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Toward Structural Optimization of MAX Phases as Epitaxial Thin Films

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Prompted by the increased focus on MAX phase materials and their two-dimensional counterparts MXenes, a brief review of the current state of affairs in the synthesis of MAX phases as epitaxial thin films is given. Current methods for synthesis are discussed and suggestions are given on how to increase the material quality even further as well as arrive at those conditions faster. Samples were prepared to exemplify the most common issues involved with the synthesis, and through suggested paths for resolving these issues we attain samples of a quality beyond what has previously been reported.

Keywords: MAX Phase, Thin Films, Reproducible Materials Synthesis, Sample Quality

Impact Statement: We aim to address the quality of MAX phase thin films and suggest a more robust route for the synthesis of samples of consistent reproducible quality.

Introduction MAX phases are a family of laminated ternary carbide or nitride materials that have received considerable amount of interest in the past two decades. They have the general chemical formula $M_{n+1}AX_n$ ($n = 1 - 3$), where M is an early transition metal, A is an A-group element and X is carbon or nitrogen.[1,2] The structure is inherently nanolaminated where the constituting elements form complete separate layers. As an example, the so-called 211 phase ($n = 1$) has the repeated $M - X - M - A$ stacking sequence, but the bonding between the layers is different; the $M - A$ bonds are more metallic and weak, while the $M - X$ bonds are covalent and much stronger. This gives the material unique properties that are both metallic; good electrical and thermal conductivity, and ceramic; high thermal stability and high melting point.[3] Additionally, the layered structure causes properties such as electrical conductivity to be anisotropic.[4] MAX phases are commonly synthesized using bulk methods such as pressureless sintering, hot pressing and reactive hot isostatic pressing.[5] Bulk methods yield polycrystalline samples of varying phase purities although phase pure samples are not uncommon. The quality of such samples is typically evaluated based on the phase purity as well as the grain size. More

recently very large (area of a few mm^2) single crystal samples have been obtained from high-temperature solution growth.[6] This is promising for the characterization and evaluation of the intrinsic anisotropic properties of these materials, but if they are to be integrated in functional electronic devices for instance, other methods to obtain high-quality samples are needed.

Since 2002,[7] MAX phases have been increasingly synthesized as thin film materials for potential applications such as oxidation-resistant and protective coatings on, e.g. turbine blades,[8] bond coatings on sapphire fibers,[9] and low friction and oxidation-resistant contacts.[10] In the latter examples the focus is primarily on achieving single-phase films of high density, but steps toward making high-quality single crystal samples have mostly been taken in the past 5 years. A routine method to synthesize these materials in thin film form is physical vapor deposition, such as cathodic arc,[11,12,13] but most often magnetron sputtering [1,14,15] which combined with a suitable substrate and co-deposition from elemental targets at a relatively high temperature can yield epitaxial single-phase thin films of high crystal quality. Commonly, a buffer layer is grown on the substrate in order to levitate any mismatch between the

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film and substrate, and this layer is typically chosen as the corresponding carbide to the MAX phase, e.g. TiC in the case of Ti_2AlC . A common optimization procedure for film growth is thus to find the parameters for synthesis of the binary carbide and then add the A element, double the amount of M and vary until the MAX phase is attained. The initial values of the deposition parameters are then based on some estimations or calibrations, but the procedure quickly becomes a trial-and-error one.

As the quality of sputtered films has progressively improved, work has started to focus on creating single crystal films for more detailed measurements of the intrinsic properties, initially most commonly with respect to conduction [4,16] but more recently also magnetism.[17–21] In order to realize the full potential of this family of inherently layered materials, the reproducibility and quality of samples have to be improved. To review the current state of affairs, identifying the most important parameters involved and proposing a more consistent synthesis route is the focus of the present paper. An approach, reducing the amount of ad hoc materials synthesis, is presented, allowing faster identification of optimal deposition conditions and reproducible film depositions. Transfer of procedures between different deposition systems is also simplified.

