Electronic and optical characterization of 2D Ti$_2$C and Nb$_2$C (MXene) thin films

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Abstract
Two-dimensional (2D) transition metal carbides and/or nitrides (MXenes) are a new class of 2D materials, with extensive opportunities for property tailoring due to the numerous possibilities for varying chemistries and surface terminations. Here, Ti$_2$AlC and Nb$_2$AlC MAX phase epitaxial thin films were deposited on sapphire substrates by physical vapor deposition. The films were then etched in LiF/HCl solutions, yielding Li-intercalated, 2D Ti$_2$CT$_z$ and Nb$_2$CT$_z$ films, whose terminations, transport and optical properties were characterized. The former exhibits metallic conductivity, with weak localization below 50 K. In contrast, the Nb-based film exhibits an increase in resistivity with decreasing temperature from RT down to 40 K consistent with variable range hopping transport. The optical properties of both films were determined from spectroscopic ellipsometry in the 0.75 to 3.50 eV range. The results for Ti$_2$CT$_z$ films confirm the metallic behavior. In contrast, no evidence of metallic behavior is observed for the Nb$_2$CT$_z$ film. The present work therefore demonstrates that one fruitful approach to alter the electronic and optical properties of MXenes is to change the nature of the transition metal.

Keywords: MXene, thin films, transport properties, transition metal carbide

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

1. Introduction
Two-dimensional (2D) solids have been shown to be promising candidates for electronic and optical applications [1, 2]. For instance, graphene possesses ballistic conductivity and high electron mobility reaching $2 \times 10^5$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature (RT) and transmits 97.7% of the light in the near-infrared (IR) to ultraviolet (UV) range [3]. This combination allows graphene to excel in optoelectronic applications such as transparent conductive electrodes which can be used for touch screens [4, 5]. Other 2D materials have different electronic properties such as the semiconducting MoS$_2$ which can be used in applications such as transistors, sensors, and memory devices [6, 7].
Recently, a new family of 2D materials based on transition metal carbides and nitrides, labelled ‘MXene’ was discovered [8, 9]. MXenes are mostly produced by etching the A element from the MAX phases. The latter are a family of hexagonal layered ternary transition metal carbides and/or nitrides with a general formula of $M_{n+1}AX_n$, where M stands for an early transition metal, A stands for mainly group 13 and 14 elements, X stands for carbon and/or nitrogen and $n = 1$, 2, or 3 [10].

Various acidic solutions containing fluoride ions (HF, NH$_4$HF$_2$, LiF + HCl, HF + LiCl, or NaF + HCl) are used to selectively etch the A layers (usually Al, but more recently Ga and Si), to convert MAX phases into MXenes [9, 11–17]. The A layers are replaced with oxygen, hydroxyl and/or fluoride surface terminations, $T$, such that the proper MXene designation is $M_{n+1}X_nT_x$ [18]. Using the appropriate solutions, MXenes can be delaminated as single flakes in colloidal suspensions [19–21]. MXenes were first synthesized in powder or colloidal suspension form. In 2014, the first MXene thin films, Ti$_3$C$_2T_2$, were produced by etching—using HF or NH$_4$HF$_2$ [12]—physical vapor deposited (PVD) films of the MAX phase Ti$_3$AlC$_2$ on sapphire substrates. Later, other methods were used to produce Ti$_3$C$_2T_2$ thin films, such as spin coating, spray coating and electrohydrodynamic atomization [22–25].

MXenes have the potential to be used for various applications, such as battery electrodes, supercapacitors, fuel cells, transparent conducting electrodes, photocatalytic applications, water treatment, electromagnetic shielding, gas sensors, and biosensors among many others [26–28]. For most, if not all, of these applications it is crucial to understand electron transport, a topic that is still very much a work in progress since there are many variables to consider, including the nature of the terminations, the multiple chemistries and defects at various levels. To put the difficulty in perspective we note that electron transport situation for the relatively much simpler MAX phases is still far from being understood since the transport depends on the shape of the Fermi surfaces, among other variables [29].

In general, transport in Ti$_3$C$_2T_2$ is metal-like, with a resistance, $\rho$, that decreases linearly with decreasing temperatures. This response is not only true for thin films, but also for single flakes [12, 30].

Before proceeding much further it is instructive to review the variable range hopping, VRH, mechanism since it has been shown to be applicable to several MXenes, including Nb$_2$CT$_2$ explored herein. In the VRH model the DC conductivity, $\sigma$, is assumed to vary as

$$\sigma = \sigma_0 \exp \left( \frac{T_0}{T} \right)^{\frac{x}{d + p + 1}}$$  \hspace{1cm} (1)

where $T$ is the absolute temperature, $\sigma_0$ is a conductivity prefactor and $T_0$ a characteristic temperature with an exponent $x$ that depends on dimensionality, $d$, of the transport, and a term $p$ characterizing the variation of the density of states at the Fermi level $D(E_F)$ with energy [31, 32]. $p$ and $d$ are related by

$$x = (p + 1) / (d + p + 1).$$  \hspace{1cm} (2)

If, as assumed here, the $D(E_F)$ is not a strong function of energy, then $p = 0$ and $x$ reduces to 1/4 for $d = 3$, and 1/3 for $d = 2$ [33]. In the Efros–Shklovskii VHR model, where prominent charging or Coulomb effects are operative [32], $x$ is equal to 1/2 and is independent of $d$ [34].

