Transparent Conductive Two-Dimensional Titanium Carbide Epitaxial Thin Films

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INTRODUCTION

Since the discovery of graphene,\(^1\)\(^-\)\(^3\) two-dimensional (2D) solids have attracted considerable attention due to the unique properties bestowed upon them by their reduced dimensionality. These are currently being considered for a multitude of applications, including electronic, photonic, and energy storage devices.\(^4\)\(^-\)\(^6\) For instance, graphene has an electron mobility of 2 \(\times\) 10\(^5\) cm\(^2\)/Vs at room temperature, which shows a weak dependence on temperature.\(^5\)\(^,\)\(^7\) Furthermore, a single layer of graphene transmits 97.7\% of light in the near-infrared to ultraviolet range.\(^8\) This combination of unique electronic and optical properties has positioned graphene as a promising material for transparent conductive electrodes.

The immense interest generated by graphene has renewed efforts to identify and characterize other 2D solids such as BN,\(^9\) MoS\(_2\),\(^10\)\(^,\)\(^11\) that may possess equally attractive properties. Recently, we discovered a new family of 2D materials that is both metallically conducting and hydrophilic, an uncommon combination. To date MXenes have been produced as powders, flakes, and colloidal solutions. Herein, we report on the fabrication of \(\sim 1\times 1\) cm\(^2\) Ti\(_3\)C\(_2\) films by selective etching of Al, from sputter-deposited epitaxial Ti\(_3\)AlC\(_2\) films, in aqueous HF or NH\(_2\)HF\(_2\). Films that were about 19 nm thick, etched with NH\(_2\)HF\(_2\), transmit \(\sim 90\%\) of the light in the visible-to-infrared range and exhibit metallic conductivity down to \(\sim 100\) K. Below 100 K, the films’ resistivity increases with decreasing temperature and they exhibit negative magnetoresistance—both observations consistent with a weak localization phenomenon characteristic of many 2D defective solids. This advance opens the door for the use of MXenes in electronic, photonic, and sensing applications.

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The Ti continuous scan of a step size with 0.017 transparency for wavelengths in the visible to infrared range. Magnetoresistance down to 2 K. These films show high transparency for wavelengths in the visible to infrared range.

Table 1. Thickness, Etching Duration, Resistivity, and Light Transmittance (at a Wavelength of 700 nm) of the As-Deposited and Etched Ti3AlC2 Thin Films

<table>
<thead>
<tr>
<th></th>
<th>deposition time [min]</th>
<th>thickness [nm]</th>
<th>etching duration [minutes]</th>
<th>resistivity [$\mu$Ωm]</th>
<th>transmittance [%]</th>
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</thead>
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<tr>
<td>set 1</td>
<td>Ti3AlC2</td>
<td>15.2 ± 0.5°</td>
<td>4.5 ± 0.1</td>
<td>31</td>
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<tr>
<td></td>
<td>Ti3C2Tx</td>
<td>17.2 ± 0.8°</td>
<td>9.5</td>
<td>39.2 ± 1.21</td>
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<td>Ti3C2Tx-IC</td>
<td>18.7 ± 0.6°</td>
<td>150</td>
<td>4472 ± 323</td>
<td>85</td>
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<tr>
<td>set 2</td>
<td>Ti3AlC2</td>
<td>27.7 ± 0.8°</td>
<td>0.34 ± 0.01</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti3C2Tx</td>
<td>28.4 ± 1.8°</td>
<td>15</td>
<td>2.28 ± 0.04</td>
<td>49</td>
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<tr>
<td></td>
<td>Ti3C2Tx-IC</td>
<td>31.3 ± 1.2°</td>
<td>160</td>
<td>5.01 ± 0.03</td>
<td>37</td>
</tr>
<tr>
<td>set 3</td>
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<td>0.31 ± 0.01</td>
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<tr>
<td></td>
<td>Ti3C2Tx</td>
<td>47.1 ± 3.5°</td>
<td>60</td>
<td>22.27 ± 0.43</td>
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<tr>
<td></td>
<td>Ti3C2Tx-IC</td>
<td>52.8 ± 2.5°</td>
<td>420</td>
<td>31 ± 2.8</td>
<td>28</td>
</tr>
<tr>
<td>set 4</td>
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<td>0.35 ± 0.01</td>
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<td></td>
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<tr>
<td></td>
<td>Ti3C2Tx</td>
<td>67.4 ± 5.3°</td>
<td>160</td>
<td>1.76 ± 0.02</td>
<td>15</td>
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<tr>
<td></td>
<td>Ti3C2Tx-IC</td>
<td>74.7 ± 3.7°</td>
<td>660</td>
<td>54 ± 4.51</td>
<td>14</td>
</tr>
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</table>