In general, the deposition parameters that define the material's quality, of sputtered thin films, both in terms of structure and composition, are the deposition temperature, pressure, the power applied to the magnetrons, i.e. the outgoing/incoming material flux, and the choice of the substrate. The geometry of the system as well as more subtle parameters such as the placement of pumps and gas inlets influence the results as well though they remain constant. For MAX phase synthesis, competing binary or ternary phases that are close in composition and/or structure are an issue that needs to be considered. These parameters will be discussed in the following sections accompanied by examples of their influence on the film growth. We limit the discussion to carbide MAX phases, being far more explored than corresponding nitrides. Still, even if the discussion is pertinent to nitride MAX phases, the added complications of dealing with reactive sputtering are beyond the scope of the present study.

Quality Definition and Materials Synthesis To start with, we need to define what is meant by MAX phase quality. In the present paper, we focus on epitaxial thin films oriented with the 0001 planes out of the substrate surface, and define the highest quality films as being a single phase, single crystal, smooth film. Samples that are not single phase or have crystal grains that are tilted in different directions are therefore considered to be of lesser quality. When the films have been optimized the point where they are single phase and only oriented in

one direction, X-ray diffraction (XRD) rocking curves of the highest intensity basal peaks are used as a measure of quality, more narrow peaks indicating higher quality. It should be noted, however, that the main part of the discussion below concerning optimizing the deposition conditions pertains also to the synthesis of the polycrystalline material. In general, if crystallinity is a measure of quality, it would move from amorphous to polycrystalline with small grains, to bigger grains, to textured films with increasing degree of texture. Next the texture would extend to the in-plane direction until finally coming to epitaxy. Generally, when textured or polycrystalline films are being used for a specific application, quality is measured by the performance of parameter such as hardness, conduction and resistance to corrosion that may or may not be correlated with crystal quality which then may not be studied in depth.

Another issue that needs to be considered is the composition of the material, both in terms of vacancies and possible variations of composition from composite targets for example. The films can look perfect from XRD while only high-resolution transmission electron microscopy combined with energy-dispersive X-ray spectroscopy (EDX) can be used to map out the elemental composition and determine the quality from a more broad perspective. The present discussion focuses on structural quality so the influence of composition is only relevant when it affects the structure.

As illustrative examples, selected samples were deposited for the present study (not published elsewhere). The films were grown in a confocal magnetron sputtering system (ultra-high vacuum) described in detail in [22]. Prior to growth the substrates were cleaned in acetone, ethanol and isopropanol for 10 min each in an ultrasonic bath. They were then loaded into the system and heated to the desired temperature where they were kept for at least 10 min prior to growth. The temperature was measured with a reference thermocouple close to the heater and a pyrometer. Structural information post deposition was obtained by XRD and reflection (XRR) using a Panalytical Empyrean MRD system equipped with a CuK source. For $\theta - 2\theta$ measurements, the tube was in line focus with a hybrid mirror on the incident side and a 0.27° collimator on the diffracted side.

1. Important Parameters for Optimal Film Growth

1.1. Substrate Temperature; the Case of Ti_2AlC .

Generally, MAX phases require high deposition temperatures, such as $900\text{--}1000^\circ\text{C}$ (Ti_3SiC_2 , Ti_3GeC_2 , Ti_2AlC , Ti_3AlC_2), in order to form although they are moderate for the growth of thin films compared with bulk synthesis.[23] This is generally attributed to the layered crystal structure since atoms need to transverse whole

layers in order to diffuse through the film.[24] This high temperature can cause several issues when trying to arrive at the optimal growth conditions due to the vastly different sublimation rates of the elements. A typical example would be Ti_2AlC that routinely is deposited at 900°C on Al_2O_3 [0001] substrates. First to notice is the well-known reaction between the routinely grown buffer layer TiC_x and the substrate seen by Wilhelmsen et al. [24] and further studied by Persson et al. [25] who state that their results indicate that Al_2O_3 is not an ideal substrate for the growth of transition metal carbides or MAX phase films. Such a reaction can also be seen in the case of $\text{Ti}_2\text{AlC} - \text{TiN} - \text{Al}_2\text{O}_3$ [26] and for Si-based MAX phases.[27] Secondly, by using tabulated values of the vapor pressure at different temperatures the rate of sublimation r_{sub} can be derived from

$$r_{\text{sub}} = \frac{P_v N_A}{\sqrt{2\pi MRT}}, \quad (1)$$

where P_v is the vapor pressure, M the molar mass, R the gas constant, N_A Avogadro's constant and T the temperature. Using this equation we arrive at, for Al 1.9×10^{19} [atoms/(second cm^2)], Ti 3.7×10^{13} [atoms/(second cm^2)] at $T = 900^\circ\text{C}$, a difference of six orders of magnitude. Clearly, this is valid for single element material, and the dynamics during multi-element deposition is more complicated and not all Al is evaporated when the MAX phase starts to form. However, it does show that aiming for the correct element ratios with respect to the desired phase is not possible.