This brief review of VRH is important for understanding electron transport in MXenes other than Ti-based. For example, in Mo-containing MXene thin films $\rho$ increases with decreasing temperatures and was thus termed ‘semiconductor-like’ [16, 35, 36]. Recently we measured $\sigma$ of Mo$_2$CT$_2$, Mo$_{1.33}$CT$_2$, Mo$_2$Ti$_2$C$_2$, and Mo$_2$Ti$_2$C$_2$T$_2$ thin films—made by filtering colloidal suspensions—in the 10–300 K temperature range and concluded that, with the exception of the heavily defective Mo$_{1.33}$CT$_2$ composition, VRH, between individual 2D sheets is the operative conduction mechanism, especially at the lower temperatures [37]. Most importantly, for this work, $\rho$ of the highly defective Mo$_{1.33}$CT$_2$ composition, was also concluded to be by VRH, however, in that case, it was surmised that the VRH within individual flakes was rate limiting. This is important because this is the conclusion reached herein concerning transport in our Nb$_2$CT$_2$ films. The motivation for this work is two fold. One is scientific in that we are trying to systematically understand electronic transport in MXene films [12, 16, 36, 37]. From a practical point of view, we have shown that spincoast transparent conductive Ti$_2$CT$_2$ films on glass were as promising as Ti$_3$C$_2T_2$ or undoped chemically vapor-deposited graphene films [46]. Conversely, Nb$_2$CT$_2$ has attracted some interest recently since it has shown promise in several applications such as Li-ion battery electrodes [21, 38], a photocatalyst for hydrogen evolution [39], photothermal tumor eradication [40], and support for platinum catalysts [41], among others. To date, and as far as we are aware, there have been no experimental studies on the electronic and optical properties of Nb$_2$CT$_2$. The only systematic study on a Nb-containing MXene was recently reported by Halim et al who measured the temperature dependencies of the resistivity of thin films of heavily defective Nb$_{1.33}$CT$_2$ films [42]. Here again it was concluded that the VRH model was applicable.

In this report, physically vapor-deposited epitaxial Ti$_2$AlC and Nb$_2$AlC thin films grown on sapphire substrates were converted to their respective MXenes, viz Nb$_2$CT$_2$ and Ti$_2$CT$_2$, by etching them using a mixture of LiF and HCl. We subsequently measured the electronic and optical properties and showed them to depend on the transition metal.

2. Experimental details

2.1. Deposition of Ti$_2$AlC and Nb$_2$AlC

The Ti$_2$AlC and Nb$_2$AlC thin films were deposited using DC magnetron sputtering in an ultrahigh vacuum system described elsewhere [43–45]. The sputter-deposition was performed in an Ar gas (99.9999% purity) environment at a constant pressure of 4.8 mbar. The substrates were c-axis-oriented sapphire Al$_2$O$_3$ (0001), with area of $10 \times 10$ mm$^2$ and thickness of 0.5 cm (MTI Corp., Richmond, CA, United States of America). Prior to deposition, the substrates were cleaned by sonication in an
acetone bath, followed by sonication in isopropanol, each for 10 min, and dried by blowing nitrogen, N₂, gas. The substrates were preheated in the deposition chamber at 750 °C for 1 h. The Ti₂AlC films were ~15 to 30 nm thick and deposited from three elemental targets (Ti, Al, and C with diameters of 75, 50 and 75 mm, respectively). First, the Ti and C targets were ignited at 106 W and 138 W, respectively, at 875 °C and 110, 120 and 120 W, respectively, to grow Ti₂AlC films. Previous works [44] have shown that a TiC incubation layer facilitates the growth of Ti-based MAX phases such as Ti₃AlC₂ and Ti₂AlC. Ti₂AlC thin film sputtered for 2.5 min were used for XRD, transport and optical characterization, while the Ti₂AlC thin film sputtered for 5 min was used for TEM characterization. A 15 nm thick Nb₂AlC film was deposited also from three elemental targets (Nb, Al, and C with diameters of 75, 50 and 75 mm, respectively) at 950 °C for 2.5 min. The power used on the Nb, Al and C sputtering targets were, respectively, 98 W, 88 W, and 138 W.