“Determined by XRR (Supporting Information Figure S1a,b). Interpolated (Supporting Information Figure S1c). Obtained from direct measurement in TEM (Supporting Information Figure S9a for Ti3C2Tx). Obtained from direct measurement in TEM after accounting for the decrease in thickness due to partial deintercalation.

shown that ammonium bifluoride, NH4HF2, can be used instead; (3) the one-step synthesis of a MXene, intercalated with ammonia, is demonstrated; (4) the availability of epitaxial films on transparent and insulating sapphire substrates enabled the measurement of some of the fundamental physical properties, such as optical absorption, in a broad wavelength range, and the temperature dependence of conductivity and magnetoresistance down to 2 K. These films show high transparency for wavelengths in the visible to infrared range.

Methods

Deposition of Ti3AlC2. The Ti3AlC2 thin films were deposited from three elemental targets (Ti, Al, and C with diameters of 75, 50, and 75 mm, respectively) using DC magnetron sputtering in an ultrahigh vacuum system described elsewhere.38,39 The sputtering process gas was Ar (99.9999% purity) at a constant pressure of 4.8 mbar. The substrates were c-axis-oriented sapphire, Al2O3 (0001), with surface areas of 10 × 10 mm2 and thicknesses of 0.5 cm (MTI Corp. CA). Prior to deposition, the substrates were cleaned using acetone, rinsed with isopropanol, dried by nitrogen gas, and finally preheated inside the deposition chamber at 780 °C for 60 min. Deposition was performed at 780 °C. Titanium and carbon targets were ignited for 5 s followed by the growth of a TiC incubation layer 5 nm thick. Previous work has shown that a TiC incubation layer facilitates the growth of epitaxial Ti3AlC2.30,38,40

Synthesis of Ti3C2Tx. Two chemicals were used to etch, at room temperature, the Ti3AlC2 films. The first was 50% concentrated HF (Sigma Aldrich, Stockholm, Sweden). Samples of nominal thickness of 15, 28, 43, and 60 nm were etched for 10, 15, 60, and 160 min, respectively. The second was 1 M NH4HF2 (Sigma Aldrich, Stockholm, Sweden). Samples of the same thickness as those mentioned above were etched for 150, 160, 420, and 660 min, respectively. After etching, the samples were rinsed in deionized water, then in ethanol.

Chemical and Morphological Characterization. X-ray diffraction (XRD) of the films was performed using an XPert Powder diffractometer (PANalytical, Almelo, The Netherlands), with a 2θ/20 continuous scan of a step size with 0.017° and 40 s dwell time. XRD of the Ti3C2Tx-IC powders and deintercalated Ti3C2Tx thin films were carried out using a diffractometer (SmartLab, Rigaku, Tokyo, Japan) with a 2θ/20 continuous scan of a step size of 0.02° and 1 s dwell time. X-ray reflectometry (XRR) continuous scans were performed using an XPert Powder diffractometer (PANalytical, Almelo, The Netherlands), with a step size of 0.01° and 1.67 s dwell time. Simulation for the XRR results was carried out using the XPert Reflectivity software produced by PANalytical B.V.