This sensitivity of the sublimation to the temperature means that by changing the deposition temperature one is effectively also changing the ratio of the incoming elements. A typical optimization procedure is to start with a given temperature; the composition (fluxes) is varied until the phase starts to form and then the temperature is changed for further optimization. With the sublimation in mind, it should be clear that for each temperature, the ratios have to be tuned again, at least for those MAX phases that contain materials with low vapor pressure and require high deposition temperatures.

Another aspect arises when using a target composed of two elements that have vastly different sublimation rates. Here, the issue is similar; the ratio of the two elements in the film will depend on the temperature of the substrate with no way to adjust the rates. This can cause problems with reproducibility since in order to obtain the same results from different runs, the temperature needs to be precisely the same and the optimization procedure gets more complex since one cannot compensate for the lack of one element by increasing the individual flux. The sensitivity of the quality of a grown film to the substrate temperature is also apparent when sublimation is not a large issue such as for $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$ deposited from a composite Cr/Mn target along with Ga

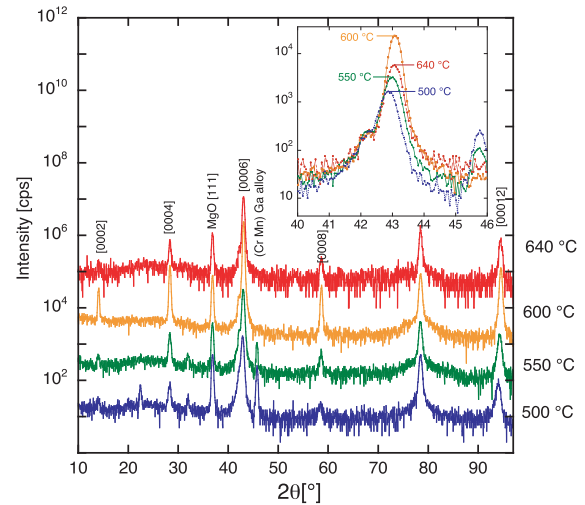


Figure 1. (Colour online) Diffractograms of four $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$ films grown on MgO at different temperatures. The scans are offset for clarity and the inset shows a zoom in on the 0006 peak to show clearly the difference in quality with temperature.

and C. Resulting high-quality material has been grown epitaxially on MgO, SiC and sapphire, see [21]. Figure 1 shows diffractograms of films grown on MgO at the same conditions but at different substrate temperatures. It is clearly shown that there is an optimal temperature for attaining the highest quality, and with a significant reduction in quality at $\sim 40^\circ$ higher or lower temperature. The figure also shows the appearance of a competing phase at lower temperature, most likely a (Cr Mn)Ga intermetallic alloy at lower temperatures with peaks appearing at $\sim 22^\circ$, 32° and 46° .

1.2. Choice of Substrate; the Case of Mn_2GaC .

If we focus on epitaxial growth of MAX phases with the 000/ direction out-of-plane the substrate needs to have a hexagonal lattice in-plane and an a -parameter between 2.80 and $3.5 \text{ \AA}$. This allows some hexagonal materials as well as cubic materials oriented in the (111)-direction. Table 1 lists commonly used substrates as well as potential choices. It should be noted that for cubic materials such as MgO, the in-plane epitaxial relationship will be $[11\bar{2}0]_{\text{MAX}} \parallel [10\bar{1}]_{\text{MgO}}$ in the film plane and $(0001)_{\text{MAX}} \parallel (111)_{\text{MgO}}$ out of the plane. It should also be said that finding the epitaxial relationship between the MAX phase and the most commonly used substrate, sapphire is not trivial. Commonly, the $[11\bar{2}0]$ plane in the MAX phase is found to be parallel with the $[100]$ in sapphire as in the case of Ti_2AlC were it is rotated 30° with respect to the $[110]$ [28] but how exactly the film fits on the substrate and what number to use to determine the lattice mismatch can be different between MAX phases, possibly due to domain matching epitaxy allowing for many different orientations.

