Synthesis and Characterization of 2D Nanocrystals and Thin Films of Transition Metal Carbides (MXenes)

Joseph Halim

Thin Film Physics Division
Department of Physics, Chemistry and Biology
Linköping University, Sweden
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ABSTRACT

Two dimensional (2D) materials have received growing interest because of their unique properties compared to their bulk counterparts. Graphene is the archetype 2D solid, but other materials beyond graphene, such as MoS$_2$ and BN have become potential candidates for several applications. Recently, a new family of 2D materials of early transition metal carbides and carbonitrides (Ti$_2$CT$_x$, Ti$_3$C$_2$T$_x$, Ti$_3$CNT$_x$, Ta$_4$C$_3$T$_x$, and more), labelled MXenes, has been discovered, where T stands for the surface-terminating groups.

Before the present work, MXenes had only been synthesized in the form of exfoliated and delaminated powders, which is not suitable for electronic applications. In this thesis, I demonstrate the synthesis of MXenes as epitaxial thin films, a more suitable form for electronic and photonic applications. Results show that 2D epitaxial Ti$_3$C$_2$T$_x$ films - produced by HF and NH$_4$HF$_2$ etching of magnetron sputter-grown Ti$_3$AlC$_2$ - exhibit metallic conductive behaviour down to 100 K and are 90% transparent to light in the visible-infrared range. The results from this work may open the door for MXenes as potential candidates for transparent conductive electrodes as well as in electronic, photonic and sensing applications.

MXenes have been shown to intercalate cations and molecules between their layers that in turn can alter the surface termination groups. There is therefore a need to study the surface chemistries of synthesitized MXenes to be able to study the effect of intercalation as well as altering the surface termination groups on the electronic structure and chemical states of the elements present in MXene layers. X-ray Photoelectron Spectroscopy (XPS) in-depth characterization was used to investigate surface chemistries of Ti$_3$C$_2$T$_x$ and Ti$_2$CT$_x$. This thesis includes the discussion of the effect of Ar$^+$ sputtering and the number of layers on the surface chemistry of MXenes. This study serves as a baseline for chemical modification and tailoring of the surface chemistry groups to potential uses and applications.

New MXene phases, Nb$_2$CT$_x$ and V$_2$CT$_x$, are shown in this thesis to be produced from HF chemical etching of Nb$_2$AlC and V$_2$AlC powders. Characterization of the produced MXenes was carried out using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Transmission Electron Microscope (TEM) and XPS. Nb$_2$CT$_x$ and V$_2$CT$_x$ showed promising performance as electrodes for Li-ion batteries.
In this thesis, electrochemical etching was used in an attempt to produce 2D metal carbides (MXene) from their ternary metal carbides, Ti$_3$SiC$_2$, Ti$_3$AlC$_2$ and Ti$_2$AlC MAX phases. MAX phases in the form of highly dense bulk produced by Hot Isostatic Press. Several etching solutions were used such as HF, NaCl and HCl. Unlike the HF chemical etching of MAX phases, which results in MXenes, the electrochemical etching resulted in Carbide Derived Carbon (CDC). Here, I show the characterization of the produced CDC using several techniques such as XRD, TEM, Raman spectroscopy, and XPS. Electrochemical characterization was performed in the form of cyclic voltammetry, which sheds light on the etching mechanism.
This thesis summarizes my research work from January 2012 to September 2014. The main focus of this work is to synthesize and characterize MXenes in the form of nanocrystals and epitaxial thin films. Furthermore, this work investigates the ability of production of 2D transition metal carbides (MXenes) by electrochemical etching instead of purely chemical etching of MAX phases. The main results of my studies are presented in the appended papers. This work has been conducted equally in the Thin Films Physics Division at the Department of Physics, Biology, and Chemistry (IFM) at Linköping University and at the Materials Science and Engineering Department at Drexel University. The work has been funded by the Swedish Research Council (VR), Grant Nos. 621-2012-4430 and 621-2011-4420, the VR Linnaeus Strong Research Environment LiLi-NFM, and the Swedish Foundation for Strategic Research (SSF) through the Synergy Grant FUNCASE.
LIST OF PAPERS

I. Room-Temperature Carbide-Derived Carbon Synthesis by Electrochemical Etching of MAX Phases


II. New Two-Dimensional Niobium and Vanadium Carbides as Promising Materials for Li-Ion Batteries

M. Naguib, J. Halim, J. Lu, K.M. Cook, L. Hultman, Y. Gogotsi, and M.W. Barsoum


III. Transparent Conductive Two-Dimensional Titanium Carbide Epitaxial Thin Films


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IV. X-ray Photoelectron Spectroscopy Characterization of Two-Dimensional Transition Metal Carbides (MXenes)


Manuscript in preparation
List of Papers

Author’s contributions:

**PAPER I:** I along with M.R. Lukatskaya planned and performed the electrochemical etching experiments, performed the XPS measurements and performed the peak fitting. Also I took part in writing and editing the manuscript.

**PAPER II:** I with M. Naguib planned and performed the synthesis and etching of the Nb₂AlC and V₂AlC. I analysed the TEM data and took part in the discussion of the XPS analysis. Also I took part in writing and editing the manuscript.

**PAPER III:** I planned and performed the thin film depositions, performed and developed the etching process; performed XRD and XRR of the films before and after etching; and measured the room temperature resistivities. I also analysed the TEM micrographs and the XPS results. I wrote the manuscript.

**PAPER IV:** The paper is based on my idea. The XPS analysis was done by me in cooperation with L.-Å. Näslund and K.M. Cook. I wrote the manuscript with the help of K.M. Cook.
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1. INTRODUCTION

1.1 Graphene and other 2D materials

In 2004, Novoselov et al. [1] managed to isolate a single atomic layer of graphene, measured its electronic properties and reported its ballistic conductivity. This achievement enthralled the scientific community for the last decade. It is worth noting that exfoliation of 3D materials and converting them to 2D materials was already reported in 1859 by Brodie [2] who showed that exfoliation of graphite to single sheets is possible. Furthermore in 1986 Joensen et al. [3] reported on the exfoliation of MoS$_2$ single layers. However, before 2004 no characterization of these single sheets was performed.

According to Geim et al. [4], a 2D crystal is a single atomic plane (monolayer), in the case of graphene one atomic layer of carbon 0.34 nm thick. In contrast, if we have 100 atomic layers of carbon that would be a thin film of graphite (3D material). The question is: if only a monolayer of material is regarded as 2D material or if there is a certain range of thickness for a material to be called 2D material? In the case of graphene, Bianco et al. [5] defined the range of graphene to be considered as 2D material to be from 1 to 10 layers; whereas more than 10 layers would be considered as 3D. This definition was based on the electronic structure of graphene which changes from being a zero-gap semiconductor (often referred to as semimetals) for a monolayer of graphene to the graphitic 3D bulk electronic structure when exceeding 10 atomic layers. Thus, in general one can define the range of thickness for 2D materials to be from one atomic layer to the extent that the electronic structure of such a material approaches that of the 3D bulk.

Graphene is by far the most researched member of the 2D materials owing to its ballistic conductivity, high thermal conductivity, high in-plane mechanical strength, optical transparency of 97.7% per monolayer of the visible light and the possibility of tuning its properties, thus finding its way into many applications [4, 6, 7]. For example, the high mobility of charge carriers in graphene enabled it to be used in the field of transistors. Lin et al. were able to fabricate a 100-GHz transistor from wafer-scale epitaxial graphene [8]. Also taking advantage of its high optical transparency as well as its high flexibility, the dream of obtaining flexible transparent electronic devices is becoming true. Eda et al. produced transparent flexible conductive material of reduced graphene oxides [9]. Kobayashi et al. developed an industrial method that can produce 100 m long high
quality transparent conductive graphene [10]. Such a material can be used in several applications as solar cells, light emitting devices, and touch screens [11].

The rapid advancement in the field of graphene has encouraged several countries, funding agents, as well as companies to focus on graphene. In 2013, the European Commission has awarded 1 billion Euros to the Graphene Flagship [12], a 10-year project aiming to exploit graphene, while in South Korea since 2012 about 200 million US$ has been invested in research on graphene. Interestingly, a large amount of such investments came from private companies such as Samsung [13].

Despite the growing interest in graphene, the lack of a natural bandgap and the existence of very few methods to open a bandgap such as functionalization [14,15] and/or the introduction of defects [16-18], have encouraged scientists to explore other 2D materials. Among these other 2D materials are hexagonal BN [19], transition metal oxides and hydroxides [20], chalcogenides [21] and, a new family of early transitional metals (MXenes) [22-25]. Such a number of 2D materials comes with a variation of properties; thus, each can be used for a certain application, as well as combining several 2D materials to build heterostructure devices. For example, Bertolazzi et al. [26] took advantage of the ballistic conductivity and high mobility of charge carriers for graphene as well as the natural bandgap for MoS$_2$ and built a memory cell device. In that device, graphene is used as conductive electrodes while MoS$_2$ is used as the channel.