To characterize the chemical states of elements in the thin films before and after etching, X-ray photoelectron spectroscopy (XPS) was performed using a surface analysis system (Kratos AXIS Ultra DLD, Manchester, U.K.). Monochromatic Al Kα X-rays irradiated the samples at an angle of 45°, with respect to the surface; X-ray spot size was 300 × 800 μm. The electron energy analyzer accepted the photoelectrons perpendicular to the sample surface with an acceptance angle of ±15°. The high-resolution spectra were recorded using a pass energy of 20 eV and a step size of 0.1 eV. To avoid broadening of the XPS spectra caused by sample charging, an electron flood gun was used while recording the data. The binding energy scale of all XPS spectra was therefore referenced to the Fermi level which was set to a binding energy of 0 eV. Peak assignments of the spectra were supported through an analysis of a TiC bulk sample of known stoichiometry (1:1) and a TiO2 thin film of known stoichiometry (1:2). The quantification and peak fitting were carried out using CasaXPS Version 2.3.16 RP 1.6.

Transmission electron microscopy (TEM) imaging, film thickness measurement, and selected area electron diffraction (SAED) acquisition was carried out using a TEM (FEI Tecnai G2 TF20 UT) operated at 200 kV with a point resolution of 0.19 nm. High-resolution scanning TEM imaging (HR STEM), and energy-dispersive X-ray spectroscopy (EDX) were performed using a HRTEM instrument (FEI image/probe double C, corrected Titan3 G2 60–300, Eindhoven, The Netherlands) operated at 300 kV with an ultrathin window silicon drift detection X-ray energy-dispersive spectrometer and a monochromator.

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. Scanning electron microscopy (SEM) (Zeiss Supra 50VP, Germany) was used to investigate the morphology of the Ti3AlC2 and Ti3C2Tx films.

Optical and Electrical Characterization. Transmittance values of the films were obtained using a spectrophotometer (Perkin-Elmer Lambda 950 UV–vis) with a 2-mm slit width and resolution. Spectra were corrected with both 100% and 0% transmittance background spectra. A bare sapphire substrate was used as a reference. The number of MXene layers obtained for Figure 3b were calculated by dividing the total film thicknesses by c/2, where c is the lattice parameters obtained from XRD.

Room-temperature resistivities were measured using a four-point probe method. Three sheet-resistance measurements were taken for each sample. The errors reported in Table 1 and Supporting Information Table S4 were calculated from these three measurements.
The resistivity was obtained by multiplying the sheet resistance with the corresponding average film thickness.

The temperature-dependent in-plane resistivity 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 the magnetic field up to 10 T applied out of the plane of the film.

■ RESULTS AND DISCUSSION

The films used were 15 to 60 nm thick Ti$_3$AlC$_2$ films deposited onto sapphire (0001) substrates by magnetron sputtering. More details can be found in Supporting Information Section I. Scheme 1a shows the process starting from the sputter-deposition of Ti$_3$AlC$_2$ (with initial formation of a TiC incubation layer). This is followed by etching of the Al layers resulting in 2D Ti$_3$C$_2$T$_x$ layers (Scheme 1b), where T$_x$ stands for the surface $-\text{O}$, $-\text{OH}$, or $-\text{F}$ terminations resulting from the aqueous HF etchant. In Scheme 1b, the Ti$_3$C$_2$ surfaces are presumed to be OH-terminated. STEM image of the interface between the TiC incubation layer and Ti$_3$C$_2$T$_x$ is shown in Scheme 1c. The fact that the very first MXene layer has an ordered structure bodes well for the production of single layer MXene films. To date, the only etchant reported for producing MXenes has been HF.$^{13,15,16}$ Herein, we show that, NH$_4$HF$_2$ can be used for the same purpose. The main advantage of the latter is that it is less hazardous than HF$^{23}$ and is a milder etchant. Its use leads to the concomitant intercalation of cations during the etching process. For the sake of brevity, these films will be referred to as Ti$_3$C$_2$T$_x$-IC, where the IC represents the intercalated species, viz. NH$_4^+$ and NH$_3$.$^{25}$
Figure 2. Cross-sectional STEM images of (a) Ti$_3$AlC$_2$, (b) Ti$_3$C$_2$T$_x$ and (c) Ti$_3$C$_2$T$_x$-IC films (60 nm nominal thickness) grown on a sapphire substrate with a TiC incubation layer. Insets show SAED of the film and the substrate. The subscripts A and T correspond to Al$_2$O$_3$ and Ti$_3$AlC$_2$, respectively. High-resolution STEM images of (d) Ti$_3$AlC$_2$, (e) Ti$_3$C$_2$T$_x$, and (f) Ti$_3$C$_2$T$_x$-IC films along the [1120] zone axis. The inset in panel d shows Ti, Al, and C atoms in yellow, gray, and black, respectively. Scale bars for low resolution (a, b, and c) and high-resolution (d, e, and f) images correspond to 5 and 1 nm, respectively.