2.2. Synthesis of Ti₂CT₂ and Nb₂CT₂

Thin MXene Ti₂CT, and Nb₂CT films were produced via selective etching of the Al layers using a solution of LiF (Alfa Aesar, Ward Hill, MA, United States of America) and HCl (Fisher Scientific, TraceMetal grade, Fair Lawn, NJ, United States of America). The LiF + HCl solution, for etching the Ti₂AlC film, was prepared by adding 1.2 g of LiF salt to 20 ml of 12 M HCl. The solution was stirred using a Teflon coated magnetic stirrer on a magnetic stir plate for 15 min at RT to ensure the complete dissolution of the LiF salt in the HCl. Subsequently, the stirring was stopped and the Ti₂AlC thin film was immersed in the solution for 0.3 h at RT. For the Nb₂AlC thin film, the LiF + HCl solution was prepared by adding 3 g of LiF to 40 ml of 12 M HCl and stirred using a Teflon coated magnetic stirrer on a magnetic stir plate for 15 min. After stirring, the Nb₂AlC films were immersed in the etching solution for 3 h at 55 °C, rinsed in distilled water, followed by ethanol and lastly dried by blowing Ar gas. Because at this stage the multilayers are intercalated with Li, they will henceforth be referred to as Ti₂CT₂-yLi and Nb₂CT₂-yLi.

2.3. Structural and chemical characterization

X-ray diffraction (XRD) of the films was performed using an X’Pert Powder diffractometer (PANalytical, Almelo, Netherlands), with a θ – 2θ continuous scan of a step size of 0.017° and a 40 s dwell time.

A transmission electron microscope (TEM) FEI Tecnai G² TF20 UT operated at 200kV, was used to measure the film thickness. Selected area electron diffraction acquisition was carried out in the same TEM.

High-resolution scanning TEM imaging and high-angle annular dark-field scanning TEM (HAADF-STEM) was performed in the Linköping double-C₁₂-corrected Titan³ G² 60-300 (FEI, Eindhoven, Netherlands) operated at 300 kV. Cross-sectional TEM samples were prepared by sandwiching two cross-sectioned samples in a Ti grid that was, in turn, mechanically polished down to 70 µm, followed by ion milling to electron transparency.

X-ray photoelectron spectroscopy, XPS, analysis of the films followed previously optimized characterization methods [18]. XPS measurements were performed using a surface analysis system (Physical Electronics, VersaProbe 5000, Chanhassen, MN) employing a 100 µm monochromatic Al-Kα x-ray beam to irradiate the sample surface. Photoelectrons were collected using a 180° takeoff angle between the sample surface and the path to the analyzer. Charge neutralization was performed using a dual beam charge neutralizer that irradiated the sample with low-energy electrons and ions to avoid shifts in the recorded binding energy (BE). Survey spectra were taken at a pass energy of 117.5 eV, with a step size of 0.1 eV. High-resolution spectra for Nb 3d, Ti 2p, C 1s, O 1s, F 1s, Li 1s and Al 2p were taken at a pass energy of 11.75 eV with a step size of 0.05 eV. The binding energy scale of all XPS spectra was referenced to the Fermi-edge (E_f), which was set to a BE of 0 eV.

To obtain the spectra, the sample was mounted on doublesided tape and ground using a copper wire. The quantification, using the obtained core-level intensities, and peak fitting of the core-level spectra was performed using a software package (CasaXPS Version 2.3.16 RP 1.6). Prior to both the quantification and peak fitting the background contributions were subtracted using a Shirley function. The intensity ratios of the Nb 3d₅/₂ and Nb 3d₇/₂ and Ti 2p₃/₂ and Ti 2p₁/₂ peaks were constrained to 3:2 and 2:1, respectively.

2.4. Optical and electrical characterization

Spectroscopic ellipsometry measurements were performed using an ellipsometer (M2000, J.A. Woollam Co., Inc., Lincoln, NE) in the 0.75 to 3.50 eV spectral range. Focusing probes were used to avoid backside reflections. The temperature-dependent in-plane resistance measurements were performed in a Physical Property Measurement System (Quantum Design, San Diego) using an external current source (Keithley 6220, Ohio) and a nanovoltmeter (Keithley 2182A). A linear four-point probe geometry was used. Gold wires were attached to the films using silver paint. Positive and negative currents were applied at each temperature to eliminate any thermal offsets. The magnetoresistance, MR, measurements were performed with a magnetic field applied out of the plane of the film.