1.2 Aim

The aims of this thesis are to: 1. produce MXene in the form of 2D epitaxial thin films to investigate its electrical and optical properties; 2. study the chemical states of the elements in MXene as well as the electronic structure using XPS; 3. explore new MXene phases of different M elements, Nb and V, and; 4. investigate other methods than chemical etching, such as electrochemical etching for production of MXenes.

In order to investigate the electronic and optical properties of MXenes, we needed to produce MXene in the form of thin films. Thus came the idea of deposition of MAX phase Ti$_3$AlC$_2$ by DC sputtering to form epitaxial films that could be etched to obtain 2D epitaxial Ti$_3$C$_2$Tx films. These were then characterized focusing on their application as transparent conductive electrodes.

The in-depth study of Ti$_3$C$_2$Tx and Ti$_5$CTx using X-ray Photoelectron Spectroscopy (XPS) came from the need to understand the MXene structures and how the
termination groups are bound to the MXenes as well as the influence of changing the number of layers.

The reason behind exploring new MXene phases, with different M elements, is to study the effect of changing the M element on the capacity, and the charging/discharging rates for MXenes when used as electrodes for Li-ion batteries.

Electrochemical etching of MAX phase was proposed as another technique for obtaining MXene which could be more industrially used compared to the current used technique which is chemical etching of MAX phase. In addition to investigating other etchants which are less harmful and more environmentally friendly such as HCl and NaCl.

1.3 Outline

This thesis begins with a general introduction to 2D materials. Chapter 2 discusses the structure, synthesis techniques, properties and applications of MAX phases which act as precursors to MXenes, while chapter 3 is concerned with MXenes, illustrating their method of synthesis, effect of processing parameters, structure, exfoliation and intercalation, and properties and applications. Chapter 4 discusses the main characterization techniques used in this work. Chapter 5 summarises the main results in the appended papers. Chapter 6 discusses future work.
2. MAX PHASES

MAX phases are ternary carbides and nitrides forming a large family of more than 60 phases, having a general formula of $M_{n+1}AX_n$, where $n = 1, 2$ or $3$, $M$ is an early transitional metal, $A$ is an A-group element, and $X$ is C and/or N as shown in Figure 1 [27].

These phases have a layered hexagonal crystal structure with two formula units per unit cell. The near-closed-packed M-layers are interleaved with pure A-group element layers, while X-atoms are occupying the octahedral sites between the M layers (Figure 2). This structure provides these compounds with anisotropic behaviour.

**Figure 1.** Periodic table containing elements from which MAX phases are composed, M: early transition metal (red), A: group A element (blue) and X: C and/or N (black) [28-30].

**Figure 2.** Crystal structure unit cells of various MAX phases $M_2AX$ (211), $M_3AX_2$ (312) and, $M_4AX_3$ [31].
2. MAX Phases

2.1 Synthesis of MAX phases

MAX phases can be synthesized in the form of bulk material or thin films.

2.1.1 Bulk synthesis techniques

Several bulk synthesis techniques have been used to produce bulk MAX phases such as pressureless sintering [32], hot pressing [33], Hot Isostatic Pressing (HIP) [34], self-propagating high-temperature synthesis [35], pulse discharge sintering [36] and solid-liquid reaction synthesis [37]. More details about pressureless sintering as well as hot pressing techniques are discussed below since they were used in the production of MAX phase used in papers I and II.

Sintering is a common method for production of ceramics and pottery. Fine powders are mixed with water to form a slurry which is formed into a desired shape. Then, the object is subjected to high temperature which leads into the transformation of that mixture into a more compact and rigid object. That process is called sintering. If one of the constituents of the fine powders has a melting point lower than the sintering temperature, it would transform into liquid while sintering. In that case, the process is called liquid-phase sintering (Figure 3.a). If no liquid phase occurs during the sintering process, it is called solid-state sintering (Figure 3.b).

Like any thermodynamically governed process, the driving force of sintering is reducing the free energy. This can be achieved either through (1) coarsening, through which the total surface area is reduced by increasing the average particle size and/or (2) grain growth followed by densification where the free energy is decreased by the reduction and elimination of the pores between the particles, densification, creating grain boundaries followed by grain growth. Densification and coarsening are two competing mechanisms. The first leads to shrinkage of the sintered object and to an increase of its density, while the latter leads to an increase of the pore size as well as the particle size.

![Figure 3. (a) Liquid-phase sintering; (b) Solid-state sintering.](image-url)
Figure 4. Schematic showing both routes for reduction of free energy during sintering: (a) densification; (b) coarsening.

For densification to take place, the grain boundary energy $\gamma_{gb}$ has to be less than twice the solid/vapor surface energy $\gamma_{sv}$. This can take place when the angle, $\phi$, between the 2 $\gamma_{sv}$ at the intersection between 2 particles (Figure 5) is less than 180°. The relationship between $\gamma_{gb}$ and $\gamma_{sv}$ can be described by the equation below [38]:

$$\gamma_{gb} = 2\gamma_{sv} \cos \frac{\phi}{2} \quad (1)$$

Figure 5. Equilibrium between grain boundary and solid/vapour energies.

There are several factors that can affect the solid-state sintering process and contribute to favour densification rather than coarsening. These factors are:

1. Temperature: increasing the temperature leads to an increase in the diffusion rate, thus increasing the grain boundary diffusion thus densification will dominate over the coarsening process.

2. Density of the object before sintering: increasing the density of the object before sintering would result in decreasing the amount of pores that needs to
be eliminated during sintering. Hence, there would be more chance to obtain a higher dense object after sintering.

3. Atmosphere: choosing the correct atmosphere for sintering is crucial. Certain gases might promote densification while others might promote coarsening. The used gas can increase the diffusivity of the sintered species thus promoting densification or increase the vapour pressure leading to coarsening.

4. Size distribution: the narrower the particle size distribution is, the more homogenous the product is after sintering. Wide particle size distribution would lead to abnormal grain growth which would result in a non-uniform grain size distribution after sintering.

Pressureless sintering technique has been used to produce Nb$_2$AlC and V$_2$AlC MAX phases from their elemental powders. Nb$_2$AlC and V$_2$AlC were used as precursor for synthesis of Nb$_2$CT$_x$ and V$_2$CT$_x$ respectively as mentioned in Paper II.

Fully dense MAX phases can be achieved by applying pressure during sintering. Applying pressure on the sample leads to the decrease of the pore size and promoting the densification process. The relationship between the stress $C_{\text{stress}}$ subject to a certain area and the concentration of vacancies in that area can be defined by the following equation [38]:

$$C_{\text{stress}} = \left(1 + \frac{V_m \sigma_b}{RT}\right) C_v \quad (2)$$

where $\sigma_b$ is the effective stress at the boundary due to the applied stress, $V_m$ is the molar volume, $R$ is the gas constant and $T$ is the temperature. If the pressure is applied uniaxially the process is called hot pressing. Barsoum et al. [39] were able to obtain Ti$_3$SiC$_2$ of more than 99% of the theoretical density using hot pressing technique. This technique also results in a more uniform microstructure and finer grain size compared to sintering technique.

2.1.2 Thin film synthesis techniques

Thin film is a term usually referred to films which have a thickness ranging from several Å to tens of μm. They are usually used to alter the properties of the surface of bulk materials, for example, providing protection against corrosion, wear resistance, or acting as a barrier against gas penetration. Also thin films can be used for their own properties, not in order to enhance the properties of a bulk material, when size reduction is required in the out of plane direction, such as in memory chips and transistors.
Among the techniques used for MAX thin film synthesis, Physical Vapour Deposition (PVD), especially sputtering, is the most used [31]. Unlike bulk synthesis techniques, sputter-deposition is a non-equilibrium process. Thus it can deposit films of compositions and phases that are not constrained by the thermodynamical phase diagrams. This can allow for the synthesis of MAX phase thin films that are not achievable in bulk form.

*Sputtering* is the ejection of atoms by the bombardment of a solid or liquid target by energetic particles such as ions [40]. A negative voltage is applied to the target (material source), which attracts the ions (Figure 6). These ions bombard the target atoms, which are ejected from the target leading to condensation on a substrate forming the thin film of the desired material.

