Layered ternary $M_{n+1}AX_n$ phases and their 2D derivative MXene: an overview from a thin-film perspective

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Received 31 October 2016, revised 20 December 2016
Accepted for publication 9 January 2017
Published 14 February 2017

Abstract

Inherently and artificially layered materials are commonly investigated both for fundamental scientific purposes and for technological application. When a layered material is thinned or delaminated to its physical limits, a two-dimensional (2D) material is formed and exhibits novel properties compared to its bulk parent phase. The complex layered phases known as ‘MAX phases’ (where $M$ = early transition metal, $A$ = A-group element, e.g. Al or Si, and $X$ = C or N) are an exciting model system for materials design and the understanding of process-structure-property relationships. When the A layers are selectively etched from the MAX phases, a new type of 2D material is formed, named MXene to emphasize the relation to the MAX phases and the parallel with graphene. Since their discovery in 2011, MXenes have rapidly become established as a novel class of 2D materials with remarkable possibilities for composition variations and property tuning. This article gives a brief overview of MAX phases and MXene from a thin-film perspective, reviewing theory, characterization by electron microscopy, properties and how these are affected by the change in dimensionality, and outstanding challenges.

Keywords: Ti$_3$SiC$_2$, physical vapor deposition, sputtering, electron microscopy, MXene, ceramics, 2D materials

(Some figures may appear in colour only in the online journal)
with a few examples being h-BN, MoS$_2$ and WS$_2$. There are numerous reviews of these classes of non-graphene 2D materials [1–14].

More complex layered structures occur in a wide range of ceramic materials. The so-called ‘MAX phases’ are an exciting playground for property tuning and understanding of process-structure-property relationships. They stand out because of the large variations in chemistry—and hence design opportunities—within the same materials family. The history of the MAX phases began in the 1960s, when Hans Nowotny’s group in Vienna discovered [15] more than 100 new carbides and nitrides. Among them were the so-called ‘H phases’ and their relatives Ti$_3$SiC$_2$ and Ti$_3$GeC$_2$. These phases remained largely unexploited until the mid-1990s, when Barsoum and El-Raghy [16] synthesized relatively phase-pure samples of Ti$_3$SiC$_2$ and revealed a material with a remarkable combination of metallic and ceramic properties: it is a good electrical and thermal conductor, machinable, and resistant to thermal shock and oxidation. They later discovered Ti$_3$AlN$_3$, making it clear that these phases are a large family described by the general formula M$_{3+n/2}$AX$_n$ phases (n = 1, 2, or 3) or ‘MAX phases’, where M is a transition metal, A is an A-group element, and X is C and/or N [17, 18]. This structure endows the MAX phases with unique chemical, physical, electrical, and mechanical properties stemming from their layered structure and the mixed metallic-covalent nature of the strong M–X bonds together with M–A bonds that are relatively weak. Because of this unusual property combination, the MAX phases show promise for a wide range of uses in high temperature structural applications, protective coatings, sensors, electrical contacts, microelectromechanical systems, and many more.

In 2011, it was demonstrated that the A layers can be selectively etched from the MAX phases [19], to form a new type of 2D material, named MXene to emphasize the relation to the MAX phases and the parallel with graphene. MXenes have rapidly become established as a novel class of 2D materials with remarkable possibilities for composition variations and property tuning.

The purpose of this article is to give a brief overview of MAX phases and MXene from a thin-film perspective, integrating a discussion on theoretical approaches and physical properties, in particular how these are affected by the step from 3D to 2D. This article is complementary to other reviews on MAX phases, e.g. [20–24]. For an in-depth treatment of the fundamentals of the MAX phases, we refer to Barsoum’s initial review from 2000 [17], his more recent textbook [25] and our previous comprehensive review of the field of materials science and thin-film processing of MAX phases [26]. Furthermore, good introductory treatments of MAX phases are given in several brief overviews [18, 27–29], and specific subtopics are treated in a number of focused reviews, for example the relation to related layered phases [30–32], summaries on individual phases [33–35], tribology [36], magnetism [37], spectroscopy and electronic structure [38], elastic and mechanical properties [39], and oxidation [40].

Figure 1 is an illustration of the hexagonal unit cells of the 211, 312, and 413 MAX phases. From [26], adapted from Högbom et al [28] and an earlier version by Barsoum [17]. © Elsevier, reproduced with permission.

2. M$_{3+n/2}$AX$_n$ phases

2.1. Definition and crystal structure

The MAX phases [17], are carbides and nitrides (the ‘X’ indicating C or N) with the general formula M$_{3+n/2}$AX$_n$ (n = 1, 2, or 3), often referred to as 211 (n = 1), 312 (n = 2), and 413 (n = 3) phases. The M elements are mainly group-4, group-5, and group-6 transition metals (primarily Ti, Zr, Hf, V, Nb, Ta, Cr, and Mo), while the A element is from groups 12 (Cd), 13 (Al, Ga, In, Tl), 14 (Si, Ge, Sn, Pb), 15 (P, As), or 16 (S). The origin of the label ‘A’ is the old American nomenclature for the periodic table [26].