3. Results and discussion

Figure 1 shows XRD diffractograms of as-deposited and etched Ti-based (figure 1(a)) and Nb-based (figure 1(b)) films. Consistent with previous work, the as-deposited films are epitaxial since they (bottom curves in figure 1) exhibit only 00l (l = 2, 4, 6, …) peaks [43, 44]. The corresponding c lattice parameters, LPs, are 13.61 Å and 13.85 Å for Ti₂AlC and Nb₂AlC, respectively, again in agreement with previous
work \cite{43, 45}. After etching (top curves in figure 1), the 0 0 2 peaks are shifted to lower angles and all other 0 0 l peaks are so reduced in intensity that they are barely visible (figure S6 for Ti2CT z–y Li and figure S7 for Nb2CT z–y Li). The etching therefore increases the interlayer spacing, \( \delta \) (=c/2) from 6.805 Å to 11.35 Å for the Ti-based films and from 6.925 Å to 11.65 Å for the Nb-based films. In general, the large expansion in \( \delta \) is a characteristic of the MAX to MXene transformation \cite{9, 38}. More specifically, it is typical for LiF etched MXene. The expansion is due to the intercalation of water and Li between the 2D carbide layers \cite{11, 13, 22, 46}. It follows that the proper designation of our films should be: Ti2CT z–y Li and Nb2CT z–y Li, with \( z \) represents the various termination and -y Li denotes intercalated Li. Evidence for the presence of Li is given below.

Figure 2 shows HAADF-STEM images of the Ti- and Nb-based films of 40 and 20 nm thick, respectively. Figures 2(a) and S8 are a typical overview image of Ti2CT z–y Li on top of the Ti2AlC–TiC mixed incubation layer grown on Al2O3. Figure 2(b) shows atomically resolved Ti2CT z–y Li layers. Figures 2(c) and S8 are typical overview images of the Nb2CT z–y Li films and figure 2(d) shows the atomically resolved image of the Nb2CT z–y Li films. At 11.4 ± 0.2 and 11.8 ± 0.3 Å, the \( \delta \) values for the Ti and Nb-based films, respectively, estimated from the TEM micrographs, are in good agreement with the values obtained from XRD. The overall chemical composition of the films, determined by XPS measurements, were found to be Ti2CO0.4(OH)0.5F0.6·0.1H2O–0.2Li and Nb2CO0.5(OH)0.8F0.4·0.3H2O–0.3Li. Detailed analysis of the XPS data is given in the supplementary information (stacks.iop.org/JPhysCM/31/165301/mmedia). As typical of most MXenes, both contain mixed terminations of comparable ratios.

As in our previous work on Ti2CT z and Nb2CT z cold pressed from multilayers, the sum of the terminations, \( z \), are \( \approx 1.5 \pm 0.2 \) and 1.7 ± 0.2, respectively \cite{18}. When all termination sites are occupied, the total of the O, OH and F terminations should be 2 \cite{47}. The fact that here \( z \) here is <2, implies that not all M atoms are terminated. The exact reason for this state of affairs is unclear at this time. The most likely explanation is that some of the terminations desorb in the high vacuum of the XPS. These comment notwithstanding, thermodynamically, it
is almost impossible for these terminations to be absent when the films are in air and the assumption made hereafter is that all M atoms are terminated during characterization in air.

Figures 3(a) and (c) plot the temperature dependencies of $\rho$ for Ti- and Nb-based films, respectively. Figure 3(c) also plots the results of previous MXene work in which $T_0$ was determined to be $>10^4$ (see below) [37, 42]. The former exhibits metallic behavior, with a linear increase in $\rho$ with temperature in the range from ~80 to 300 K temperature range. The RT resistivity, $\rho_{RT}$, is ~4.4 $\mu\Omega \cdot m$. Below 50 K, $\rho$ increases weakly with decreasing temperature, which can possibly be attributed to weak localization in this 2D metallic material.

This is indirectly evidenced by the fit to a weak-localization model, WL, shown in figure 3(b). The metallic behavior at high temperatures and WL at low temperatures for Ti$_2$CT$_z$–$\gamma$Li is reminiscent of that of Ti$_3$C$_2$T$_z$ thin films, made from sputter-deposited epitaxial films [12].

In sharp contrast, $\rho$ of Nb-based film increases more than two orders of magnitude in the 5 K to 300 K temperature range (figure 3(c)). In this case, at 414 $\mu\Omega \cdot m$, $\rho_{RT}$ is roughly two orders of magnitude higher than $\rho_{RT}$ of the Ti-based films. At 50 K the difference is more than four orders of magnitude. Note, no results were obtained at $T < 35$ K because the resistances of the epitaxial films were simply too high given their extreme thinness ($\approx$20 nm).

As done previously [16, 37], the transport mechanism was evaluated by fitting the transport data to several transport models including simple thermal activation (figure S3(a)) a power law model (figure S3(b)) and various VRH (equation (1)) models. A comparison of the various fits indicated that the 3D VRH mechanism showed the best fit (figure 3(d)) over the 40 to 300 K temperature range. As discussed in more detail in our previous work, in general it is difficult to distinguish between the various VRH mechanisms, viz between, the 3D, Efros–Shklovskii, or 2D models, the fits for which are shown in figures 3(b), S3(c) and S3(d), respectively. In this case, what can be ruled out are the Efros–Shklovskii VRH and the thermal activation models. The fit for the 3D model is ever so slightly better than the 2D, which is why it is the one shown in figure 3(d). However, based on these results we simply cannot differentiate between power-law models, 2D or 3D VRH ones (figures 3(d), S3(b) and (d)).