![Sputter deposition setup](image)

**Figure 6.** Sputter deposition setup.

The *sputter yield* ($Y$) is the rate of removal of surface atoms, which is the ratio between the number of sputter-ejected atoms and the number of incident projectiles. The sputter yield is an important factor as it determines when the target will be consumed and needed to be replaced and also affects the deposition rate. $Y$ depends on many factors such as the ion energy and the target material. The sputter yield for a certain material increases as the ion energy for a certain ion size increases. Below a certain ion energy (threshold energy) the sputter yield is almost negligible.
The sputter yield at low ion energy (near threshold) can be calculated from the equation (3) which is based on the theory introduced by P. Sigmund [41]:

$$Y = \frac{3}{4\pi^2} \alpha \frac{4M_1M_2}{(M_1+M_2)^2} \frac{E}{U_s}$$  \hspace{1cm} (3)$$

where: $E$ is the energy of the projectile
- $M_1$ is the mass of the projectile atom in atomic mass unit (amu)
- $M_2$ is the mass of the target atom in amu
- $U_s$ is the surface binding energy, and
- $\alpha$ is a dimensionless parameter depending on the mass ratio and the ion energy.

At low energy and $M_2/M_1$ lower than 1, $\alpha$ is of the order of 0.2. Equation (3) can be explained as follows: when an ion hits the surface of the target, its momentum transfers to the target atoms, as expressed in the term $\frac{4M_1M_2}{(M_1+M_2)^2}$. The transferred momentum reaches maximum when $M_1 = M_2$. For an atom to be removed from the surface of the target, the momentum transfer must be greater than the surface binding energy $U_s$, thus as $U_s$ decreases $Y$ increases. Also based on that equation the sputter yield increases linearly with increasing the ion energy.

As mentioned previously, sputtering is based on ion bombardment of the target to eject the surface atoms of the target. The most widely used ion source is plasma which is composed of free electrons and positively charged ions. A plasma-based sputter deposition apparatus is composed of a cathode (target) and anode placed opposite each other in a vacuum chamber of a base pressure typically lower than $10^{-4}$ Pa. Various pumps are used to reach that pressure, for example a rotary pump is used to lower the pressure from the atmospheric pressure ($10^5$ Pa) to 1 Pa, followed by a turbomolecular pump which used to bring the chamber to the desired pressure, i.e. less than $10^{-4}$ Pa [42]. A noble gas such as argon is introduced to the chamber after reaching the desired base pressure which is ionized by applying a high potential difference of about 2000 V between cathode and anode and a glow discharge is ignited.

The electric circuit creating the discharge contains an external ohmic resistance described by the following equation:

$$\text{EMF} = V + RI$$  \hspace{1cm} (4)$$

where EMF is the electromotive force in volts,
- $V$ is the voltage of the gas discharge in volts,
- $R$ is the external ohmic resistance in ohms, and
- $I$ is the current in ampères.
This equation is also presented in figure 7, by the straight line called load line which upon intersecting the I-V characteristics, gives the actual I and V values in a discharge.

**Figure 7.** The three primary regions of a gas discharge. The straight line is a typical load line.

The glow discharge can be discussed through the characteristic I-V diagram shown in Figure 7. I-V diagram can be divided into three regions as follows:

1. The first regime (Dark discharge): through this region there is no visible light for the discharge except for the corona and the breakdown voltage. From A to B there is a slight increase in the current by increasing the voltage which is due to the movement of the ions and electrons formed by the background ionization towards the electrodes. After the voltage reaches point B, the current is constant as all ions and electrons reach the electrodes, this region is called the saturation regime. Then the current increases again when the voltage reaches a value higher than point C, as more ions receive enough energy to collide with the electrodes producing more ions. The region C to E is called Townsend regime. The corona discharge takes place from the middle of the Townsend regime till its ending (D to E). Corona discharge occurs in regions of high electric field such as near sharp points and edges. The visibility of the corona depends on the electric current. If the electric current is low, the corona is not visible to the eye; however, if the electric current is high enough the corona becomes visible.
to the eye and, in that case it is more or less a glow discharge. When ions and photons collide, secondary electrons are emitted from the cathode, thus the gas becomes electrically conductive, i.e. a breakdown voltage occur. The breakdown voltage is described by Paschen’s law as follows [40]:

$$V_{\text{breakdown}} = \frac{BPd}{\ln(APd)+\ln(\ln\left(\frac{1}{\gamma}+1\right))} \quad (5)$$

where, $P$ is the pressure inside the chamber,
$d$ is the gap distance between the electrodes,
$\gamma$ is the electron emission yield induced by photon and ion bombardment,
$A$ and $B$ are constants which depend on the gas used.

Based upon Paschen’s law, the breakdown voltage, for a certain gas and electrode material, depends on the product of the pressure and the distance between the electrodes. Thus the larger that product is the higher the breakdown voltage will be.

2. The second regime (glow discharge): in this regime the plasma is visible to the eye unlike the dark discharge regime. The glow discharge regime is divided into two modes. The first region is called the normal glow discharge, which takes place when the glow discharge is covering a part of the cathode. In this mode the current density is independent of the discharge voltage, so by increasing the current density the plasma region increases covering more area of the cathode while the voltage remains constant as shown from point F to G. As soon as the plasma covers the entire area of the cathode the second mode begins (abnormal glow discharge), which is characterized by the dependence of the voltage on the current density, (i.e. as the current density increases the voltage increases as well). Sputtering is performed in the abnormal glow discharge mode from G to H.

3. The third regime (arc discharge): in this regime, the cathode becomes hot enough so that electrons are emitted thermionically and discharge is changed from glow to arc.

The main drawback of DC (diode) glow discharge sputtering is the inability of ensuring that electrons accelerated from the cathode will ionize enough gas atoms to sustain the glow discharge. One way to overcome this drawback of the DC glow discharge system is by introducing a magnetic field that would trap the electrons in the discharge region longer, thus increasing the probability of ionizing the gas atoms while the electron is travelling from the cathode to the anode. By that way, enough gas atoms will be ionized and in the same time the ions will reach the substrate with no loss of energy and with a very few collisions (Figure 8). This technique is called magnetron sputtering.
In magnetrons, the magnetic field, \( \vec{B} \), is applied parallel to the target and perpendicular to the electric field. The electrons emitted from the target due to the ion collision are forced to move in cycloidal orbits as a result of the applied magnetic field. The electron path is described by the Lorenz equation as in the following equation:

\[
\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})
\]  

Where \( \vec{F} \) is the Lorenz force, 
q is the electron charge,  
\( \vec{v} \) is the velocity of electron,  
\( \vec{B} \) is the magnetic field, and  
\( \vec{E} \) is the electric field.

According to the equation above, the Lorenz force on the electron depends on both the velocity of the electron and the strength of the magnetic field and is perpendicular on their directions.

The electron motion consists of three components; the first component is the movement of the electron along the magnetic field. The second component is the rotation of the electron around the magnetic field, where the radius of rotation (Larmor radius) depends on the mass of electron \( m \), the velocity component perpendicular to the magnetic field \( v_{\perp} \), the electron charge \( q \) and the magnetic field \( B \).

\[
r_L = \frac{mv_{\perp}}{qB}
\]  

The third and final component is due to the effect of both the magnetic field \( B \) and electric field \( E \) (Hall Effect), where the electron moves in a helical orbit perpendicular to both the electric and magnetic fields.
There are several methods for powering the target such as direct current (DC) which is used for conductive targets, and radio frequency (RF) which is used for non-conductive targets. Moreover, a reactive gas might be added to the plasma to deposit a thin film of a compound containing the species found in that gas, such as the deposition of TiN thin films using a DC magnetron sputtering system, titanium target and nitrogen gas [44]. A three target DC magnetron sputtering system was used for synthesis of Ti$_3$AlC$_2$ thin films reported in paper III. The main reason for using a three target deposition system is to have control over the flux of each element which helps in controlling the deposited film composition.

The deposition parameters have a strong influence on the film morphology and microstructure. Thus it is essential to know how such parameters affect the morphology and microstructure of the deposited film in order to grow the films of desired morphology. Structure zone models (SZM) have been developed to show the effect of the deposition parameters on the morphology and microstructure of the deposited films. The SZM published by Thornton in 1974 [45] has been used as a base for many several studies later in time (Figure 10). SZM’s are usually represented as a function of the ratio between the substrate temperature T and the melting temperature of the deposited material $T_m$.

Zone I occurs when $T/T_m$ is low, about 0.1, sputtered particles will simply stick to the growing film at the place they arrive. That is because the particles do not have enough energy to cross the diffusion barrier, this phenomenon is often referred to as hit and stick growth. The only factor affecting the structure of the growing film is the direction of the incoming particles. Due to the inability of the particles to move, only small crystallites with amorphous like structure will form. After adequate time of deposition, the crystallites will grow into columns separated by voids. Such morphology will make the deposited film of lower density compared to the bulk material due to the voids.
The same structure can also be obtained at high temperatures provided that the deposition rate is high. In that case, the adparticles will not have enough time to diffuse to a more stable site. Although they have the enough energy to cross the diffusion barrier, they are hindered by the incoming adparticles that will be deposited over them. In that situation the process is called **burial growth process** where still zone I structure is obtained but through a different mechanism.