Figure 1 is an illustration of the hexagonal unit cells of the 211, 312, and 413 MAX phases. The unit cells consist of M$_6$X octahedra, e.g. Ti$_6$C, interleaved with layers of A elements. In the MAX phases, the MX layers are twinned with respect to each other and separated by the A layer which acts as a mirror plane. The MAX structures are anisotropic: the lattice parameters are typically around $a \sim 3$ Å and $c \sim 13$ Å (for the 211 phases), $c \sim 18$ Å (for the 312 phases), and $c \sim 23–24$ Å (for the 413 phases). The space group is $P6_3/mmc$. In principle, the value of $n$ may be higher than 3, forming the ‘514’ phases, and higher. However, there are only a few examples of such phases, e.g. (Ti$_{0.5}$, Nb$_{0.5}$)$_4$AlC$_4$, and none have been synthesized in pure form [41].

2.2. Intergrown phases

Intergrown MAX phases were first reported by Palmquist et al in the Ti-Si-C system [42], and soon thereafter observed also in the Ti-Ge-C and Ti-Al-C systems [43, 44]. These phases consist of alternating ‘211’ and ‘312’ half unit cells, to form
a ‘523’ phase, or alternating ‘312’ and ‘413’ half-unit cells to form a ‘725’ phase. This stacking needs to be repeated three times to form a complete unit cell, meaning that the c-axis is three times the average unit cell of the two constituents, and that the symmetry of the P63/mmc space group is broken. Initially, it was believed that these intergrown phases could form only as minority or intermediate phases, primarily in thin films. However, in 2011, Scabarozi et al demonstrated that Ti$_5$Si$_2$C$_3$ can be synthesized as phase-pure epitaxial thin films [45]. Figure 2 (from Scabarozi et al [45]) shows a transmission electron microscopy (TEM) of the Ti$_5$Si$_2$C$_3$ structure; the alternating ‘312’ and ‘413’ layers can be seen. Somewhat later, Ti$_5$Al$_2$C$_3$ was synthesized as a majority phase in bulk samples [46]. Initially, the structure was reported as belonging to the P3m1 space group [46, 47], but it was soon shown that the same structure can be described with a higher symmetry in the R-3m space group [48] (refer to table 1 in [49] for the structural model of Ti$_5$Al$_2$C$_3$). It should also be noted that there is an erroneous report [50] on Ti$_6$Al$_2$C$_3$ claiming a different structure, with space group P63/mmc, but this proposed structure is inconsistent with the experimentally observed structure [47].

2.3. Isostructural solid solutions

In addition to the pure ternary phases, there is a large number of synthesized isostructural solid solutions of MAX phases, which is important for understanding the role of chemistry in controlling and ultimately tuning of physical properties. In practice, important examples of this tailoring opportunity include oxidation studies, where the excellent oxidation resistance of the alumina-formers Ti$_2$AlC and Ti$_3$AlC$_2$ [40, 51, 52] is retained also for solid solutions, e.g. Ti$_3$(Si,Al)C$_2$ [53–56], thermal properties, in particular tailoring of thermal expansion [57, 58], tuning magnetic characteristics [59, 60] and the possibility to stabilize new MAX phases that are not stable in their pure ternary form [41, 61–63]. For mechanical properties, solid-solution hardening effects [64–69] are generally not very pronounced, with some exceptions [70–72]. There are also some discrepancies, particularly in the Ti$_3$AC$_2$ systems (A = Si, Ge, Al, Sn) where several investigations [64, 65, 73–75] have demonstrated that solid solution hardening is not operative, while one study argues the opposite [72]. Most recently, Gao et al [76] demonstrated that solid solutions could play a role in increasing the hardness of coarse-grained Ti$_3$(Al,Si)C$_2$, but not for fine-grained, indicating that it is not a pure solid-solution hardening effect, but rather a microstructural effect.

2.4. Ordered MAX phases

Ordered MAX phases (M', M'')$_{n+1}$AlC$_n$ have been a recent important development. These ordered phases differ from regular solid solutions in that the two elements on the M site are different. In the ideal case, one site is one transition metal M' (e.g. Ti) and the nonequivalent site in the structure is a different transition metal M'' (e.g. Cr). This was initially reported in the phases Cr$_2$TiAlC$_2$ and V$_2$CrAlC$_2$ [77, 78]. Ideally, these should then have a fixed stoichiometry. In practice, it appears that these phases exhibit a high degree of ordering, but not necessarily complete. A further important discovery in this topic is the ordered Mo$_2$TiAlC$_2$ [79] and Mo$_2$Ti$_2$AlC$_3$ [80]. In Mo$_2$TiAlC$_2$, the Ti atoms are positioned between the two Mo layers adjacent to the Al planes. Figure 3 (from Anasori et al [79]) is a high-resolution scanning TEM (HRSTEM) image with corresponding chemical analysis by energy dispersive x-ray spectroscopy (EDX) of the structure of Mo$_2$TiAlC$_2$, showing the high degree of ordering of the metal layers. The discovery of this type of structure, together with the etching of Ga from Mo$_2$Ga$_2$C (see section 4), allows for the fabrication and characterization of Mo-based MXenes.

3. Thin-film MAX phases

With their abundance of chemical variation and design opportunities, the MAX phases constitute a model class of materials for property tuning and approaches to systematic materials discoveries. In this section, we briefly summarize the most important thin-film synthesis methodologies and integrating theoretical methods.