As noted above, figure 3(c), in addition to plotting the results obtained here also plots the results for Mo$_{1.33}$CT$_z$ and Nb$_{1.33}$CT$_z$ thin filtered films. The similarities between the four is somewhat surprising given that the results for Mo$_{1.33}$CT$_z$ [37, 48] and Nb$_{1.33}$CT$_z$ (figure S4) were obtained on thin filtered films, whereas those obtained here were obtained on etched epitaxial thin films.

Table 1 summarizes the fitting parameters, $T_0$ and $\sigma_0$ (see equation (1)) for the Nb-films tested herein, together with
those of other films we tested for which \( T_0 > 10^4 \) K \[37\]. The parameters were determined for \( x = 1/4 \) and \( 1/3 \) that correspond to the 3D and 2D VRH models, respectively.

In our previous work, we argued that when \( T_0 < 10^4 \) K, the most likely rate limiting step is flake-to-flake transport \[37\]. We also made the case, that when \( T_0 > 10^4 \) K, the more likely scenario is one where transport within individual flakes is rate limiting.

In the VRH model, this conclusion was reached by first appreciating that in Mott’s VRH model, \( T_0 \) is related to the density of states at the Fermi level, \( D(E_F) \), by

\[
T_0 = a \frac{\gamma}{k_B D(E_F)} \gamma^{-3}
\]

where \( 1/\gamma \) is the decay length or reciprocal tunneling exponent of the localized states, \( a \) is a constant initially estimated by Mott to be 64 in case \( D(E_F) \) does not vary over a range \( \approx k_B T \) \[49\]. In case of an exponential DOS, \( a \) was found to exceed 300 \[49\]. In our previous work, we assumed a range of \( \gamma \) and estimated the \( D(E_F) \) using the experimental values of \( T_0 \). By doing so we showed that since in many of our films, \( T_0 \) was \( < 10^4 \) K, the jump distances were consistent with interflake conductivity.

Here we approach the problem slightly differently; we assume \( a = 310, D(E_F) = 1.5 \times 10^{22} \) eV\(^{-1}\) cm\(^{-3}\)—i.e. that of a decent metal—and making use of the experimentally determined values of \( T_0 \) (table 1) we calculate \( \gamma \) to obtain a sense for the magnitude of the jump distances involved. It is important to note that the choice of \( a = 64 \) or 310, does not affect much the calculated values of \( \gamma \). For example for Nb2CT–yLi: assuming 3D VRH, for \( a = 64, \gamma = 0.31 \) nm while for \( a = 310, \gamma = 0.52 \) nm.

Table 1. Summary of fitting parameters, \( T_0 \) and \( \sigma_0 \) (see equation (1)) for the 3D and 2D VRH models proposed. Also listed in column 4 are the characteristic jump distances one obtains from equation (3) if \( D(E_F) \) is assumed to be \( 1.5 \times 10^{22} \) eV\(^{-1}\) cm\(^{-3}\) (see text).

| Sample       | VRH 3D T0 (K) | VRH 3D \( \sigma_0 \) (S m\(^{-1}\)) | \( \gamma \) (nm) | VRH 2D T0 (K) | VRH 2D \( \sigma_0 \) (S m\(^{-1}\)) | Ref. |
|--------------|---------------|--------------------------------------|------------------|---------------|--------------------------------------|------|
| Nb2CT–yLi    | 1.7 \( \times 10^6 \) | 12.5 \( \times 10^6 \) | 0.52            | 0.62 \( \times 10^5 \) | 0.78 \( \times 10^6 \) | This work |
|              | \( \pm 0.04 \times 10^6 \) | \( \pm 0.1 \times 10^6 \) |                  | \( \pm 0.003 \times 10^5 \) | \( \pm 0.01 \times 10^6 \) |       |
| Nb1.33CTz    | 0.17 \( \times 10^6 \) | 284 \( \pm 6 \) | 1.12            | 0.1 \( \times 10^5 \) | 49.2 \( \pm 0.4 \) | [42] |
|              | \( \pm 0.001 \times 10^6 \) |                         |                  | \( \pm 0.01 \times 10^5 \) |                         |       |
| Mo1.33CTz    | 6.2 \( \times 10^6 \) | 2.84 \( \times 10^6 \) | 0.34            | 1.5 \( \times 10^5 \) | 0.11 \( \times 10^6 \) | [37] |
|              | \( \pm 1.4 \times 10^6 \) | \( \pm 0.14 \times 10^6 \) |                  | \( \pm 0.01 \times 10^5 \) | \( \pm 0.03 \times 10^6 \) |       |
| Mo1.33CTz    | 41 \( \times 10^6 \) | 3.9 \( \times 10^6 \) | 0.18            | 6.2 \( \times 10^5 \) | 3.44 \( \times 10^6 \) | [37, 48] |
|              | \( \pm 39 \times 10^6 \) | \( \pm 0.7 \times 10^6 \) |                  | \( \pm 0.02 \times 10^5 \) | \( \pm 0.01 \times 10^6 \) |       |