Table 1. Commonly used substrates as well as some candidates for epitaxial growth of MAX phases.

Substrate	'a' at RT (Å)
MgO [111]	2.982
SrTiO ₃ [111]	2.76
Sapphire [0001]	2.88 ^a
SiC [0001]	3.08
YSZ [111]	3.623

^aThe relevant parameter is not easily obtained due to the complicated nature of the substrate and several possible orientations that yield epitaxial growth.

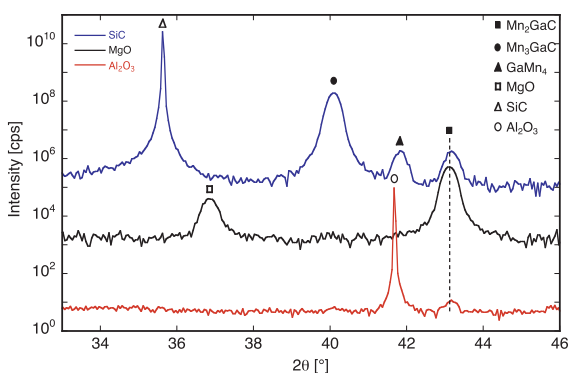


Figure 2. (Colour online) Diffractograms of Mn₂GaC grown at three different substrates. Only the film grown on MgO displayed a single phase epitaxial Mn₂GaC while the film on sapphire showed virtually no signal of the MAX phase. The film on SiC showed a significant amount of the inverse perovskite Mn₃GaC.

The issue of selecting the correct substrate is quite evident from growth of Mn₂GaC, for which $a = 2.90$ Å. Here, the appropriate substrate was found to be MgO and films grown were found to be highly crystalline and smooth.[20] However, using the same conditions, growth on any other substrate yielded little or no visible signal from the MAX phase, as illustrated in Figure 2.

Here, there is no expected or observed reaction occurring between the grown film and the substrate, so the nucleation dynamics are primarily governed by the diffusion rate of the atomic species on the substrate as well as the lattice parameter. The drastic difference in film phase formation between the different substrates can be caused by several factors, such as a slight deviation from the ideal MAX phase stoichiometry and/or several relatively stable phases in the Mn–Ga–C system (Mn₂GaC, Mn₃GaC, etc.), and small deviation in their lattice parameters relative to the substrate, which in turn may change the nucleation dynamics as well as the diffusion rates during the initial stages of growth, promoting one phase over the other. For MAX phases that are less sensitive to the choice of substrate, the sample quality can still be influenced. Figure 3 shows diffractograms from two [Cr_{0.75}Mn_{0.25}]₂GeC films grown on MgO and

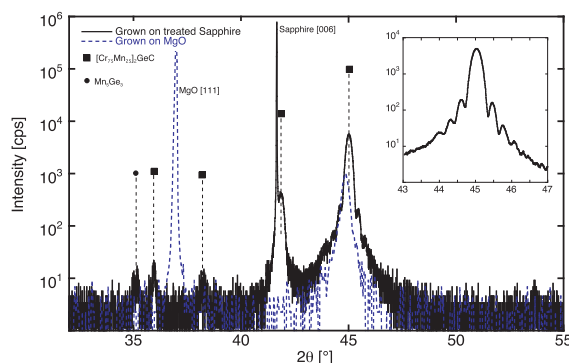


Figure 3. (Colour online) $2\theta/\omega$ scans of [Cr_{0.75}Mn_{0.25}]₂GeC grown on MgO and annealed sapphire. The inset zooms in on the 006 peak at 45 for the film grown on sapphire, illustrating the high crystal quality from the appearance of high-angle Laue fringes.