3.1. Thin-film synthesis methodologies

This section summarizes methodologies for thin-film synthesis of MAX phases, in particular chemical vapor deposition (CVD), physical vapor deposition (PVD), and solid state reaction synthesis. The summary is restricted to atomistic techniques rather than methods for growth of thick coatings such as spraying techniques, where a powder of the desired material is sprayed [81–86]. The majority of bulk synthesis methods operate (or are assumed to operate) near thermodynamic equilibrium, which is similar to the situation in CVD which is based on chemical reactions typically at high temperature.
Ti₃SiC₂ may be formed not only by the simultaneous deposition of Mo, Ti, and Al over the green arrow. From Anasori et al.[79]. Ti atoms in green and Al atoms in blue, (g) EDS line scan profile of (b)–(c). (f) Overlap of (a) and (e) showing the Mo atoms in red, axis, EDS mapping on (a) for: (b) Mo, (c) Ti, (d) Al. (e) Overlap of all elements, but by a reaction between the gas and a solid phase such as TiC [88, 90]. This concept, termed reactive CVD (RCVD), has been used by Jacques et al [92] and Faikh et al [93, 94] to synthesize Ti₃SiC₂/SiC multilayer coatings.

Overall, CVD has been used to a rather limited extent for synthesis of MAX phases, and there is room for future research, notably to synthesize MAX phases other than Ti₃SiC₂ by CVD. Particular promise should be held by the form of CVD known as atomic layer deposition (ALD) [95], which permits control of the deposition process on a layer-by-layer basis and would thus in principle be ideally suited for synthesis and tailoring of layered materials such as MAX phases. This is further underlined by the recent synthesis of 2D MXene films in the Mo₂C system by CVD (see section 4) [96].

3.1.2. PVD. Physical vapor deposition (PVD), primarily by sputtering techniques but also cathodic arc deposition, is the most common approach to thin-film synthesis of MAX phases. Much PVD syntheses have been performed at relatively high substrate temperature (700–1000 °C), which is a limiting factor both for the use of temperature-sensitive substrates and for industrial applicability. Typically, M₂AX phases with group-5 or group-6 M elements [26] can be vapor-deposited at a relatively low substrate temperature of about 300 °C. This includes V₂GeC [97], Cr₃GeC [98, 99], and Cr₂AlC [100–107], while the Ti-based MAX phases require higher temperatures. Aside from materials selection, attempted approaches to reduce the substrate temperature include ionized deposition techniques such as high-power impulse magnetron sputtering and sequential deposition of the three elements at moderate temperature (~650 °C for Ti₃SiC₂), enabling element segregation and MAX-phase formation at low temperature [108].

Sputter-deposition can be made from individual sources (targets), which is preferred for the individual control of the elements or from compound or composite targets [101, 109, 110], which is typically preferred for reproducibility under industrial conditions (see [26] for a detailed discussion). MAX-nitrides are normally grown by reactive sputtering using nitrogen gas as the source of nitrogen. Typically, the process window for growth of pure MAX-phase films is then narrow [26], and the use of reactive sputtering for MAX carbides has been quite limited. There are, however, a few studies that indicate that the technique has potential for broader use [45, 111].

Compared to sputtering, cathodic arc deposition has had more limited use for MAX-phase synthesis, for example for growth of Ti₂AlC [112–117] using a pulsed cathodic-arc setup from elemental Ti, Al, and C cathodes. A key difference with arc deposition compared to sputtering is its high degree of ionization (almost 100%) of the deposition flux, suggesting an approach for temperature reduction.

3.1.3. Solid-state reaction synthesis. Solid-state reactions as a thin-film synthesis method consists of two main variations: one based on between the film and the substrate and the other based on film–film reactions. The most important example of the former is Ti₃SiC₂ synthesized by annealing of Ti-based contacts in SiC devices [118–128]. The second

Figure 3. (a) HRSTEM of Mo₂TiAlC₂ along the [11–20] zone axis, EDS mapping on (a) for: (b) Mo, (c) Ti, (d) Al. (e) Overlap of (b)–(c). (f) Overlap of (a) and (e) showing the Mo atoms in red, Ti atoms in green and Al atoms in blue. (g) EDS line scan profile of Mo, Ti, and Al over the green arrow. From Anasori et al. [79]. ©American Institute of Physics, reproduced with permission.
category involves deposition of a film containing the three elements M, A, and X in the right proportions, for example in a multilayer [129–133], or in amorphous or nanocrystalline form [134–136]. Annealing at higher temperature then initiates the transformation to the MAX phase. Additionally, film–substrate reactions were also reported to occur during deposition of substoichiometric TiX (X = C, N) on sapphire (Al₂O₃) substrates [137–139]. Al and O, originating from the decomposing substrate, were found to migrate into the growing film. Under these conditions, a MAX phase formed, at the film–substrate interface which incorporated the deposited species with the substrate species; Tiₙ₋₁Al(X,O)ₙ.