Zone T takes place at higher temperature when the adatoms have enough energy to diffuse from one grain to another. This would allow for a denser columnar structure compared to that of zone I.

In zone II the temperature is high enough to enable the mobility of incorporated atoms in the growing films which was prohibited in all the previously discussed zones as temperature was not high enough for such mobility to occur. The mobility of the incorporated atoms leads to the observation of recrystallization or restructuring of the formed islands. Less stable islands will get merged into more stable islands by ripening, cluster diffusion or grain boundary migration. A columnar structure will be formed with nearly straight columns through the entire film thickness. Increasing the temperature to higher values will increase the width of the columns. Thus for growing epitaxial films, besides the necessity of lattice match between the film and the substrate, higher temperatures would be favourable for growing denser films with larger grain size.

**Figure 10.** Schematic of the structure zone model (SZM).
2.2 Properties of MAX phases

The properties of MAX phases are a unique combination of metals and ceramics properties. They are thermally and electrically conductive, thermal shock resistant, machinable and damage tolerant like metals; also they have low density, high elastic stiffness and exhibit oxidation resistance like ceramics. For instance Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$ show a substantial resistance to creep, fatigue and oxidation [46-49].

MAX phases are layered materials where mechanical deformation takes place by basal dislocations and is very anisotropic – it can lead to partial delamination and the formation of lamellae with thicknesses ranging from tens to hundreds of nanometers as shown in Figure 11 [50]. Therefore, one would assume that exfoliation of MAX crystals to monolayers is possible, similar to graphene. However, mechanical exfoliation of MAX crystals into single layers is difficult because of the nature of bonding between the elements forming MAX crystals. In the case of graphene, layers are bonded to each other by the means of Van der Waals force which is a relatively weak bond that could be broken using mechanical exfoliation [51].

![Figure 11. Scanning Electron Microscopy (SEM) micrograph of Ti$_3$SiC$_2$ sample, its surface was scribed by a sharp metal blade showing partial delamination [50].](image)

As for MAX solids, there is a mixture of ionic, metallic and, covalent bonds between the M and X elements, while the M element is bonded to the A element layer via metallic bond which is still weaker than the bond between the M and X elements [52,53]. Thus the A layers are chemically more reactive, this is seen when heating MAX phases at high temperatures they decompose into M$_{n+1}$X$_n$ and A. The former recrystallizes forming binary carbides and/or nitrides [54].

Reacting MAX phases with chlorine gas at high temperatures results in the removal of both M and A elements, leaving only carbon, which is named carbide derived carbon (CDC) [55-57].
3.2D TRANSITION METAL CARBIDES (MXENES)

3.1 Synthesis of MXenes

Taking advantage of the fact that the A element in MAX phase is more chemically reactive than the MX, Naguib et al. [23] were able to chemically etch the A element (Al) from Ti$_3$AlC$_2$ powders using aqueous solution of HF. This resulted in exfoliated M$_{n+1}$X$_n$ (Ti$_3$C$_2$) layers which are named MXenes. The reactions of HF with Ti$_3$AlC$_2$ have been proposed to be as follows [23]:

$$\text{Ti}_3\text{AlC}_2 + 3\text{HF} = \text{AlF}_3 + 3/2\text{H}_2 + \text{Ti}_3\text{C}_2 \quad (1)$$
$$\text{Ti}_3\text{C}_2 + 2\text{H}_2\text{O} = \text{Ti}_3\text{C}_2(\text{OH})_2 + \text{H}_2 \quad (2)$$
$$\text{Ti}_3\text{C}_2 + 2\text{HF} = \text{Ti}_3\text{C}_2\text{F}_2 + \text{H}_2 \quad (3)$$

When HF reacts with Ti$_3$AlC$_2$, Al and F form AlF$_3$ (reaction 1), which is removed while washing the powder from HF with deionized water. The Al in Ti$_3$AlC$_2$ is replaced by OH, O and/or F (reaction 2 and 3), referred to as surface terminating functional groups. Thus the general formula of MXenes containing these functional groups is M$_{n+1}$X$_n$T$_x$ where T stands for the surface-terminating groups. Figure 12 is a schematic of the production process of MXene from MAX.

**Figure 12.** Schematic diagram of the production of MXenes from MAX phases [24].
3.1.1 Factors Influencing the Production of MXenes

Following the success in obtaining the first MXene compound, more MXene phases have been synthesized. Nine MXene phases, obtained from MAX powder, have been reported (Ti$_3$C$_2$Tx [23], Ti$_2$CT$_x$ [24], Ti$_3$CNT$_x$ [24], (Ti$_{0.5}$Nb$_{0.5}$)$_2$CT$_x$[24], Ta$_2$CT$_x$[24], (V$_{0.5}$Cr$_{0.5}$)$_2$CT$_x$ [24], Nb$_2$CT$_x$ [22,58], Nb$_4$C$_3$T$_x$ [22], and V$_2$CT$_x$ [22]). These results show that MAX phases of different layers, $n = 1, 2$ and $3$, and different M elements Ti, Nb, and V, can be converted to MXene as well as MAX phases having solid solutions of two different M elements V and Cr. Table 1 summarizes: 1) the etching conditions used to produce the MXenes mentioned above, 2) the $c$ lattice parameters before and after the HF treatment and 3) the MXene yield based on the weight of the powder after etching divided by the weight of the powder before etching multiplied by 100.

The process of synthesizing MXenes depends on many factors such as the particle size of the starting MAX phase powder, etching time, and HF concentration [22]. Thus, tuning these factors leads to increased yield, reduced etching time and improved quality of the produced MXenes. For example reducing the particle size of Ti$_3$AlC$_2$ from above 53 μm to less than 38 μm resulted in the decrease in the time needed for a complete conversion of Ti$_3$AlC$_2$ to Ti$_3$C$_2$T$_x$ in 50% HF conc. from 19 hours to only 2 hours [59]. The same holds true for V$_2$AlC, it is demonstrated in paper II that decreasing the particle size by using the attrition mill instead of the titanium-nitride-coated milling bit led to the reduction of etching time from 90 to 8 hours. This method decreased the yield of the process.

Several other factors affect the etching conditions. These factors are related to the chemistry and structure of the MAX phase among them is the effect of changing the M element as well as changing the number of layers, $n$. MAX phases of different M element will possess different M-Al binding energies which will affect the etching conditions. Conversion of Ti$_2$AlC to Ti$_2$CT$_x$ needs shorter etching time and lower HF concentrations than those needed for converting Nb$_2$AlC to Nb$_2$C (Table 1). This could be explained when comparing the binding energy of Ti-Al to that of Nb-Al in Ti$_2$AlC, and Nb$_2$AlC, respectively. Ti-Al has a lower binding energy of 0.98 eV compared to that for Nb-Al, (1.21 eV) and V-Al (1.09 eV) [60]. More interesting, as the number of layers increases the chemical stability of the MXenes increases. For example Ti$_3$C$_2$T$_x$, etched in 50% conc. HF, has a yield of 100% whereas, 10% conc. of HF is sufficient to produce Ti$_2$CT$_x$ of a 60% yield (Table 1).
### 3. 2D Transition Metal Carbides (MXenes)

#### Table 1. Summary of MXenes being reported to date, the etching conditions at room temperature, c lattice parameter before c$_i$, and after, c$_f$, HF treatment as well as the yield of the process estimated by weighting the powders before and after HF treatment.