sapphire that had been annealed according to the procedure described by Wölfling et al.[29] The figure shows high-quality MAX phase, however, the film on treated sapphire is of superior crystal quality as seen by the appearance of high-angle Laue fringes, not previously reported for MAX phases, and the drastic difference in the FWHM of the 006 rocking curves; 0.7° for the one on MgO compared with 0.003° (2520 and 11 arcsec, respectively) for the one grown on sapphire. Additionally, the film on sapphire shows the presence of Mn₅Ge₃ as well as some tilted grains of the MAX phase (the (103) direction growing out of plane). The film on MgO has a lower crystal quality but negligible amount of another phase and no trace of tilted grains. Obviously, the issue is then how to define sample quality. On one hand, the MAX phase on sapphire has far superior crystal quality but the film on MgO was chosen for further analysis as it contained no competing phases or tilted grains.[19] The results do show, however, that obtaining MAX phase films of a quality comparable to that of electronic grade nitrides for instance is possible and should be a goal for further detailed studies of these materials.

The inherent substrate quality is also an issue, as illustrated in a recent publication by Schroeder et al.[30] They show specifically for MgO how substrates sold as single crystal are not always that, and provide a scheme for substrate evaluation prior to film synthesis aimed at high sample quality. The effect of inconsistent substrate quality is that results can be skewed toward lower sample quality even if conditions during growth should promote higher quality. Though the discussion was focused on MgO substrates where this is a widespread problem, monitoring substrate quality applies for other materials as well.

In the event that no appropriate substrate is available that fits the MAX phase in question, growing a complacent buffer layer is possible. This can be done for example by selecting a substrate with a larger lattice

parameter than needed and then deposit a substoichiometric nitride alleviating the lattice mismatch between the MAX phase and substrate.

1.3. Buffer Layer; the Case of Ti_2AlC . The combined effect of initial reactions at the surface and different sublimation rates is the need for a buffer layer, here exemplified in the case of Ti_2AlC . The TiC_x layer is consumed by the substrate to form a MAX phase which in turn facilitates its continued growth. This initial MAX phase, at least for Ti_2AlC growth on Al_2O_3 , will be rich in oxygen, originating from the substrate and substituting for C.[13,25,31] If the buffer layer is either too thick or too thin and the surface seen by the incoming atoms is not the MAX phase, then the Al will sublimate resulting in the delayed growth of the MAX phase. Eventually enough Al is incorporated into the growing film to form the MAX phase.[24] This is illustrated in Figure 4, which shows the diffractogram of two films grown at the same time, one on sapphire and the other on a thick (~ 100 nm) TiN layer grown on sapphire. Both films were deposited with a TiC buffer layer, motivated by previous work. The quality of the MAX phase in both cases is similar as measured with XRD, even slightly better on TiN, with the FWHM of a rocking curve across 0002 peak measuring 0.428° compared with 0.539° for the film grown directly on sapphire. The figure shows diffraction peaks from the MAX phase as well as the substrate. The film grown on TiN additionally shows the TiN 111 and 222 peaks. Both films show the TiC peaks but the intensity of those peaks is much higher in the film grown on TiN (note the scale is logarithmic). This indicates that sapphire supplies Al and oxygen to the grown TiC film in the initial stages of growth allowing for faster formation of a MAX phase, while for TiN there is no supply of Al or O and therefore Al sublimates. There is then a delay in the MAX phase nucleation, resulting in a thicker TiC

layer. The result is that in order to obtain a high-quality Ti_2AlC film on sapphire one should ideally optimize the buffer layer in such a way that it is completely consumed by the substrate, forming a MAX phase layer that in turn can act as a nucleation site for the deposited MAX phase film. If the film is to be phase pure Ti_2AlC , then obtaining this on sapphire will be difficult since the first layer close to the interface will inherently contain O substituting C. If another substrate is chosen, one that does not contain Al, then during the initial nucleation of the film an excess of Al has to be supplied and then reduced once the first layer has been formed. If this is not done there will be a layer of TiC between the substrate and the film, which, depending on the application, might be unacceptable.