A typical XRD pattern of an as-deposited Ti$_3$AlC$_2$ film (Figure 1a, I) shows the (000) peaks from Ti$_3$AlC$_2$, a TiC incubation layer) and the sapphire substrate. The presence of only peaks corresponding to basal-plane oriented Ti$_3$AlC$_2$ indicates epitaxial growth, a fact also confirmed by TEM and SAED (Figure 2a). The Ti$_3$C$_2$T$_x$ XRD pattern (Figure 1a, II) on the other hand, shows a shift to a lower angle of the 000 peaks corresponding to an increase in the c lattice parameter from 18.6 Å for Ti$_3$AlC$_2$ to 19.8 Å for Ti$_3$C$_2$T$_x$. The latter value agrees with previous work on Ti$_3$C$_2$T$_x$ synthesized from Ti$_3$AlC$_2$ powders. The XRD pattern of Ti$_3$C$_2$T$_x$-IC (Figure 1a, III), is similar to the other two, except that now c is further increased to 24.7 Å.

Similar behavior was observed when Ti$_3$AlC$_2$ powders were intercalated with NH$_4$OH or NH$_4$F after HF etching. In both cases, the c lattice expansion was of the order of 25% (see Supporting Information Figure S5a). The independence of the increase in the c lattice parameter on the nature of the anion of the etching solution strongly suggests that the cations (NH$_4^+$) and/or (NH$_3$), and not the anions, are the intercalated species. We note in passing that the present work is in contradistinction to the recent work by Lukatskaya et al. who intercalated NH$_4$OH into Ti$_3$C$_2$T$_x$ in a two-step process. Herein, the etching and intercalation occur in a single step. This is an important result because it considerably simplifies the intercalation process.

The XPS results, shown in Figure 1b—d for films, with a nominal thickness of 60 nm, demonstrate a shift in the Ti 2p and C 1s (Figure 1b and c) toward higher binding energies for the titanium carbide species in Ti$_3$AlC$_2$, Ti$_3$C$_2$T$_x$, and Ti$_3$C$_2$T$_x$-IC, compared to those of binary TiC (shown in Figure 1b and c as thin vertical lines), indicating the change in the nature of bonding between the Ti and C atoms in Ti$_3$AlC$_2$ and the corresponding MXenes. The latter most likely occurs because valence electrons are withdrawn from the Ti atoms, and subsequently from the C atoms, in the MXene layers by the surface functional groups, as well as from the interaction of the surface with the intercalated compounds. The removal of Al is verified by the high-resolution spectra in the Al 2p region for Ti$_3$C$_2$T$_x$ and Ti$_3$C$_2$T$_x$-IC (Figure 1d), in which a very weak Al signal—most probably originating from aluminum fluoride (see Supporting Information section I)—is recorded. The Ti$_3$AlC$_2$, Al 2p signal corresponds to Al bonded to Ti, as well as, to surface aluminum oxide.