<table>
<thead>
<tr>
<th>MAX</th>
<th>MXene</th>
<th>HF, conc. %</th>
<th>Time, h</th>
<th>C$_i$, Å</th>
<th>C$_f$, Å</th>
<th>Yield, %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$AlC$_2$</td>
<td>Ti$_3$C$_2$Tx</td>
<td>50</td>
<td>2</td>
<td>18.4</td>
<td>20.5</td>
<td>100</td>
<td>[23]</td>
</tr>
<tr>
<td>Ti$_3$CIC</td>
<td>Ti$_3$CTx</td>
<td>10</td>
<td>10</td>
<td>13.6</td>
<td>15.0</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$AlCN</td>
<td>Ti$_3$CNTx</td>
<td>30</td>
<td>18</td>
<td>18.4</td>
<td>22.3</td>
<td>80</td>
<td>[24]</td>
</tr>
<tr>
<td>(Ti$<em>5$(Nb$</em>{5.5}$)$_3$AlC)</td>
<td>(Ti$<em>5$(Nb$</em>{5.5}$)CTx</td>
<td>50</td>
<td>28</td>
<td>13.8</td>
<td>14.9</td>
<td>80</td>
<td>[24]</td>
</tr>
<tr>
<td>Ta$_3$AlC$_2$</td>
<td>Ta$_3$AlC$_3$</td>
<td>50</td>
<td>72</td>
<td>24.1</td>
<td>30.3</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>(V$<em>3$(Cr$</em>{6.5}$)$_3$AlC)</td>
<td>(V$<em>3$(Cr$</em>{6.5}$)CTx</td>
<td>50</td>
<td>69</td>
<td>17.7</td>
<td>24.3</td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>Nb$_3$AlC</td>
<td>Nb$_3$CTx</td>
<td>50</td>
<td>90</td>
<td>13.9</td>
<td>22.3</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Nb$_3$AlCN</td>
<td>Nb$_3$C$_2$Tx</td>
<td>50</td>
<td>96</td>
<td>24.2</td>
<td>30.5</td>
<td>77</td>
<td>[58]</td>
</tr>
<tr>
<td>V$_2$AlC</td>
<td>V$_2$CTx</td>
<td>50</td>
<td>8*</td>
<td>13.1</td>
<td>24.0</td>
<td>55</td>
<td></td>
</tr>
</tbody>
</table>

* V$_2$AlC powder was obtained by milling the sintered V$_2$AlC sample using the attrition mill while the rest of the sintered phases were milled using a titanium-nitride-coated milling bit.

#### 3.2 Structure of MXenes

The crystal structure of MXenes is similar to that of the MAX phases with the exception of replacing the A element with the terminated functionalization groups, T$_x$. The first proposed models for multilayered Ti$_3$C$_2$T$_x$ were based upon density functional theory, DFT, simulations [23]. In those models all T$_x$ were assumed to be either OH or F. Simulated XRD diffraction patterns were obtained from these models and compared with XRD diffraction patterns obtained experimentally for Ti$_3$C$_2$T$_x$ as shown in Figure 13. The Ti$_3$C$_2$(OH)$_2$ is the closest to the experimental one, however experimental results obtained from XPS analysis show the presence of OH, O and F terminations [61].

Later on, the theoretical work on MXenes focused on solving a fundamental problem which is finding the most energetically favourable position of T. Enyashin et al. [62] proposed and studied three configurations (Figure 14). Configuration I: OH groups are positioned in the empty space between the three carbon atoms on the two sides of the MXene layer (Figure 14b, and e), configuration II: OH groups are located right above the C atoms on both sides of the MXene layer (Figure 14c, and f), while configuration III (Figure 14d) is a combination of configurations I and II, where each configuration I and II occupy one side of the MXene layer. It was found by comparing the relative total energies for the three configurations that the least stable is configuration I, while the most stable is configuration II. The same results were also obtained for Ti$_3$C$_2$F$_2$ [63].
Figure 13. XRD patterns for Ti$_3$AlC$_2$ before and after HF treatment, Ti$_3$C$_2$Tx after sonication in water (exfoliated) and simulated XRD patterns of Ti$_3$C$_2$F$_2$, Ti$_3$C$_2$(OH)$_2$ structure models [23].

Figure 14. Atomic structures of: (a) Ti$_3$C$_2$ layer without any terminations. (b) Ti$_3$C$_2$ layer with OH terminations in configuration I. (c) Ti$_3$C$_2$ layer with OH terminations in configuration II. (d) Ti$_3$C$_2$ layer with OH terminations in configuration III. (e) Top view of Ti$_3$C$_2$ layer with OH termination in configuration I. (f) Top view of Ti$_3$C$_2$ layer with OH termination in configuration II [62].
3.3 Exfoliation, Intercalation and Delamination of MXenes

Delamination trials for the exfoliated MXenes have been carried out in order to separate the stacked layers into single flakes. The first approach was to sonicate the exfoliated MXenes in isopropanol or methanol. This process resulted in a low yield of single flakes and a relatively small size of the produced flakes [24].

Although after Al removal, the bond between the MXene layers is weaker. It is not weak enough to be broken by sonication alone. This is reason the behind the low yield of delaminated flakes after sonication. One approach which is commonly used for obtaining 2D layers is intercalation of a compound between the layers, which breaks the bonds between the layers and isolating the layers from each other. This method was used decades ago to exfoliate vermiculite [64] as well as other clays [65]. Nowadays, it is one of the methods used to obtain single layers of 2D materials such as graphene [66] and MoS₂ [67].

Using this technique Mashtalir et al. [61] intercalated Ti₃C₂Tx with dimethylsulfoxide (DMSO). Immersion of Ti₃C₂Tx in DMSO resulted in an increase in the c lattice parameter from 19.5 to 35 Å as shown in Figure 15 (a), a clear evidence of intercalation taking place. After sonication in water, the XRD pattern shows the loss of non-basal peaks at about 2θ = 60° which leads to loss of
order along all planes except [000l]. This indicates that a complete delamination takes place. Figure 15 (b) is a schematic explanation of the entire process starting from MAX phase to delaminated MXene along with SEM micrographs of the materials after each process.

Ti$_3$C$_2$Tx powders have not only shown to be intercalated by DMSO, but also other molecules such as hydrazine, urea along with also cations such as (Na$^+$, K$^+$ and Mg$^{2+}$) [61,68]. Not only Ti$_3$C$_2$Tx show the intercalation phenomenon but also other MXenes such as Ti$_3$CNT$_x$ and TiNbCT$_x$. However, only Ti$_3$C$_2$Tx has been delaminated to date; there are no reports of delamination of other MXenes.

### 3.4 Properties and Applications of MXenes

Similar to graphene, modifying the surface terminations can result in tuning the properties of MXenes to suit specific applications. Much theoretical work using DFT was done to understand the electronic structure of MXenes and how they change by changing the surface terminations and what is the influence of that change on the properties of MXenes [23,63,69-73].

DFT calculations predict that MXene monolayers without surface terminations are metallic and that their electron density of states, DOS, near the Fermi level, $E_F$, are higher than that of their parent MAX phases [23,63,69,70]. In MAX phases, taking Ti$_2$AlC as an example, the valence states below $E_F$ are divided into two sub-bands. One of them which is the nearest to $E_F$ is mainly composed of a hybridization between Ti 3d and Al 3p orbitals, this sub-band is denoted sub-band A (Figure 16). The other sub-band, denoted B, is located further away from $E_F$ between -10 and -3 eV and is formed from the hybridization between Ti 3d and C 2p orbitals. In MXenes, the removal of the A element leads to the reformation of sub-band A due to the removal of Al 3p orbitals. Thus sub-band A will be composed of only Ti 3d orbitals meaning that the nature of the bonding become a metallic Ti-Ti bonding resulting in the increase in an electron DOS near the $E_F$ of Ti$_2$C compared to Ti$_2$AlC [71].

These findings have a strong influence on the magnetic properties of MXenes. The increase in the electron DOS near the $E_F$ caused by the d orbitals of M, leads could potentially lead to magnetic properties [69,70,74]. For example DFT calculations predict that Cr$_2$C, Cr$_2$N [70] and Ta$_3$C$_2$ [74] are ferromagnetic while Ti$_3$C$_2$ and Ti$_3$N$_2$ [69] are antiferromagnetic. Such magnetic properties disappear as soon as the MXenes are terminated with any functional groups due to changes in the sub-band A from M-M bonding to M-T bonding causing a reduction in electron DOS near the $E_F$. That is not true for Cr$_2$C and Cr$_2$N where theoretical calculations show
that Cr$_2$CT$_x$ will stay magnetic up to almost room temperature [70]. It is worth noting that no one has reported the production of Cr$_{n+1}$X$_n$T$_x$ experimentally.

As surface terminations are important factors influencing the magnetic properties of MXenes, they also influence whether a particular MXene compound is a metal, semiconductor or insulator. Through theoretical calculations, the band gaps of bare MXenes and MXenes with various surface terminations were predicted. As stated above bare MXenes surfaces are predicted to be metallic-like conductors. However surface terminated MXenes vary from being semiconductor with a very small band gap to large direct or indirect band gap as show in Table 2. The key to understanding the reason behind the changes in band gap is how the electron DOS near $E_f$ changes when MXenes are surface terminated as shown in Figure 16 [4,37,44,45]. The existence of the surface terminations results in the formation of a third sub-band, sub-band C, located below sub-band B. The latter is formed due to the M-T bonds moving the gap between sub-band A and B to lower energies.