3.2. Theory-guided materials discovery and optimization

3.2.1. Materials discovery. New materials are continuously being discovered in today’s materials science. Historically, this was approached in a trial-and-error manner, which emphasizes the need for development of and improved theoretical guidance and has led to a tremendous increase in predictions of hypothetical novel materials. Traditionally, it was typically approached by calculating only the cohesive energy of the hypothetical compound itself, which yields a local energy minimum in a vast parameter space. This can, however, often lead to misleading results. A classic example is the prediction of the β-C₃N₄ phase with a Si₃N₄ structure, which was suggested to be stable and harder than diamond [140]. While some have claimed to have synthesized the β-C₃N₄ phase, it is by now established that it most likely does not exist [141–143]. Data-mining methods to predict new crystal structures have existed for some time [144–147], but in their basic form these approaches do not directly address the question of whether a hypothetical compound can be expected to exist experimentally. Rather, they predict the most likely crystal structure given the premise that a material with a specific composition is known to exist. For predicting the existence of hypothetical phases, realistic stability calculations considering relevant competing phases are therefore necessary. Traditionally, the selected competing phases were chosen ad hoc. Reliable results require systematic optimization approaches, which have been applied to simulate temperature dependence and reaction paths in known systems (see, e.g. [148, 149]), and are now a systematic approach to predicting new phases, considering all known competing phases as well as hypothetical competing phases based on neighboring and similar systems. Thus, the relative stability of any hypothetical phase can be calculated relative to the most stable combination of competing phases [150, 151].

In the MAX-phase area, this approach has been shown to have substantial predictive power in predicting numerous new phases [152–154], but the opposite is also generally true, i.e. that phases with positive formation enthalpy typically turn out to be at best metastable and very difficult to synthesize. It should be noted here that one usually makes a substantial simplification in accounting only for enthalpy terms (i.e. a 0K calculation), not entropy or vibrational contributions to the Gibbs free energy. While these contributions can be added, it increases the computational complexity of the problem and thus the time scale of the computations. Nevertheless, the temperature effects appear to essentially cancel out in most relevant MAX-phase systems [155] rendering the 0K prediction reliable for this class of materials. However, for example quaternary MAX phases displaying out-of-plane chemical order, an estimation of the configurational entropy and its contribution to Gibbs free energy is essential for estimating stability and order/disorder of the alloy [156]. It should be stressed, though, that these observations for MAX phases do not necessarily hold true for other material classes.

Recently, important steps have been taken towards implementing a data-mining stage also for the determination of competing phases [157], taking full advantage of the emergence of large databases such as the Materials Project [158] and potentially enabling a fully systematic and even automated approach to predicting new compounds. At present, this approach remains limited by the content of databases, but limited computational power is no longer the hurdle it once was. A fully automated approach to predictions of hypothetical phases is therefore within reach.

An alternative manner of approaching the systematic discoveries of new compounds is to instead start with a desired property that can be described by a suitable descriptor, a parameter directly connected to the property of interest (for example, piezoelectric coupling coefficients for ABO₃ perovskites where A and B are any metals) [159]. This can then be optimized for a very large number of chemical compositions in a given crystal structure. This will yield ‘islands’ of perhaps a few hundred candidate materials. To be experimentally relevant, these should subsequently be reduced to an experimentally manageable number by adding a phase-stability step. These approaches to modern materials discoveries further underline the need also for reliable calculations of materials properties, which is essential both for predicting new materials with interesting properties and for fundamental understanding of existing materials.

3.2.2. Property calculations. Accurate ab initio calculation of properties of materials is a challenge which has very different levels of complexity depending on what set of properties are of interest. For example, elastic constants are relatively straightforward to calculate from first principles, in that complexity is mainly due to their tensorial nature [160]. For some materials (e.g. containing Cr, Mn, or Fe), magnetic ordering also needs to be properly accounted for to obtain reliable elastic properties [161–164]. It follows that piezoelectric responses of a wide range of materials can be reliably obtained, since they depend on second-order strain-derivatives of ground state energies, elastic constants, and first-order strain-derivatives of polarization [165], which are relatively straightforward to calculate accurately.

In contrast, the properties needed for understanding electrical-transport and thermoelectric properties of a material are a challenge to compute from first principles, because of the involvement of both electronic and thermal transport as well as non-equilibrium transport processes [161]. This has turned out to be an important challenge in the MAX and MXene research topics (see section 5.3). Boltzmann transport theory
[166] is the standard approach, but is performed within the relaxation-time approximation and thus involves an unknown scattering parameter, the relaxation time $\tau$. In the calculation of the Seebeck coefficient (and Hall coefficient), $\tau$ is cancelled out under the conditions that it is isotropic and constant with respect to energy. This is often not a satisfactory assumption [159]. However, even if this assumption is accepted, the issue still remains that electrical and (electronic) thermal conductivities can only be determined numerically by fitting to experimentally determined values [167] of $\tau$, for a specific material. Alternatively, the electrical conductivity is determined only as a function of an unknown $\tau$. Thus, such calculations are not truly ab initio, but remain limited to materials with experimentally determined $\tau$ values available. This is an important limitation in terms of applicability, since it precludes predictions of transport properties for materials that are not yet synthesized or insufficiently experimentally characterized (see section 5). Current method development therefore strives to find approaches for first-principles computation of these properties, e.g., an ab initio approach in the low-electric-field limit [168] and efforts to incorporate phonon drag [169, 170].