For Ti2CT–yLi, an absorption feature is found in the visible and a strong decrease of \( \varepsilon_2 \) and an increase of \( \varepsilon_1 \) is observed towards the infrared, IR, spectral range—for the Ti and Nb-based films, respectively. Straight lines represent results from model-dielectric-functions (MDF) based analysis employing several parametrized contributions (dashed lines). Further details on the data analysis are given in the supplementary information.

For Ti3CT–yLi, the value for \( \gamma \) is 1.12 nm which is close to the interlayer distance in MXene and the size of the cluster vacancies in the flakes, thus in this case the conductivity could be dominated by either interflake or intraflake hopping. Lastly, it is important to note that given the high resistivities measured it is reasonable to assume that the charge carriers percolate between flakes acting in series with the hops within flakes. Without this assumption, no current would be measured. This assumption is thus consistent with the significantly higher \( \rho \) measured for the Nb-films compared to their Ti-based counterparts.

Figures 4(a) and (b) plot the magnetoresistances, MRs, of the Ti- and Nb-based films as a function of applied magnetic field at 10 K, respectively. The negative MR for Ti2CT–yLi (figure 4(a)) is reminiscent of that of Ti3C2T (figure 4(b)) positive. In that respect it is similar to that for Mo3CT, Mo2TiC2T2 and Mo2Ti3C2T2 (MXenes) [16, 35], but somewhat surprisingly, opposite in sign to Nb1.33CT and Mo1.33CT [37, 42]. This reversal in sign in MR is clearly important but at this stage is not understood. More theoretical work is indicated, although the problem has proven to be anything but trivial.

Figures 5(a) and (b) display the dielectric functions—determined from analysis of spectroscopic ellipsometry data in the 0.73 eV to 3.34 eV spectral range—for the Ti and Nb-based films, respectively. Straight lines represent results from model-dielectric-functions (MDF) based analysis employing several parametrized contributions (dashed lines). Further details on the data analysis are given in the supplementary information.
Furthermore, the model includes a Lorentz oscillator and a UV-pole for UV absorptions to adequately model the experimental data.

In comparison, the Nb-based film exhibits significantly different behavior. Here both $\varepsilon_1$ and $\varepsilon_2$ increase towards the IR spectral range indicating an absorption in the near IR. In contrast to Ti-based film this behavior differs significantly from that of the corresponding MAX phase Nb$_2$AlC [50]. The absorption coefficient $\alpha$ ranges between $2.5 \times 10^5$ cm$^{-1}$ and $5.7 \times 10^5$ cm$^{-1}$ in the investigated spectral range, with a value of $\alpha^{550} = 5.7 \times 10^5$ cm$^{-1}$ at 550 nm. The near IR absorption is modeled by a Lorentz MDF. While the Lorentz MDF describes $\varepsilon_2$ sufficiently well over the whole measured range, an offset mainly in $\varepsilon_1$ remains. This offset decreases with increasing photon energy and can possibly originate from different mechanisms, for example further IR absorptions or free charge carriers that behave unlike a metal, e.g. carriers with a high mobility and low concentration. In addition, carrier localization and hopping may also play a role. For consistency we use Drude MDF to model the offset. The data analysis provides a resistivity value of 0.1 $\mu\Omega\cdot$m, which differs significantly from values from electrical measurements. However the uncertainty of the resistivity value is high due to depolarization in the sample. In addition, carrier localization and hopping may also play a role. The exact nature of the free charge carrier properties in Nb$_2$CT$_z$–yLi cannot be determined from the experimental data acquired here and more detailed work is needed.

Since both MXenes contain mixed terminations of comparable ratios, and, as importantly, comparable interlayer distances, our results show that the electrical and optical properties arise from the electronic configuration of the M elements, i.e. Ti is in group 4 and Nb is in group 5 and their bonding with the C atoms and surface terminations. This addition of an extra valence electron is proposed to cause the difference in electronic transport properties from metallic behavior to VRH transport. The 2D nature of the properties of Ti$_2$CT$_z$–yLi is evidenced by the low-temperature resistivity and MR. The low-temperature behavior of Nb$_2$CT$_z$–yLi is more complex, but consistent with VRH models.