2. Competing Phases For synthesis of a MAX phase as a thin film or in bulk form, having knowledge about the stability of the phase with respect to competing phases can be extremely helpful. Dahlqvist et al. [32] have developed a method to assess the feasibility of attempted synthesis by establishing the stability of a given phase with respect to all known competing phases, and with the identification of most competing phases likely to be expected during synthesis. This has led to discoveries of several novel MAX phases, e.g. Nb_2GeC [33] and Mn_2GaC . [20]

The issue of competing phases can be a particularly difficult one when synthesizing thin films due to the textured or epitaxial nature of the structure and since competing phases will potentially have related crystal structures that in some orientations will be almost indistinguishable from that of the MAX phase. Most notable is the example of the Cr_2AlC MAX phase.[34] Here the competing Cr_5Al_8 phase has a BCC structure with a lattice parameter of $a = 9.05 \text{ \AA}$ which grows with the [110] direction out of the plane on for example sapphire. The 110 peak will then be at a position of 13.8° for $\text{CuK}\alpha$ radiation, exactly where the 0002 peak of the corresponding Cr_2AlC MAX phase is expected. The subsequent basal plane peaks of the MAX phase are actually all matched with corresponding $l/0$ peaks of the Cr_5Al_8 , 220 with 0004, 330 with 0006, etc, see, ref. [34] It is therefore extremely difficult to distinguish between the two phases using simple $\theta - 2\theta$ XRD scans only; pole figures and/or other characterization techniques have to be employed to identify and quantify the phases. This also means that when characterizing bulk samples with powder diffraction there is a danger that although identified as phase pure, the samples may contain considerable amounts of competing phases where diffraction peaks that could allow for discriminating between the MAX phase and other phases fall below the detection limit, while those that are visible overlap with the ones from the MAX phase.

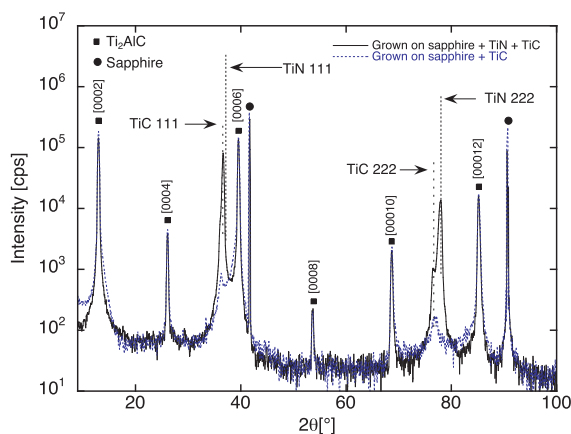


Figure 4. (Colour online) Two diffractograms showing the difference between a Ti_2AlC film grown on sapphire with TiC and sapphire with TiN + TiC.

3. Reproducible Materials Synthesis Having reviewed the inherent issues when optimizing the condition for thin film growth of MAX phases, we have laid the foundation allowing identification of an improved procedure for arriving at optimal synthesis conditions. The ultimate goal is to be able to define the perfect conditions for a specific material system being grown in a specific deposition system. At present, this is not possible, mostly due to the fact that in reality, conditions drift over time and maintaining a system in a state that can be fully mapped out and used consistently is very difficult. What can be done is to minimize the time spent on trial and error, arriving sooner at conditions yielding the desired material. A goal is then also to define parameters that can be used to communicate effectively the conditions needed for reproducing reported material synthesis. Commonly researchers report the applied power to the target or power densities (to account for different target size) when communicating the conditions used. It should be clear, that even between sessions in the same deposition system such numbers do not necessarily yield the same material and stating the current and/or power values in publications regarding growth of MAX phases is not sufficient if one is to reproduce the results and really of no use if further information is not given.

To arrive at a procedure for accurately describing the conditions needed for the synthesis of a particular MAX phase, let us imagine that we have the correct conditions for deposition of a high-quality film of that phase. We know all the relevant parameters and want to communicate them to the community. Since the applied power/power density is not very informative, the next step would be to find the sputter yield of the material for the applied voltage (tabulated values or simulated), to multiply this with the current and one coulomb (6.241×10^{18} electrons), and to arrive at a measure of the flux of ejected atoms from the target. These flux numbers will, however, only apply for that particular deposition system and the specific configuration of magnetrons that those conditions were applied for. The ratio between the atoms ejected from the target and the amount that ends up on the substrate is a function of the system geometry as well as all the other parameters that define the system; angles, distances, pressure etc. Even for depositions in the same system the relationship between the power and this flux is very sensitive to parameters such as the strength of the magnets in the magnetrons, e.g. how far they are from the target surface, the target thickness, etc. These are parameters that routinely can change between sessions and so further information is needed if the optimized conditions are to be communicated.