Figure 16. Partial density of states of Ti$_2$AlC, and Ti$_2$CT$_x$, where $T_x$ is O$_2$, F$_2$, H$_2$ or (OH)$_2$ [71].
3. 2D Transition Metal Carbides (MXenes)

Table 2. Band gap values calculated theoretically for various MXenes with different surface terminations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band gap, eV</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$C$_2$(OH)$_2$</td>
<td>0.05</td>
<td>[23]</td>
</tr>
<tr>
<td>Ti$_3$C$_2$(F)$_2$</td>
<td>0.10</td>
<td>[23]</td>
</tr>
<tr>
<td>Ti$_2$CO$_2$</td>
<td>1.03*</td>
<td>[70]</td>
</tr>
<tr>
<td>Sc$_2$C(OH)$_2$</td>
<td>0.45**</td>
<td>[70]</td>
</tr>
<tr>
<td>Sc$_2$C(F)$_2$</td>
<td>1.80*</td>
<td>[70]</td>
</tr>
<tr>
<td>Sc$_2$CO$_2$</td>
<td>0.24*</td>
<td>[70]</td>
</tr>
<tr>
<td>Zr$_2$CO$_2$</td>
<td>0.88*</td>
<td>[70]</td>
</tr>
<tr>
<td>Hf$_2$CO$_2$</td>
<td>1.00*</td>
<td>[70]</td>
</tr>
</tbody>
</table>

*indirect band gap, **direct band gap

Theoretical results obtained for different MXenes cannot be directly implemented on the MXenes produced experimentally, due to the lack of a structure model that takes into consideration the fact that the surface terminating groups, T, in MXenes are not composed of one functional group but more than one. Another problem with the theoretical studies is that they only predict properties for isolated layers when the obtained MXenes experimentally are in the form of stacked layers. However, still theoretical predictions of MXene properties based upon the proposed models become useful in directing the experimental work to the MXenes of interesting properties.

Similar to the MAX phases, MXenes of different elements and n layers vary in their electrical resistivities [75]. The resistivity of cold pressed freestanding discs for different exfoliated MXenes is about four times higher than that for their parent MAX phases. For example the resistivity of cold pressed Ti$_3$AlC$_2$ is 1200 μΩm while that for Ti$_3$C$_2$T$_x$ is 5000 μΩm. The sheet resistance values reported for MXenes are comparable to those for multilayered graphene [1, 76, 77]. The etching time as well as intercalation of various compounds in MXenes were found to play an important role in changing the resistivities of cold pressed MXenes discs [59]. Increasing etching time of Ti$_3$AlC$_2$ results in a significant increase in resistivity of the produced Ti$_3$C$_2$T$_x$ [2]. Mashtalir et. al [34], reported on the increase of resistivity of cold pressed discs of Ti$_3$C$_2$T$_x$, Ti$_3$CNT$_x$, Nb$_2$CT$_x$, and TiNbCT$_x$ after intercalation with hydrazine monohydrate, this behaviour is similar to other 2D materials such as the intercalation of TaS$_2$ with hydrazine [78]. MXenes have also been reported to be hydrophilic, by measuring the contact angle on cold pressed discs. The hydrophobicity of the MXenes would be an advantage when using MXenes in energy storage devices containing aqueous electrolytes or dispersing them in water or alcohol.
The mechanical properties of MXenes have been of an interest to investigate due to the strong M-X bonds. Their elastic properties have been predicted by calculating the elastic constant when stretched along the basal planes, $c_{11}$, using DFT calculations [23,79]. MXenes show high values of $c_{11}$ compared to their parent MAX phases; however, these values are lower than that what was reported for graphene [80].

Energy storage applications are considered of the early explored potential applications for MXenes specially lithium ion batteries (LIBs). Theoretical as well as experimental studies show promising behaviour for MXenes as anodes in LIBs [22,63,69,81]. Theoretical calculations predict that Ti$_3$C$_2$ could achieve a better performance as an anode in LIBs compared to TiO$_2$ because of its higher electrical conductivity due to its metallic nature, its lower open circuit potential and its high charge/discharge rates [63]. Although several MXenes (Ti$_3$C$_2$Tx [61], Ti$_2$CTx [81], V$_2$CTx [22] and Nb$_2$CTx [22]) have been experimentally studied for their performance as anodes in (LIBs) but the most exciting results were obtained for delaminated Ti$_3$C$_2$Tx [61]. Delaminated Ti$_3$C$_2$Tx was used as an anode without any additives for (LIBs). The delaminated Ti$_3$C$_2$Tx anodes show a reversible capacity 4 times higher than that of exfoliated Ti$_3$C$_2$Tx as shown in Figure 17. Furthermore, delaminated Ti$_3$C$_2$Tx paper proved to have the capability of maintaining good capacity at high rate (110 mAh g$^{-1}$ at 36 C after 700 cycles). Also in the same field of energy storage, MXenes show a volumetric capacitance exceeding 300 F/cm$^3$ which is much higher than for porous carbon currently used in electrochemical capacitors [68].

![Figure 17](image.png)

**Figure 17.** Performance of exfoliated and delaminated Ti$_3$C$_2$Tx as anodes in LIBs. Inset showing the delaminated Ti$_3$C$_2$Tx after filtration through the alumina membrane, scale bar is 4 μm long [35].
Ti$_3$C$_2$Tx was used as a supporting material for platinum nanoparticles [82]. The Ti$_3$C$_2$Tx/Pt catalysts showed extraordinary stability and durability compared to the conventionally used Pt/C catalysts for proton exchange membrane fuel cells. Very recently, MXenes were investigated for their hydrogen storage properties. Using both DFT calculations and molecular dynamics simulations, the hydrogen storage properties for Ti$_2$C, Sc$_2$C and V$_2$C were studied showing the possibility of hydrogen storage up to about 3.4 wt.% reversibly at room temperature [83].
4. Characterization Techniques

4. CHARACTERIZATION TECHNIQUES

This chapter describes the most important techniques used in characterizing the present work.

4.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is one of the most common techniques used to characterize the structure of materials whether it is powder, bulk or thin films. It is a non-destructive technique and it does not need extensive sample preparation. The technique is based on the scattering of X-rays by atoms. Constructive interference is achieved at certain angles governed by Bragg’s law [84].

\[ n\lambda = 2dsin \theta \] (8)

Where \( n \) is an integer,
- \( \lambda \) is the wavelength of the probing rays,
- \( \theta \) is the angle between the incident rays and the surface of the crystal, and
- \( d \) is the spacing between layers of atoms.

Constructive interference would give peaks at characteristic positions in the X-ray diffractogram from which the lattice parameters as well as phase identification is possible using a mode called \( \theta/2\theta \) scan, where \( \theta \) is the angle between the incident beam and the sample, and \( 2\theta \) is the angle between the incident beam and the detector.

The XRD \( \theta/2\theta \) scans in this thesis were performed for phase identification as well as measurement of lattice parameters. The latter was used to determine the conversion of MAX to MXene as well as whether intercalation of the produced thin film MXenes Ti\(_3\)C\(_2\) when Ti\(_3\)AlC\(_2\) is etched by NH\(_4\)HF\(_2\). As shown in Figure 18, the (002) peak for Ti\(_3\)AlC\(_2\) thin film etched by HF is shifted to lower \( 2\theta \) values compared to the film before etching. This is due to the removal of the Al layers as well as the exfoliation of the films resulting in an increase in the \( c \)-lattice parameter from 18.6 to 19.8 Å. While the film etched by NH\(_4\)HF\(_2\), Ti\(_3\)C\(_2\)Tx-IC, IC stands for intercalated compound, is shifted further to the left compared to that of Ti\(_3\)AlC\(_2\) thin film etched by HF. This shift is attributed to an increase in the \( c \)-lattice parameter.
4. Characterization Techniques

parameter to 24.7 Å, indicating that intercalation took place while etching the thin film using NH₄HF₂.

![XRD patterns](image)

**Figure 18.** XRD patterns for thin films of Ti₃AlC₂, Ti₃C₂Tx and Ti₃C₂Tx-IC.

4.2 X-ray Reflectivity (XRR)

X-ray reflectivity (XRR) is another nondestructive technique that is used to measure the thickness, roughness, and density of thin films [84]. XRR uses the same θ/2θ configuration as for phase identification, but it is performed using parallel beam where the beam divergence does not exceed 0.05° compared to the wide angle beam used for phase identification. Moreover, the θ angle for XRR is much smaller from 0 to 10° compared to what is usually used for θ/2θ scans. However XRR has several limitations of which is the ability to measure films’ thickness up to 1μm. Thickness cannot be measured for thin films of roughness exceeding 50 nm. The technique itself doesn’t work if there is no electron density difference between the thin film and the substrate.