4. Conclusions

The MXenes Ti$_2$CT$_z$–yLi and Nb$_2$CT$_z$–yLi were produced by etching Ti$_2$AlC and Nb$_2$AlC epitaxial thin films deposited by PVD on sapphire substrates and their structure, surface terminations, and electrical and optical properties were characterized. XPS of the films revealed their chemistry to be, respectively,

$\text{Ti}_3\text{CO}_0.4(\text{OH})_{0.6}\cdot 0.1\text{H}_2\text{O}_{ads} - 0.2\text{Li}$ and
$\text{Nb}_2\text{CO}_{0.5}(\text{OH})_{0.8}\cdot 0.4\cdot 0.3\text{H}_2\text{O} - 0.3\text{Li}$.
The Ti-based films exhibit typical metallic behavior with a room temperature $\rho \sim 4.4 \ \mu\Omega \cdot \text{m}$. The optical properties determined from spectroscopic ellipsometry measurements confirm the metallic behavior, where $\varepsilon_1$ decreases and $\varepsilon_2$ increases. The optically determined resistivity parameter is close to the one determined from the electrical measurements. In contrast, $\rho$ of the Nb-based films increases with decreasing temperature. With a room temperature $\rho$ of 414.1 $\mu\Omega \cdot \text{m}$, this film is two orders of magnitude more resistant than its Ti-based counterpart. At 50 K the difference is $\approx 4$ orders of magnitude.

The optical properties of the Nb-based films, ascribed to a percolation between flakes. The optical response of the Nb-based film is also different than its Ti-based counterpart, since both $\varepsilon_1$ and $\varepsilon_2$ increase towards the IR spectral range indicating an absorption in the near IR.

The present work therefore clearly demonstrates how the electronic and optical properties of MXenes can be tailored, by the choice of the transition metal.

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Conflicts of interest

There are no conflicts to declare.