The reactions of HF with Ti$_3$AlC$_2$ have been postulated by Naguib et al. to be

\[
\text{Ti}_3\text{AlC}_2 + 3\text{HF} = \text{AlF}_3 + 3/2\text{H}_2 + \text{Ti}_3\text{C}_2
\]

(1)

\[
\text{Ti}_3\text{C}_2 + 2\text{H}_2\text{O} = \text{Ti}_3\text{C}_2(\text{OH})_2 + \text{H}_2
\]

(2)

\[
\text{Ti}_3\text{C}_2 + 2\text{HF} = \text{Ti}_3\text{C}_2\text{F}_2 + \text{H}_2
\]

(3)

Reaction 1 is followed by reactions 2 and 3, which result in OH and F terminated Ti$_3$C$_2$ surfaces or Ti$_3$C$_2$T$_x$. The elemental ratio obtained from the analysis of high-resolution (XPS) spectra is Ti$_3$C$_2$O$_2$F$_{0.6}$ (see Supporting Information section II). As indicated by XPS, terminal hydroxyl and fluoride groups exist on the surface of the material, thereby indirectly confirming the aforementioned reactions. EDX mapping in the TEM (Supporting Information Figure S7) also confirms the presence of F and O atoms between the Ti$_3$C$_2$ layers.

As discussed above for the NH$_4$HF$_2$ etched Ti$_3$AlC$_2$, the etching of the Al and the intercalation of ammonium species occur concomitantly. It is thus reasonable to conclude that in this case the following reactions are operative:

\[
\text{Ti}_3\text{AlC}_2 + 3\text{NH}_4\text{HF}_2 = (\text{NH}_4)_3\text{AlF}_6 + \text{Ti}_3\text{C}_2 + 3/2\text{H}_2
\]

(4)

\[
\text{Ti}_3\text{AlC}_2 + 3\text{NH}_4\text{F} = (\text{NH}_4)_3\text{AlF}_6 + \text{Ti}_3\text{C}_2 + 3/2\text{H}_2
\]
Figure 3. (a) Transmittance spectra and visual images (on right) for (I) Ti₃AlC₂, (II) Ti₃C₂Tₓ, and (III) Ti₃C₂Tₓ-IC films of 15 nm nominal thickness. The films are ≥1 x 1 cm² in area; (b) light absorbance at wavelengths of 240 and 800 nm vs thickness of Ti₃C₂Tₓ and Ti₃C₂Tₓ-IC films.

\[
\text{Ti}_3\text{C}_2 + a\text{NH}_4\text{HF}_2 + b\text{H}_2\text{O} = (\text{NH}_4)_a\text{Ti}_3\text{C}_2(\text{OH})_b\text{F}_c
\]

Unlike HF etching, NH₄HF₂ etching results in formation of (NH₄)₃AlF₆ according to reaction 4 (see Supporting Information section III). Reaction 5 depicts the intercalation of NH₄ and NH₄⁺ between the Ti₃C₂Tₓ layers. In order to confirm the intercalation of NH₄ and NH₄⁺ between the Ti₃C₂Tₓ layers.  

The elemental ratio obtained from the analysis of high-resolution XPS spectra (see Supporting Information section II) of Ti₃C₂ produced by NH₄HF₂ etching is Ti₃C₂(O₃F₀.5N₂)₂. Here again, the XPS analysis indicates the presence of terminal hydroxyl and fluoride groups.

Cross-sectional scanning TEM micrographs of as-deposited Ti₃AlC₂ films, before (Figure 2a and d) and after etching with HF (Figure 2b and e) or NH₄HF₂ (Figure 2c and f) clearly show the presence of the TiC incubation layers and the effects of etching on the microstructures of the films. The SAED patterns confirm the out-of-plane epitaxial relationship Ti₃AlC₂(0001)//TiC(111)//Al₂O₃(0001). At 18.6 Å, the c lattice parameter for Ti₃AlC₂, obtained from the SAED pattern and TEM micrographs (see Supporting Information section VIII), is in excellent agreement with that calculated from XRD (18.6 Å). At 19.5–20 Å, the c lattice parameters of Ti₃C₂Tₓ obtained from the SAED patterns match the ones obtained from XRD (19.8 Å). However, at 21 ± 0.5 Å, the average c for Ti₃C₂Tₓ-IC measured from the SAED pattern is considerably lower than that obtained from XRD (25 Å). The most probable reason for this state of affairs is the deintercalation of the ammonium species during TEM sample preparation and/or observation (see Methods and Supporting Information section IV).