What is needed is a way to measure and quantify the amount of material that arrives to the substrate and fit this number to the applied power. This can be done by performing calibrations for individual targets

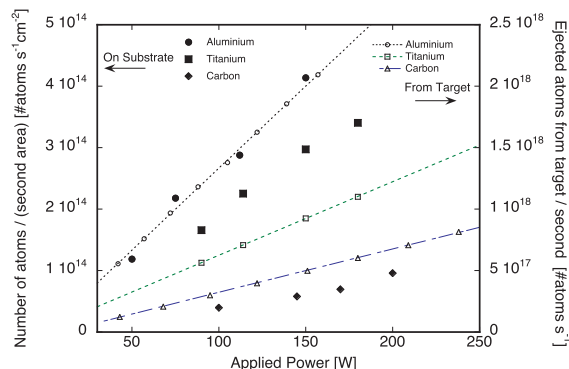


Figure 5. Measured deposition rates of Al, Ti and C at RT (single filled icons) compared with fluxes from the targets (open icons). The applied power is adjusted, the voltage (and thereby yield), and current read and subsequently the flux is calculated for each measured value.

prior to eventual co-depositions. Films of the single elements are therefore deposited at room temperature at different power values and analyzed using X-ray reflectivity (XRR). By fitting the XRR curves using, e.g. the Parrat formalism [35] implemented through commercial software, the thickness d and density ρ of the films can be obtained and the rate of atomic flux per cm^2 calculated by

$$\text{atoms/area} = \frac{\rho * d * N_A}{M_A}, \quad (2)$$

where M_A is the atomic density and N_A is Avogadro's constant. Any other reliable method to obtain the thickness or density can of course be used. This combined with the deposition time gives the rate of flux of the material to the substrate, which can then be related to the applied power to the target so that the incoming flux can be controlled very precisely. Figure 5 shows how this applies for Ti, Al and C (filled icons). Also shown is the calculated flux from the same targets using only the conditions on the magnetrons and tabulated values of the yield from each measured voltage value (open icons). The figure shows clearly that in both cases the flux correlates linearly with power but that the slope is different between the materials. This in turn means that in order to change the fluxes by a certain amount, in a controlled way, this slope needs to be known. The difference of four orders of magnitude between these two approaches is then a measure of the amount of material that is lost during deposition, i.e. only about 0.1% of the atoms leaving the target end up on the substrate. This is expected and is related to the area of the substrate as a section of a sphere, expanding from the target with the radius of the target/substrate distance.

By using this method of calibration, we can arrive at the set of parameters that yield a high-quality MAX phase, and that can easily be transferred between deposition systems. Table 2 shows selected MAX phases that

Table 2. Deposition condition for synthesis of selected MAX phases as epitaxial thin films. The unit of flux to the substrate is atoms $\times 10^{14}/\text{cm}^2$.

Material	Substrate	Temp ($^{\circ}\text{C}$)	M-flux	A-flux	X-flux	Pressure (mbar)
Ti ₂ AlC	Sapphire	900	2.7	4.32	1.15	6.9
Cr ₂ GeC	MgO	600	2.26	1.42	1.17	6.0
Cr ₂ AlC	MgO	600	2.65	1.42	1.17	6.0
Mn ₂ GaC	MgO	550	1.91	NA	1.19	5.7
(Cr _{0.5} Mn _{0.5})GaC	MgO	600	2.77	NA	1.27	3.9

have been optimized so that high-quality films have been achieved. The table gives a set of conditions that could be used in order to reproduce these materials, or at least be a very good starting point for further optimization. It should be added that the pressure was not a part of the optimization process. How the pressure generally affects the quality of MAX phases remains unexplored although we can speculate that a lower pressure is beneficial due to lower loss of energy of impinging atoms through collisions with gas atoms.