Since in XRR we are more concerned with the refracted beam, Bragg’s law require modification as follows:

\[
m\lambda = 2d \sin\theta \sqrt{1 + \frac{n^2 - 1}{\sin^2 \theta}} \quad (9)
\]

where m is an integer number representing the order of Kiessig fringe (Figure 19),
\( \lambda \) is the wave length of the probing rays,
\( d \) is the film thickness,
\( \theta \) is the angle at which m is at, and
\( n \) is the refractive index.
The thickness can be deduced from plotting sin^2 θ vs. m² and obtaining the slope, then substituting in the following equation:

\[ d = \frac{\lambda}{2\sqrt{\text{slope}}} \]  

(10)

**Figure 19.** X-ray reflectometry measurements for Ti₃AlC₂ thin film sputter-deposited for 10 min, resulting in a thickness of 28 nm.

### 4.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique that is used for compositional and chemical state analysis of the surfaces of materials [85]. The basic principle of XPS is the knocking out of electrons from the core level of the atoms via photons as shown in Figure 20. The electrons that manage to reach the detector without energy loss are shown as photoelectron peaks that represent the binding energy (BE). Each element in each specific chemical state has a characteristic binding energy which is determined from the measured kinetic energy (KE) by the following equation [85]:

\[ BE = h\nu - KE - \Phi \]  

(11)

where \( h\nu \) is the energy of the X-ray photon and,

\( \Phi \) is the work function of the spectrometer.

Since the electrons that preserve their energy are the only ones that contribute to the XPS spectrum as peaks, these electrons can only be ejected from the surface of
the sample since any electrons that are buried deep in the material would suffer from inelastic scattering and would lose its energy before reaching the detector. For this reason, XPS analysis is limited to measuring the elemental composition down to 8 to 10 nm depth in the sample.

For compositional analysis, survey scans mode is used where the spectrum ranges are 1000 eV. However for chemical state analysis high resolution spectra mode is used where the spectrum window is narrower about 100 eV and the scanning step is smaller while the time per step is longer.

Surface contaminations are very important parameters that affect the XPS results since the technique is extremely surface sensitive. Thus, the samples have to be either kept under vacuum all the time, or if that is not practically possible, Ar⁺ sputtering can be used to sputtering clean the surface of the sample. However care should be taken to avoid sputtering damage to the structure and chemical changes. Figure 21 shows the effect of sputtering on carbon of a Ti₃C₂Tx thin film at the C 1s core level. After sputtering the Ti-C peak at 282 eV is shifted to higher binding energy, while the C-C peak at 285 eV is decreased significantly and shifted to lower binding energy. Furthermore the organic contamination peak at 289 eV has disappeared after sputtering, indicating the removal of surface contaminations after Ar⁺ sputtering.

**Figure 20.** Schematic diagram showing the basic principle of the XPS technique.
4. Characterization Techniques

**Figure 21.** High resolution XPS spectra for C 1s core level before and after sputtering for Ti$_3$C$_2$T$_x$ thin film.

Besides obtaining information from the core level of the atoms, XPS can be used to determine the density of states (DOS) of the valence band. As expected, valence electrons have lower binding energy compared to the core level electrons as they are positioned further away from the nucleus. Thus, the photoemissions from the valence electrons are located very close to the Fermi level as the valence band is usually at a binding energy of the range of 0 to 15 or even 25 eV.

In order to have a proper identification of the chemical species based upon the XPS spectra, calibration is essential. Such calibration can be done by calibrating with respect to the binding energy of a certain element where the most common is adventitious carbon [85]. However, this method is not accurate when Ar$^+$ sputtering is performed, as this species is removed and/or altered due to the effect of sputtering. So, the best method in that case as in Papers III and IV, is to calibrate the XPS spectra with respect to the zero eV Fermi level.

In papers I to IV, the XPS technique was used for compositional analysis as well as identification of chemical species through peak fitting of the high resolution spectra. Moreover, in paper VI, the XPS valence band was compared to the simulated DOS.

### 4.4 Electron Microscopy

Electron microscopes use electrons which have a shorter wavelength compared to optical microscopes which use the visible light which has longer wavelength. The main reason for using a light source with shorter wavelength is to increase the resolution and magnification of the structures reaching to a resolution of about 1 Å.

Transmission Electron Microscope (TEM) [86] depends on the transmission of the electron beam through the sample for imaging and acquiring microstructural information. Lattice imagining can be obtained using high-resolution TEM.
4. Characterization Techniques

(HRTEM) which is useful for studying the crystal structure and defects at an atomic level. For the electron beam to be transmitted through the sample, the sample has to be very thin, below 100 nm thick. TEM and HRTEM have been used in papers I to III for microstructure investigation and atomic resolution imaging.

More information regarding the crystal structure and grain orientation can also be achieved by acquiring selected-area electron diffraction (SAED). SAED was used in papers I to III for obtaining the lattice parameters of the crystalline structures and identifying if certain structures are crystalline or amorphous.

Scanning transmission electron microscope (STEM) focuses the electron beam into a narrow spot which is scanned over the sample in a raster and then electrons are transmitted to form the image. Using both abilities, the scanning and transmitting of electrons, it is possible to acquire atomic imaging. This technique was used in paper III to image the atomic structure of Ti₃C₂Tx thin films. Armed with Electron Dispersive X-ray Spectroscopy (EDS), elemental mapping can be acquired in STEM and TEM.

4.5 Ultraviolet-Visible Spectroscopy

Ultraviolet-Visible Spectroscopy (UV-Vis) [87] uses light in the visible and ultraviolet ranges to detect the absorption of materials to light in such ranges. It measures the intensity of light after passing through the sample (I) and compares it to the intensity of light before passing through the sample (Iₒ), where I/Iₒ is called the transmittance and is usually expressed as percentage (%T). UV-Vis was used in paper III to obtain the transmittance for MAX and MXene thin films.

4.6 Electrical Characterization

The four point probe technique is usually used for measuring the electrical resistivity of thin films [88]. This technique consists of four equidistant probes that come in contact with the surface of the film as shown in Figure 22. The current is being applied through the outer two probes while the voltage the voltage between the two inner probes is measured. The value obtained is the sheet resistance (Rₛ) which is the resistivity (ρ) divided by the thickness of the film (t) and multiplied by a geometrical factor to account for the geometry of the sample measured. This technique was used in measuring the resistivity of the MAX and MXene thin films in paper III.
Figure 22. Schematic demonstrating the setup of the four-point probe technique.
5. SUMMARY OF THE INCLUDED PAPERS

5.1 An attempt for Synthesis of MXene by Electrochemical Etching

MXenes have been produced by chemical etching of MAX phase powders using HF. However this technique is neither favourable for mass production nor environmentally friendly. Thus, the idea is to use electrochemical etching to produce MXene out of bulk MAX phases. Using bulk MAX phases would enable us to save time and effort in crushing the bulk sintered MAX phases into powders. Moreover, electrochemical industrial scan cells are already used for various other applications. Other solutions that are less harmful to the environment than HF were investigated for production of MXene. Paper I shows the electrochemical etching of several MAX phases, Ti$_3$AlC$_2$, Ti$_2$AlC and Ti$_3$SiC$_2$, in various solutions, 5 wt.% NaCl, 10 wt.% HCl and 5wt.% HF.

Cyclic voltammograms (CVs) obtained for electrochemical etching of Ti$_3$SiC$_2$ in HF showed oxidation and dissolution taking place at potentials greater than 0.5 V (vs. Ag/AgCl), while the resulting material after the termination of the electrochemical process was carbon as characterized by XRD, and Raman spectroscopy. While electrochemical etching of Ti$_3$SiC$_2$ in HCl resulted in pitting which was accompanied by gas evolution at potentials higher than 2 V.

The CVs for Ti$_3$AlC$_2$ and Ti$_2$AlC showed two peaks, which are related to the oxidation and dissolution of two species. Given the fact that the Ti-Al bond is weaker than that of the Ti-C bond, it is reasonable to assume that the electrochemical process is done in two steps. The first one is the removal of Al which is followed by the removal of both Ti and Al. The electrochemical etching of both phases in HF, HCl and NaCl results in the formation of black films that detach from the bulk MAX phase. These black films were characterized by TEM, EDS, Raman and XPS. The characterization shows that the films are composed of amorphous carbon functionalized by oxygen, fluorine and hydroxyl groups.

Although electrochemical etching of Ti$_3$SiC$_2$, Ti$_3$AlC$_2$ and Ti$_2$AlC MAX phases did not produce MXenes, the method can be used for the production of CDC at room temperature unlike the current method which involve elevated temperatures as well as chlorine gas which is toxic. Whereas the investigation of the CVs for electrochemical etching of Ti$_3$AlC$_2$ and Ti$_2$AlC showed the transformation of the MAX phase to CDC on two steps, the first step is the etching and dissolution of...
Al. Thus by tuning the electrochemical conditions, in principle one can achieve MXene.