The light elements of the surface termination groups (O, H, and F) cannot be seen between the layers, but the larger and nonuniform spacing seen in Figure 2b, c, e, and f indirectly confirm the weak interactions between the MXene layers after etching and the formation of a 2D structure. The nonuniform interlayer spacing observed in the STEM images of the HF-etched sample (Figure 2b) could also account for the peak broadening observed in XRD (Figure 2a).

Prior to etching, the initial thicknesses of the films examined in TEM were 60 nm (Figure 2a). However, as a result of the increase in c and the separation between the MXene layers, due to exfoliation, the etched films were thicker than the initial films (Table 1). Comparing the atomic layers in Ti₃C₂Tₓ-IC (Figure 2c and f) to those of the Ti₃C₂Tₓ layers (Figures 3b, e), it is obvious that the former are more uniformly spaced. This result most probably reflects the milder nature of NH₄HF₂ as compared to HF. For the latter, the reaction is faster (Table 1) and more vigorous than the former. Another possible explanation is that the intercalation of ammonia species leads to stronger interactions between MXene layers, essentially “gluing” them together as observed for other MXene intercalation compounds.

In terms of light transmittance, both Ti₃C₂Tₓ and Ti₃C₂Tₓ-IC films are significantly more transparent than Ti₃AlC₂ of the same initial thickness, 15 nm (Figure 3a, and Table 1). The increased transparency of Ti₃C₂Tₓ and Ti₃C₂Tₓ-IC, compared to that of Ti₃AlC₂ is also evident visually (Figure 3, middle inset).

With 90% transmittance, the Ti₃C₂Tₓ-IC films were the most transparent, followed by the Ti₃C₂Tₓ films at 70%. With a transmittance of 30%, the Ti₃AlC₂ films were the least transparent. It is worth noting here that the transmittance of all films would have been higher had the TiC incubation layer been absent.

A linear dependence of the absorbance—that is independent of the wavelength of the light—on the thickness of the Ti₃C₂Tₓ and Ti₃C₂Tₓ-IC films was observed (Figure 3b). Given the similarities in the transmittance curves and the linear dependencies of absorbance values for both samples, it is reasonable to conclude that Ti₃C₂Tₓ and Ti₃C₂Tₓ-IC are quite similar in structure. A crude estimation of the transmittance of a single MXene layer, d, (since each length c is comprised of two MXene layers, d is approximately equal to the film thickness divided by 2c) could be obtained from the linear fits of absorbance vs d. The transmittances, calculated at a wavelength of 240 nm, for single layers of Ti₃C₂Tₓ and Ti₃C₂Tₓ-IC are about 90.5% and 91.5%, respectively; the corresponding transmittances, at a wavelength of 800 nm, are 97.3% and 97.1% respectively. The latter values are quite close to those reported for graphene single layers. Note that to obtain these values, both the thickness and absorbance of the TiC incubation layer were neglected.
We next turn to the electrical properties, which confirm the metallic-like nature of the conductivities of all etched films despite their optical transparency. As expected, and consistent with previous work\textsuperscript{31} the Ti\textsubscript{3}AlC\textsubscript{2} films are metallic with resistivity, $\rho$, values in the range from 0.37 to 0.45 $\mu\Omega$ m. The latter increase linearly with increasing temperature (Figure 3a). Furthermore, $\rho$ increases with decreasing film thickness (Table 1 and Supporting Information Figure S10). The resistivity values of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}-IC films are systematically higher than those produced by HF etching. For instance, 28 nm nominally thick Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}-IC films have $\rho$ values of 2.3 and 5.0 $\mu\Omega$ m, respectively. This result is also consistent with previous work that has shown that intercalation of MXenes with organic compounds increases their resistivity.\textsuperscript{30} The resistivities of the etched films also depend significantly on etching time; longer etching times lead to higher $\rho$ values presumably due to the formation of defects (see Supporting Information Table S2), in agreement with previous work.\textsuperscript{32} The results listed in Table 1 are those obtained upon the full MAX to MXene conversion. The latter was determined by intermittently etching each film, followed by XRD. When the Ti\textsubscript{3}AlC\textsubscript{2} peaks disappeared, the etching process was halted (Supporting Information Figure S6). We note in passing that there were no changes in the c lattice parameter with etching time. Furthermore, the fact that the conductivities are affected by the intercalants, suggests that MXenes can potentially be used as sensors.

