimisation of deposition conditions is necessary, for fine control of film stoichiometry.

Although sputtering from a liquid Ga target has to our knowledge previously been limited to reactive sputter deposition of GaN[10,11], the present letter demonstrates that the method can be used also for synthesis of epitaxial Cr_2GaC MAX phase. There are, however, crucial steps to be considered for a successful process control. Ga and Al can readily form a eutectic alloy at 2.1 at.% Al[24] which could cause embrittlement of Al by Ga diffusion along grain boundaries[25]. Therefore, direct Ga-Al contact should be avoided. Furthermore, the discharge gas can get trapped inside the liquid Ga target during sputtering. Corresponding gas accumulation can lead to bursts of the target material and formation of Ga droplets reaching the substrate, which in turn can be detrimental to film quality. This can be avoided by balancing cooling efficiency of the sputtering target with the sputtering power. During co-sputtering of several targets, the Ga surface can become contaminated by impurities, which is evident from partial solidification of the target surface after some time of operation. The presence of these foreign species do not exceed 1-2 at.%, as measured by EDX, and can be further reduced by shielding.

To conclude, *ab-initio* calculations of $\text{Cr}_{n+1}\text{GaC}_n$ MAX phases predicts phase stability of exclusively Cr_2GaC . It is at least in part stabilized by an in-plane antiferromagnetic spin configuration. We have also demonstrated thin film growth of epitaxial Cr_2GaC MAX phase from elemental targets, including liquid Ga. Hence, a new physical vapour deposition method for depositing Ga-based MAX phases is presented, allowing a reduction of synthesis temperature of at least 600 °C. These results are encouraging for thin film studies of other Ga-based materials.

Acknowledgements The research was funded by the European Research Council under the European Community Seventh Framework Program (FP7/2007-2013)/ERC Grant agree-

ment no [258509]. J. Rosen acknowledges funding from the Swedish Research Council (VR) grant no. 621-2012-442, and from the Knut and Alice Wallenberg (KAW) Fellowship program. P.O.Å Persson acknowledges VR for funding. L. Hultman and P.O.Å Persson acknowledge the KAW Foundation for the Ultra Electron Microscopy Laboratory in Linköping. The calculations were carried out using supercomputer resources provided by the Swedish National Infrastructure for Computing (SNIC) at the High Performance Computing Centre North (HPC2N).

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