4. From 3D to 2D: MXene

4.1. Overall summary

In 2011, a new 2D nanocrystal based on MAX phases was synthesized through immersion of Ti$_3$AlC$_2$ in hydrofluoric acid (HF). Removal of the $A$ layer resulted in 2D M$_{n+1}$X$_n$ layers that were labelled MXene [19], to denote the loss of the $A$ element and emphasize the structural similarities with graphene. MXenes constitute a new family of 2D materials that, generally speaking, combine the metallic conductivity (see section 5.2) of transition metal carbides with the hydrophilic nature of their hydroxyl (OH) or oxygen (O) terminated surfaces. A common notation for the MXenes is M$_{n+1}$X$_n$T$_x$, where T$_x$ represents the surface functional groups, mostly O, OH, and fluorine (F). The terminations originate from the choice of etching procedure, typically using HF, ammonium bifluoride (NH$_4$HF$_2$) or a solution of lithium fluoride (LiF) and hydrochloric acid (HCl).

The MXenes synthesized to date include, for example, Ti$_3$C$_2$T$_x$, Ti$_2$CT$_x$, V$_2$CT$_x$, Nb$_2$CT$_x$, Nb$_2$C$_x$T$_x$, and Ta$_2$C$_x$T$_x$. MXenes have also been produced from laminated phases other than MAX phases, i.e. Zr$_3$Al$_2$C$_5$ by etching of Al-C units rather than Al etching [171]. This is important because while there are some recent reports on MAX phases in the Zr-Al-C and Hf-Al-C systems [172–174], the transition metals Zr and Hf primarily tend to form related phases of the type Zr$_2$Al$_x$C$_y$, Zr$_3$Al$_3$C$_5$, etc [31, 175]. Furthermore, solid solutions, such as Ti$_3$C$_2$T$_x$, (Ti$_{0.5}$,Nb$_{0.5}$)$_2$C$_2$T$_x$, and (V$_{0.5}$,Cr$_{0.5}$)$_2$C$_2$T$_x$ have been reported, in which the two transition elements are believed to randomly occupy the M-sites [176, 177]. More recently, ordered MXenes in the form of Mo$_2$TiC$_2$T$_x$, Mo$_2$Ti$_2$C$_2$T$_x$, and Cr$_2$TiC$_2$T$_x$ have been presented [178], originating from the corresponding out-of-plane chemically ordered MAX phases Mo$_2$TiAlC$_2$, Mo$_2$Ti$_2$AlC$_3$, and Cr$_2$TiAlC$_2$, respectively, for which Ti/TiC is sandwiched between two outer layers of metal (Mo/Cr) carbide layers.

Despite their young age, over 20 MXenes have been discovered, with new ones discovered continuously. They show great promise in many applications—from energy storage [179, 180], to cationic adsorption [181], conductive transparent electrodes [182–185], field effect transistors [186], and electromagnetic interference shielding [187].

4.2. Thin films

MXenes have been produced as powders, flakes, and colloidal solutions. In 2014, a breakthrough was made in the synthesis of large-area epitaxial thin films of 2D Ti$_3$C$_2$, see figure 4 [182]. Depositions on transparent and insulating sapphire substrates enabled measurements of fundamental physical properties, such as optical absorption, in a broad wavelength range, conductivity and magnetoresistances down to 2K. Most importantly, the results on electrical-transport properties unambiguously showed weak localization of charge carriers.
and thus proved that these materials are genuinely 2D in
the sense of electronic properties.

By varying the M and X elements, as well as the surface
terminations T and/or the number of layers, n, in Mn+1XnT,
it is possible to tune the MXene properties. Most MXene
compositions reported were obtained by etching the Al-layers
from Al-containing MAX phases. A related hexagonal ternary
nanolaminated carbide, Mo2Ga2C, was discovered recently in
both bulk and thin-film form [188, 189]. In this phase, two Ga
layers—instead of one, such as in the Mo2GaC MAX phase—are
stacked in a simple hexagonal arrangement in between
Mo2C layers, see figure 5 (left). A subsequent study [190]
showed the possibility of selectively etching the Ga layers—
using HF—from epitaxial Mo2Ga2C thin films, producing the
MXene Mo2CTx, see figure 5 (right). The finding of Mo2CTx
is important because it was the first MXene originating from
selective etching of Ga and because it was the first MXene
containing Mo. Later, both Mo2TiC2Tx and Mo2Ti2C3Tx were
discovered, as mentioned above.

4.3. Electron microscopy of MXene

Electron microscopy has proven an indispensable tool for
acquiring structural and elemental information of the MAX
phases. Since the introduction of aberration corrected electron
microscopy [191], it has been possible to individually detect
e.g. in MAX phases, the light and typically low-contrast X
elements [192] and to map the elemental distribution at
atomic resolution [79, 80, 153] Although electron microscopy
has been applied to a large number of studies in MXene syn-
thesis to verify the resulting sheet-like nature, the power of
the modern advanced electron microscopy is to resolve, atom
by atom, the structure of individual sheets. This has been suc-
cessfully applied in research on most of the other 2D materials
such as graphene [193] and dichalcogenides such as MoS2 [1].