5.2 Synthesis and Characterization of New MXene Phases

The main idea behind the work shown in paper II, is to demonstrate the possibility of synthesis of Nb$_2$CT$_x$ and V$_2$CT$_x$. In addition to investigating their performance as electrode materials for Li-ion batteries.

V$_2$AlC and Nb$_2$AlC are less reactive to HF compared to Ti$_2$AlC. This is demonstrated from the duration of time each phase requires in HF to produce MXene as well as the concentration of HF required. Ti$_2$AlC needs only 10 hours in 10% conc. HF. While Nb$_2$AlC and V$_2$AlC require 90 hours in 50% conc. HF. In order to decrease the etching time, the V$_2$AlC powders were milled prior to etching so as to decrease the particle size. This resulted in decreasing the etching time significantly from 90 to 8 hours.

Characterization of Nb$_2$CT$_x$ as well as V$_2$CT$_x$ was performed using XRD, TEM, EDS, and XPS. The characterization concluded that both V$_2$CT$_x$ and Nb$_2$CT$_x$ with c lattice parameter of 22.3 and 24.0 Å, respectively, were obtained. Both phases are terminated with several chemical groups: –O, –OH and –F and they both contain adsorbed water that is highly likely to be the reason of the large c lattice parameter compared to their MAX counterparts.

Testing Nb$_2$CT$_x$ and V$_2$CT$_x$ as electrodes for LIBs have demonstrated that they both can achieve high reversible capacities of 170 and 260 mA.h.g$^{-1}$ respectively, which is higher than that for Ti$_2$CT$_x$ (110 mA.h.g$^{-1}$) at the same rate. Thus, we have demonstrated the ability to synthesize two new MXenes Nb$_2$CT$_x$ and V$_2$CT$_x$. Nb$_2$CT$_x$ and V$_2$CT$_x$ show promising performance as electrodes for LIBs compared to Ti$_2$CT$_x$ and commercial graphite.

5.3 Synthesis and Characterization of Epitaxial Thin Films of Ti$_3$C$_2$Tx

In order to use MXene for electronic applications, MXenes should be produced in the form of thin films. Thus paper III discusses the synthesis of epitaxial Ti$_3$C$_2$Tx, from etching magnetron sputter deposited epitaxial Ti$_3$AlC$_2$ thin films on sapphire substrates using two different etchants, HF and NH$_4$HF$_2$.

Morphological, structural and chemical characterizations were performed using XRD, SEM, TEM, and XPS. Ti$_3$C$_2$Tx films produced by NH$_4$HF$_2$ etching show an increase of about 25% in the c lattice parameter compared to their counterparts that were produced by HF etching. This significant increase is due to the intercalation of NH$_4^+$ and NH$_3$ species according to the XPS analysis.
MXene thin films were found to be metallic-like conductors at room temperature, down to 100 K. Below that temperature the films behave like insulators. This behaviour is due to the weak localization phenomenon which is characteristic for defective 2D materials. Magnetoresistance measurements show a decrease in the resistivity of such films with increasing the magnetic field, again that is due to weak localization. The films show high transparency which reaches up to 90% in the visible-to-infrared range for the films of 19 nm thick etched by NH₄HF₂. MXene thin films demonstrate the possibility of their usage as transparent conductive electrodes. Moreover, these results open the door for the usage of MXenes in electronic, photonic and sensing applications.

5.4 XPS Characterization of MXenes

XPS is a powerful technique that is used for chemical analysis of the surfaces of materials as discussed in section 4.3. It is a very useful technique for studying the surface chemistry of 2D MXenes. This technique has been used to provide compositional quantification and identification of the chemical species in papers I to III.

In paper I, XPS analysis was used to determine the elemental composition of the material produced from electrochemical etching of MAX phases, CDC, and investigating the chemical species present. CDC obtained from electrochemical etching of Ti₃AlC₂ in HCl contains C-C and C-O species in the ratio of 5:2, while in the HF case that ratio is about 9:2. This indicates that the CDC produced in the HF case is less oxidized compared to those produced in the HCl case.

The XPS study of Nb₂CTₓ and V₂CTₓ shown in paper II was essential to identify the chemical composition as well as the chemical terminations of these MXenes. Peak fitting of high resolution XPS spectra for Nb₂CTₓ and V₂CTₓ shows that both compounds have a mixture of functional groups (–O, –OH, and –F) in addition to the adsorbed water discussed in section 5.2.

In addition to the determination of elemental composition and identification of the chemical species in MXenes, XPS played an important role in identifying the nature of the intercalants in the case of Ti₃AlC₂ thin films etched by NH₄HF₂ as indicated in section 5.3 and paper III.

Paper VI investigates the effect of the number of layers, n, in MXene as well as the Ar sputtering on the chemistry of the compounds. The phases of choice were Ti₃C₂Tx and Ti₃CTₓ. Based upon the fitting of high resolution XPS spectra of Ti₃C₂Tx and Ti₃CTₓ as well as comparison of the VB spectra to simulations based on DOS calculations, it is clear that as n increases, the MXene phase becomes less prone to oxidation. Furthermore, the MXene surface before sputtering is highly oxidized when compared to after sputtering. VB analysis confirms and supports the claim of existence of mixed functional groups of (–O, –OH, and –F). Also, it
5. Summary of The Included Papers

shows that the oxides present before Ar\textsuperscript+ sputtering are anatase and rutile. This information is very helpful when choosing various MXenes for different applications. For instance, one would favour Ti\textsubscript{3}C\textsubscript{2}Tx on Ti\textsubscript{2}CT\textsubscript{x} for electronic applications as the latter is more prone to oxidation that would result in decrease in conductivity. For applications that require a less conductive material with a catalytic surface such as photoelectronics, Ti\textsubscript{2}CT\textsubscript{x} would be more suitable than Ti\textsubscript{3}C\textsubscript{2}Tx.
6. PROPOSED FUTURE WORK

The discovery of MXenes provides an abundance of unexplored 2D materials with potential for a wide range of applications. This is especially true given the rich chemistry of transition metals. MXenes are extraordinary diverse as their surface terminations can be altered. While MXenes can as well be intercalated with ions and molecules. This would change the physical properties of MXenes and infers their ability to be favourably fine-tuned for specific applications.

Having that said, one proposed future work is to investigate the effect of the M element in thin film MXenes on their electronic and photonic properties. The MXenes of interest are: Ti$_3$C$_2$, Ti$_2$C, Nb$_2$C, V$_2$C, and (Nb$_{0.5}$, V$_{0.5}$)$_2$C. The rationale is to investigate how the electronic properties change with the change of the number of electrons in the same d-subshell, as well as, with different d-subshells for the transition metal (Ti, V, and, Nb: 3d2, 3d3, and, 4d4 respectively). Each of the proposed MXene compounds identified above has been selected in order to examine how specific chemical aspect affects the electronic and photonic properties. Ti$_3$C$_2$ and Ti$_2$C should shed light on the importance of n on electronic and photonic properties. Also (Nb$_{0.5}$, Ti$_{0.5}$)$_2$C should shed light on the effect of mixing two transition metals of different incomplete d-subshells in a solid solution. This could be done using a combination of several techniques such as XPS, Extended X-ray Absorption Fine Structure (EXAFS) and Angular Resolved Photoemission Spectroscopy (ARPES).

Furthermore, it has been shown that intercalation of MXenes with different cations, such as Na, Mg and Li and other compounds such as hydrazine, and dimethylsulphoxide is possible. Thus studying the effect of the intercalation of various compounds in MXene thin films on the electronic and photonic properties is also crucial for electronic and photonic applications.
7. REFERENCES


(12) European Graphene Flagship (http://graphene-flagship.eu/).


7. References

(40) Martin, P. M. Handbook of deposition technologies for films and coatings: science, applications and technology; William Andrew, 2009.
(41) Sigmund, P. Physical review 1969, 184, 383.
(43) Kelly, P. J.; Arnell, R. D. Vacuum 2000, 56, 159.
(49) Qian, X.; He, X.; Li, Y.; Sun, Y.; Li, H.; Xu, D. Corros. Sci. 2011, 53, 290.


(74) Lane, N. J.; Barsoum, M. W.; Rondinelli, J. M. *EPL (Europhysics Letters)* **2013**, *101*, 57004.

(85) Van der Heide, P. X-ray photoelectron spectroscopy: an introduction to principles and practices; John Wiley & Sons, 2011.
Papers

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