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References

[1] Mas-Balleste R, Gomez-Navarro C, Gomez-Herrero J and Zamora F 2011 Nanoscale 3 20
[2] Gupta A, Sakthivel T and Seal S 2015 Prog. Mater. Sci. 73 44
[3] Geim A K and Novoselov K S 2007 Nat. Mater. 6 183
[4] Bae S, Kim H, Lee Y, Xu X, Park J-S, Zheng Y, Balakrishnan J, Lei T, Kim H R and Song Y J 2010 Nat. Nanotechnol. 5 574
[5] Bonaccorso F, Sun Z, Hasan T and Ferrari A 2010 Nat. Photon. 4 611
[6] Jariwala D, Sangwan V K, Lauhon L J, Marks T J and Hersam M C 2014 ACS Nano 8 1102
[7] Radisavljevic B, Radenovic A, Brivio J, Giacometti V and Kis A 2011 Nat. Nano 6 147
[8] Naguib M, Kurtoglou M, Presser V, Lu J, Niu J, Heon M, Hultman L, Gogotsi Y and Barsoum M W 2011 Adv. Mater. 23 4248
[9] Naguib M, Mashtalir O, Carle J, Presser V, Lu J, Hultman L, Gogotsi Y and Barsoum M W 2012 ACS Nano 6 1322
[10] Barsoum M W 2013 MAX Phases: Properties of Machinable Ternary Carbides and Nitrides (New York: Wiley)
[11] Ghidiu M, Lukatskaya M R, Zhao M Q, Gogotsi Y and Barsoum M W 2014 Nature 516 78
[12] Halim J et al 2014 Chem. Mater. 26 2374
[13] Ghidiu M, Halim J, Kota S, Bish D, Gogotsi Y and Barsoum M W 2016 Chem. Mater. 28 3507
[14] Liu F, Zhou J, Wang S, Wang B, Shen C, Wang L, Hu Q, Huang Q and Zhou A 2017 J. Electrochem. Soc. 164 A708
[15] Moshkin R, Näslund L–A, Halim J, Lu J, Barsoum M W and Rosen J 2015 Scr. Mater. 108 147
[16] Halim J et al 2016 Adv. Funct. Mater. 26 3118
[17] Alhabeb M, Maleski K, Mathis T S, Sarycheva A, Hatter C B, Uzon S, Levitt A and Gogotsi Y 2018 Angew. Chem., Int. Ed. 75 5444
[18] Halim J, Cook K M, Naguib M, Eklund P, Gogotsi Y, Rosen J and Barsoum M W 2016 Appl. Surf. Sci. 362 406
[19] Lukatskaya M R, Mashtalir O, Ren C E, Dall’Agnese Y, Rozier P, Taberna P L, Naguib M, Simon P, Barsoum M W and Gogotsi Y 2013 Science 341 1502
[20] Naguib M, Uncic R R, Armstrong B L and Nanda J 2015 Dalton Trans. 44 9353
[21] Mashtalir O, Lukatskaya M R, Zhao M Q, Barsoum M W and Gogotsi Y 2015 Adv. Mater. 27 3501
[22] Dillon A D, Ghidiu M J, Krick A L, Griggs J, May S J, Gogotsi Y, Barsoum M W and Fafarman A T 2016 Adv. Funct. Mater. 26 4162
[23] Hantantasirisukal K, Zhao M Q, Urbankowski P, Halim J, Anasori B, Kota S, Ren C E, Barsoum M W and Gogotsi Y 2016 Adv. Electron. Mater. 2 1600050
[24] Ali A, Belaidi A, Ali S, Helal M I and Mahmoud K A 2016 J. Mater. Sci.: Mater. Electron. 27 5440
[25] Eklund P, Rosén J and Persson P O A 2017 J. Phys. D: Appl. Phys. 50 113001
[26] Lei J C, Zhang X and Zhou Z 2015 Frontiers Phys. 10 276
[27] Anasori B, Lukatskaya M R and Gogotsi Y 2017 Nat. Rev. Mater. 2 160098
[28] Naguib M, Rochal P N, Barsoum M W and Gogotsi Y 2014 Adv. Mater. 26 992
[29] Ouisse T and Barsoum M W 2017 Mater. Res. Lett. 5 365
[30] Miranda A, Halim J, Barsoum M and Lorke A 2016 Appl. Phys. Lett. 108 033102
[31] Pollak M 1972 J. Non-Cryst. Solids 8 486
[32] Efros A and Shklovskii B 1975 J. Phys. C: Solid State Phys. 8 149
[33] Mott N F and Davis E A 2012 Electronic Processes in Non-Crystalline Materials (Oxford: Oxford University Press)
[34] Guyot-Sionnest P 2012 *J. Phys. Chem. Lett.* **3** 1169
[35] Anasori B, Shi C, Moon E J, Xie Y, Voigt C A, Kent P R, May S J, Billinge S J, Barsoum M W and Gogotsi Y 2016 *Nanoscale Horizons* **1** 1227
[36] Kim H, Anasori B, Gogotsi Y and Alshareef H N 2017 *Chem. Mater.* **29** 6472
[37] Halim J, Moon E J, Eklund P, Rosen J, Barsoum M W and Ouisse T 2018 *Phys. Rev. B* **98** 104202
[38] Naguib M, Halim J, Lu J, Cook K M, Hultman L, Gogotsi Y and Barsoum M W 2013 *J. Am. Chem. Soc.* **135** 15966
[39] Su T, Peng R, Hood Z D, Naguib M, Ivanov I N, Keum J K, Qin Z, Guo Z and Wu Z 2017 *ChemSusChem* **11** 688
[40] Lin H, Gao S, Dai C, Chen Y and Shi J 2017 *J. Am. Chem. Soc.* **139** 16235
[41] Li Z, Cui Y, Wu Z, Milligan C, Zhou L, Mitchell G, Xu B, Shi E, Miller J T and Ribeiro F H 2018 *Nat. Catal.* **1** 349
[42] Halim J, Palisaitis J, Lu J, Thörmberg J, Moon E, Precner M, Eklund P, Persson P A, Barsoum M and Rosen J 2018 *ACS Appl. Nano Mater.* **1** 2455
[43] Frodelius J, Lu J, Jensen J, Paul D, Hultman L and Eklund P 2013 *J. Eur. Ceram. Soc.* **33** 375
[44] Wilhelmsson O, Palmquist J P, Lewin E, Emmerlich J, Eklund P, Persson P, Högberg H, Li S, Abuja R and Eriksson O 2006 *J. Cryst. Growth* **291** 290
[45] Scabbarozi T H, Roche J, Rosenfeld A, Lim S H, Salamanca-Riba L, Yong G, Takeuchi I, Barsoum M W, Hettinger J D and Lofland S E 2009 *Thin Solid Films* **517** 2920
[46] Ying G, Dillon A D, Fafarman A T and Barsoum M W 2017 *Mater. Res. Lett.* **5** 391
[47] Khazaei M, Arai M, Sasaki T, Chung C Y, Venkataramanan N S, Estili M, Sakka Y and Kawazoe Y 2013 *Adv. Funct. Mater.* **23** 2185
[48] Tao Q et al 2017 *Nat. Commun.* **8** 14949
[49] Godet C 2002 *J. Non-Cryst. Solids* **299** 333
[50] Mendoza-Galvan A, Rybka M, Järrendahl K, Arwin H, Magnuson M, Hultman L and Barsoum M 2011 *J. Appl. Phys.* **109** 013530
[51] Bai Y, Zhou K, Srikanth N, Pang J H, He X and Wang R 2016 *RSC Adv.* **6** 35731
[52] Knight S, Hofmann T, Bouhafs C, Armakavicius N, Kühne P, Stanishev V, Ivanov I G, Yakimova R, Wimer S and Schubert M 2017 *Sci. Rep.* **7** 5151