To generalize, MXenes are most easily investigated from
two perspectives; cross-section and plan-view, where with the
cross-sectional (side-view) approach the observer can identify
separation between sheets, stacking and gain information on
the functionalization of the MXene surfaces. This approach
is the most commonly used for thin films, though it is also
applicable to powders. An illustrative example can be viewed
in figure 6, which shows the (incomplete) etching of a thin-
film MAX phase to yield MXene. The series of images clearly
illustrates the interface between the MXene–MAX and how
the MXene organizes itself while still attached to the MAX
phase. Technically, the information gained from this invest-
gation is hampered by the (in most cases) unknown number
and elemental identity of the atoms which are projected in
the atomic columns and onto the image plane. Consequently,
resulting images do not reflect the individual atomic structure.
Subsequently, plan-view investigations are typically more
rewarding, where ideally only a single sheet is projected in
the image, such as in figure 7. In this case, the M2X MXene
structure projects in 2/3 of the atomic columns one M and
one X atom, and only the single M atom for 1/3 of the atomic
columns. For the M2X structures each column contains a sin-
gle M or X atom. The plan-view approach was first applied
by Karlsson et al [194] and later also by Sang et al [195] in
order to describe the structure and surface of the single Ti3C2
MXene sheet. These investigations have in particular yielded
information on point defects (vacancies and interstitials) and
the short-range organization of such defects. Detailed infor-
mation on these defects is desirable as point defects are known

Figure 5. Schematic showing Mo2Ga2C and synthesis and delamination of Mo2CTx (terminations not shown). Based on an original by Halim et al [223]. ©Wiley, used with permission.

Figure 6. The images (a)& (c) show a series of cross-sectional images with increasing magnification from a thin film MXene. In (a), the image reveals the substrate and the as-grown MAX phase—
which has been (intentionally) partly etched at the top to
yield a thin surface of MXene. (b) shows how the MXene is still
attached to the MAX phase while the A-layer has been etched. In
(c) the atomic resolution image of the MAX-MXene interface is
shown.

J. Phys. D: Appl. Phys. 50 (2017) 113001
to affect the electronic and optical properties of other 2D materials [196, 197].

In the investigation of single sheet 2D structures, the electron beam–sample interactions and radiation damage take on a critical variable as it comes to accelerating potential in the microscope. If knock-on damage dominates the radiation damage, low-voltage microscopy (accelerating potentials at or below 60 kV) is a viable route to avoid beam-induced changes in the atomic structure [198–200]. Nevertheless, significant beam-driven dynamics are present in all of these studies, especially at contamination sites, defects, and edges. The edges of a graphene sheet are still highly dynamic at 20 kV electron irradiation [200], defects in graphene easily change their shape in 80 kV image sequences [201] and defects are introduced in molybdenum disulfide [202] under irradiation.

At present, little is known of the electron beam–MXene interactions, however, the existing investigations of the atomically resolved structures suggest that the structure of the MXene sheet is stable between 60–100 kV [191, 195]. Edges and surface functional groups on the other hand are observed to be dynamic and reorganize even at 60 kV [194]. These changes may be the effect of beam induced sample heating rather than direct interactions between the beam and surface functional groups. However, beam–MXene interactions require further investigations for optimum imaging conditions.

The identification of a single sheet is most easily performed in the (S)TEM, yet the method is treacherous. In the (S)TEM, contrast differences originate from differences in the collected dark-field signal, which is determined by Rutherford scattering of the electron beam from each partially screened atomic nucleus. The scattered intensity increases with atomic number (Z) approximately according to $Z^{1.7}$ (commonly approximated to $Z^{2}$) [203]. In the plan-view approach, the double layer therefore adopts twice the intensity compared with the single layer. Despite this, the thickness of a structure cannot be unambiguously determined to a single sheet in plan-view. MXene sheets have a tendency to align themselves with M atomic columns atop M atomic columns [19, 194]. Therefore the columns contain an unknown number of M atoms. This was resolved by Karlsson et al [194] through intensity comparisons using native adatoms on the MXene sheets and by Sang et al [195] through tilting of the sheet to verify the thickness by changes in appearance.

These efforts have proven efficient in visualizing the organization of the M elements in MXene sheets, but a method for direct imaging of the surface functional groups is lacking. Potentially this can be resolved through newer methods in microscopy such as e.g. phase imaging in the STEM [204] or by annular bright field STEM [205].

5. Properties

This section summarizes some properties of MXene in correlation with those of their parent MAX phases, also pointing out remaining challenges.

5.1. Intercalation/electrochemistry

One of the more promising applications for 2D materials is in the realm of energy storage, where 2D solids are particularly attractive because of their intrinsically high specific surface areas that in turn result in higher energy and power electrodes. Consequently, the intercalation of ions into layered compounds has long been exploited in energy storage devices such as batteries and electrochemical capacitors. MXenes, typically being hydrophilic and conducting, have shown great promise as electrode materials for Li-, Na-, and K-ion batteries [177, 206, 207], Li-S batteries [208], and Li-ion and aqueous supercapacitors [179, 180, 209, 210]. For example, Ti$_3$C$_2$T$_x$ intercalated with Li$^+$ ions have shown a steady-state capacity of ~410 mAh g$^{-1}$ at 1 °C for additive-free electrodes [211]. However, few host materials are known to accommodate ions much larger than lithium, though Ti$_3$C$_2$T$_x$ have also been shown to allow spontaneous intercalation with molecules such as hydrazine, dimethyl sulfoxide (DMSO), and urea [210] as well as electrochemical intercalation of a variety of cations, including Na$^+$, K$^+$, NH$_4^+$, Mg$^{2+}$, and Al$^{3+}$ [209], the latter giving a capacitance in excess of 300 Fcm$^{-3}$. Supercapacitor performance has been elevated by synthesizing the Ti$_3$C$_2$T$_x$ MXene into a clay-like material, giving a volumetric capacitance of about 900 Fcm$^{-3}$ [179]. Furthermore, recent studies also show enhanced performance for nanocomposite electrodes hybridizing polymers and MXenes [212, 213], with capacitances up to 1000 Fcm$^{-3}$ [213]. However, the field is in its infancy, and the numbers will likely increase further as the MXene chemistry and structure, and possible hybridizing materials, are optimized.
5.2. Electrical properties