Clearly, the suggested procedure cannot be used for materials where attaining a smooth relatively dense film by deposition at room temperature is not possible, as in the case of Ga (melting temperature 30°C). For these cases calculating the expected flux from the target by using the yield, voltage and current has to be done for attaining initial estimated values of deposition parameters, but this soon becomes a trial-and-error procedure. It also should be noted that even if the values given in Table 2 have given high-quality films, they are by no means claimed to be the optimal set. It is most likely that even further improved quality can be attained by changing these and related parameters. The numbers do show clearly how attaining the phase by aiming for the correct flux ratio would be impossible. For Mn₂GaC, the ratio between Mn and C seems to be close to the expected 2:1 but for Ti₂AlC the ratio is closer to 2.3:4:1 where the expected ratio is 2:1:1. The Al deposited is therefore 4 times the amount of Al in the phase and this exemplifies the issues, covered earlier, with the temperature.

To illustrate this point further Table 3 shows the optimal values for a Ti₂AlC film from one deposition system (System 1) recalculated, from RT calibrations, for a different deposition system (System 2). The latter results in a Ti₂AlC film of comparable quality. The numbers show clearly that transferring the optimal conditions between systems would be impossible if only using the conditions on the magnetrons. The difference between the numbers comes about mostly due to different target /substrate distances but other parameters mentioned above can also come into play.

The procedure of optimizing the condition needed for the deposition of high-quality MAX phase thin films

Table 3. Comparison of the conditions for the growth parameters for an optimized Ti₂AlC film on sapphire at 900°C and at 6.9 mbar, in one deposition system (system 1) recalculated base on RT calibration for deposition in a different system (system 2).

	Ti	Al	C
System 1			
Power (W)	115	111	148
Current (mA)	302	317	285
Voltage (V)	380	347	511
Measured flux (atoms $\times 10^{14}/\text{cm}^2$)	2.7	4.39	1.17
System 2			
Power (W)	31	35	135
Current (mA)	120	92	306
Voltage (V)	256	381	437
Measured flux (atoms $\times 10^{14}/\text{cm}^2$)	2.7	4.39	1.17

cannot exclude a certain degree of trial-and-error optimization but given the large number of control parameters it is imperative not having to adjust all of them, but rather focus on the most important ones. This can only be done if we have starting parameters that are close to the optimal values. By performing the suggested RT calibrations and keeping the issues covered here in mind, this should be possible, but also importantly, will make it much easier to arrive again at previously optimized conditions in a given system. Having the ability to effectively reproduce results is undeniably important.

4. Outlook Research into the intrinsic properties of MAX phase is still somewhat in its infancy. There are numerous outstanding questions and opposing views and many of these questions will not be answered until the quality of the samples can be compared quantitatively between research groups. This can in turn not be achieved unless there is a consensus in the community on how to define quality. Although the present paper deals with epitaxial thin films, the discussion is pertinent to bulk samples where some of these issues are less apparent but some are even more problematic.

Parallels can be drawn with the field of high-temperature superconductors where at the beginning of that field there were numerous contradicting results that over time were resolved and many shown to stem from poorly defined samples. In semiconductor physics, a field that has reached a high level of maturity, quality is no longer measured with the methods described here, most notably XRD, but rather by measuring much more sensitive parameters such as resistivity. Over time these issues will be resolved in the MAX phase community and the hope is that the present paper moves toward this. Ultimately, this work should help advance the study of MAX phases more toward applications that rely not solely on their very interesting mechanical properties but rather transport, magnetic and optical properties. For this to happen, producing consistently high-quality thin films is required.

5. Summary/conclusions In conclusion, the quality of epitaxial MAX phase film has been discussed. The procedure of obtaining such films has been reviewed along with several issues that affect their quality, such as the choice of substrate, deposition temperature and applied power to the target materials. By being aware of these issues that arise during synthesis, it should be possible to communicate the conditions needed for high-quality samples more effectively than what is currently done, and a suggestion for the most important parameters that are needed for this is given. The improved material quality will advance the studies of the intrinsic properties of this family of interesting materials, will allow further exploration of their 2D counterpart, and move them beyond the poorly defined samples that make comparison of results difficult.

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