The MAX phases are metallic conductors with typical room-temperature resistivities of the order of a few tens of $\mu\Omega$ cm (in comparison, the room-temperature resistivities of Ag and Ti metals are about 1.6 $\mu\Omega$ cm and 40 $\mu\Omega$ cm, respectively). In general, the electrical properties are moderately anisotropic, in the sense that the conductivity along the c-axis and along the a-axis differ but are metallic and of the same order of magnitude [26, 214–219]. There is, however, recent work with measurements on single crystals showing that some MAX phases (V$_2$AlC and Cr$_2$AlC) have a much higher degree of anisotropy [220]. Etching out the A element to form MXene results in a 2D material where, generally speaking, the metallic-like conductivity is retained. At low temperature, the electrical-transport properties of Ti$_3$C$_2$T$_x$ thin films showed weak localization of charge carriers, i.e. a genuine 2D property [182]. Nevertheless, this depends on materials systems and terminations. The large possible variations in terminations yields a design opportunity for tuning the electronic properties and band structure, e.g. from metallic to semiconductor. This has been indicated in numerous theoretical studies, e.g. with pure O termination [221]. A challenge here is to accurately model the actual experimental termination, which is typically a complex mix of numerous termination species [222].

Measurements on Mo$_2$CT, MXene [223] indicated a semiconductor-like behavior of Mo$_2$CT in contrast to metallic Ti$_3$C$_2$T$_x$ [182], based on an increase in resistivity as the temperature is decreased from 300 K to 10 K. The result can be compared to direct thin-film synthesis of 2D $\alpha$-Mo$_2$C by CVD, for which 3.4 nm crystals (approximately 15 metal layers) display a decrease in resistivity from 300 K to 50 K [96]. A further reduction in temperature showed a logarithmic increase in resistivity which indicates a weak 2D localization effect—similar to Ti$_3$C$_2$T$_x$ thin films [182].

Furthermore, theoretical studies have shown that under certain termination conditions, Dirac points (i.e. cones in the band structure with a zero bandgap) analogous to graphene can appear in MXenes. This was first reported by Fashandi et al. [224] and opens the field for studying quantum-relativistic conduction phenomena and ‘Dirac physics’ in MXenes. Compared to graphene, the spin–orbit splitting at the Dirac points is much larger. Existence of topologically protected edge states is another consequence, leading to the possible application in topological insulators [224, 225–227]. These predictions remain to be experimentally verified; thus there is a need to further explore transport measurements and angle-resolved photoemission spectroscopy on single-sheet MXene.

5.3. Thermoelectric properties

The Seebeck coefficient (or thermopower), $S$, of a material is defined as $\Delta V/\Delta T$, the voltage $\Delta V$ developed over a material when exposed to a temperature gradient of $\Delta T$. For thermoelectric energy conversion, a large Seebeck coefficient coupled with a reasonably high electrical conductivity and a low thermal conductivity is required. The MAX phases are good, metallic conductors, and thus they generally exhibit low Seebeck coefficients. In this context, however, Ti$_3$SiC$_2$ is unique: bulk samples of Ti$_3$SiC$_2$ exhibit negligible $S$ over a very wide temperature range, from 300–850 K [228], an unique phenomenon. Based on density functional theory (DFT) calculations, Chaput et al [229, 230] predicted that two types of bands are the main contributors to the Seebeck coefficient in Ti$_3$SiC$_2$: a hole-like band in the ab-plane and an electron-like band along the c-axis, with twice the value in the c direction as that in the a direction, but with opposite sign. Therefore, the Seebeck coefficient macroscopically sums up to zero in a randomly oriented sample. This was experimentally confirmed by Magnuson et al [231], who demonstrated that the in-plane Seebeck coefficient is positive and substantial and evidenced the anisotropic states in the electronic structures, which is the underlying source of the near-zero Seebeck coefficient in bulk, polycrystalline Ti$_3$SiC$_2$.

For MXene, the thermoelectric properties remain essentially unexplored experimentally. From theoretical predictions it can be concluded that some MXenes could exhibit very high Seebeck coefficients [232, 233], but generally they would tend to also be good thermal conductors [234, 235], which would limit their use for thermoelectric applications. Going beyond this, existing theoretical predictions are difficult to assess given the limitations on the applied methodology from Boltzmann transport theory, as described in section 3.2. For example, there are misleading predictions based on using a value of the relaxation time $\tau$ that was not determined for the specific material and assuming that $\tau$ is constant with carrier concentration [236, 237], which it is not.

5.4. Superconductivity

A few MAX phases (notably Mo$_2$GaC, with a critical temperature, $T_c$, of $\sim$3.9 K [238]) were reported to be superconductors already in the 1960s. However, it is a challenge to assess these results, since little or no information about the samples is accessible. Only a $T_c$ is typically stated. It was not until 2015 that characterization on pure samples confirmed that Mo$_2$GaC is likely a superconductor [239]. Other reported superconductors among the MAX phases include Nb$_2$SC [240], Nb$_2$AsC [241], Nb$_3$InC [242] and Ti$_3$InC [243].

The key issue here, and the source of many discrepancies, is that measurements of superconductivity are highly sensitive to impurity phases. Anasori et al [79] demonstrated specifically the effect of a superconducting impurity phase (see section 3.4 and corresponding supplementary information of [79], and how this can lead to incorrect conclusions if care is not taken, i.e. that the presence of a superconducting impurity phase can yield an apparent superconductivity for the sample measured, even though the phase of interest is not superconducting. For example, for Nb$_2$SnC, there are conflicting reports [241, 244] as to whether the phase is a superconductor, likely because the samples in [241] were of higher purity, while those in [244] contained an impurity phase of (superconducting) NbC, giving a false positive result. Furthermore, it is known from measurements on highly pure bulk and thin-film samples that Ti$_2$GeC is not superconducting [245]. Despite this fact, there is an erroneous report [246] claiming superconductivity in that compound, where the samples in
question contained a very large amount of a superconducting impurity phase. Overall, these observations emphasize the need for great care in characterizing superconductivity.

For MXenes, it was therefore an important achievement that highly phase-pure, large area 2D Mo$_2$C (a few nanometers thick and $\sim$100 $\mu$m in lateral size) could be synthesized by CVD [96]. This allowed a direct measurement of the low temperature properties, and superconductivity, of ultrathin Mo$_2$C MXene, which as mentioned above exhibits a decrease in resistivity from 300K to 50K and a logarithmic increase in resistivity below 50K, indicative of weak 2D localization effect. A superconducting transition was observed just below 3K, with suppression of the superconducting transition for decreasing thickness, i.e. unambiguous evidence of intrinsic thickness-dependent superconductivity [96].

6. Retrospective and outlook

By the end of the 00s, the MAX-phase research field was maturing. MAX phases were also available in selected applications such as heating elements and ohmic contacts to SiC. Nonetheless, much remained to be done, and still does. The development of systematic theoretical methodology has provided invaluable guidance. While new phases are regularly discovered, the approach is no longer ad hoc, but rather a systematic approach to predict and search for stable phases with a view for property tailoring. Magnetic MAX phases were little more than speculation and MXenes were yet to be discovered. Today, they are reality. The discovery of MXene and its rapid acceptance in the 2D materials community [2–4] has launched a new field of research.

Five years after the first report on MXene [19], the progress has been astonishing and the field has come a long way in understanding their chemical and physical properties. Yet, many scientific questions remain and new ones continue to be posed. Further, proof-of-concept of MXene in numerous proposed applications exists, but the applicability of MXene requires taking the step to reproducible large scale synthesis, where initial progress has by now been made [247]. Furthermore, the synthesis of MXene is no longer restricted to only MAX-phase precursor materials, as MXene can now be made from, for example, Mo$_2$Ga$_3$C and Zr$_3$Al$_2$C$_5$ starting materials, or directly from the vapor phase by CVD. On the theory side, an essential remaining challenge is to improve the realism of the modeling of the surface terminations, which is typically much more complex than the sole species usually assumed in computational studies.

In addition to the wide range of synthesis methods now available for MXenes, the functionalization of MXenes by means of surface groups is in its infancy. At present, the understanding of the interaction between MXene and functional group is limited in terms of chemistry and coordination, which is an essential point to address. The broad variations available both in the MXene chemistry and the terminations leave extensive opportunities for property tailoring. However, novel properties are expected not only from MXene chemistry and termination, but also from morphology. One example is significantly improved Li-ion storage capability for Ti$_3$C$_2$/CNT by simply etching holes in the MXene [248].

While there are today numerous magnetic MAX phases [37], magnetic MXene remains to be discovered. Magnetic MAX phases to date include Cr and/or Mn [37], which are both dissolved upon etching with etching procedures used to date. However, new etching and intercalation procedures are continuously being developed, which will open up for more MXene chemistries and morphologies. Thin-film MXenes show promise for their electronic and optical properties, in particular as transparent conducting electrodes, where a broad application range is within reach contingent upon optimization and upscaling of synthesis processes and material quality.

All in all, the discovery of MXene has rapidly launched a new area of research within 2D materials. While the progress of the field has been impressive, MXenes are still early in their development, with new ones continuously being discovered, and the immense opportunities for materials design and surface tailoring in this class of materials remain to be exploited in the coming years.

Acknowledgments

The authors acknowledge support from the European Research Council under the European Community’s Seventh Framework Programme (FP/2007–2013)/ERC grant agreement no. 335383 (PE) and grant agreement no. 258509 (JR), the Knut and Alice Wallenberg Foundation through the Wallenberg Academy Fellows program and for support of the electron microscopy laboratory in Linköping, the Swedish Research Council (VR) through project grants 621-2012-4430, 621-2012-4425, 642-2013-8202, 621-2012-4359, and 622-2008-405, the Swedish Foundation for Strategic Research (SSF) through the Synergy Grant FUNCASE, the Future Research Leaders 5 program (PE) and the Research Infrastructure Fellows program (POAP), and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No 2009-00971).

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