At 1.8 $\mu\Omega$ m, a 60 nm nominally thick Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} sample is the most conductive of the HF etched films Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} films (Table 1). However, at 700 nm wavelength, its transmittance is only 15%. The 15 nm nominally thick Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} sample exhibited the highest transmittance (68% at 700 nm wavelength) with a $\rho$ of 39.2 $\mu\Omega$ m. For the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}-IC films, the lowest resistivity was 5.0 $\mu\Omega$ m, with a transmittance of about 37%; the most transparent (>85% at 700 nm wavelength) had a resistivity of $\approx$4.5 $\mu\Omega$ m.

At this juncture, it is worth comparing our results with other conductive electrodes at a wavelength of 550 nm. Referring to Supporting Information Figure S10, it is obvious that while the transmittance of our thinnest films is higher than that of indium tin oxide, ITO, their sheet resistance values are orders of magnitude higher. When compared to graphene transparent conductive electrodes, again MXene transmittance values are slightly higher, but the resistivity is about 2 orders of magnitude higher.

Why the resistivities measured herein are as high as they are, is unclear at this time. One possibility is the film morphology. As noted above, the Ti\textsubscript{3}AlC\textsubscript{2} films are predominantly c-axis oriented (Figure 2a). However, a secondary grain population, whose basal planes are not parallel to the substrate, also exists (see Supporting Information Figure S9). If the reasonable assumption is made that after etching the conductivity along [0001] is significantly lower than along [100], this secondary grain population, will act as insulating islands. Reducing the fraction of such grains should result in films that are more conductive when etched. Deintercalation of films by heat treatment can alone increase the conductivity by an order of magnitude or more.\textsuperscript{30}

Theoretical calculations predict that it is possible to alter the electronic properties of MXenes by altering their surface terminations.\textsuperscript{4,13} For example, pure Ti\textsubscript{3}C\textsubscript{2} is predicted to exhibit a metallic behavior, whereas Ti\textsubscript{3}C\textsubscript{2}F\textsubscript{2} and Ti\textsubscript{3}C\textsubscript{2}(OH)\textsubscript{2} are predicted to have band gaps of 0.05 and 0.1 eV, respectively.\textsuperscript{4,13} Thus, another potential avenue for enhancing the films’ conductivities is to eliminate the surface groups. We note in passing that several applications, such as touch screen, electromagnetic shielding for cathode ray tubes and electrostatic dissipation, require sheet resistance values which are comparable to what we report for MXene thin films, viz. 1000 to 1 $\Omega$ sq.\textsuperscript{-1}.

To elucidate the conduction mechanisms of the MXene layers, their resistivities, and magnetoresistances (MRs) from room temperature down to about 2.5 K were measured. Figure 4a shows the temperature dependent resistivity for Ti\textsubscript{3}AlC\textsubscript{2}, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}-IC films of 28 nm nominal thickness. The Ti\textsubscript{3}AlC\textsubscript{2} films exhibit metallic behavior from 300 K down to about 10 K. For the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}-IC films, on the other hand, metallic behavior is observed from 300 to about 100 K; below 100 K the resistivity increases with decreasing temperature (Figure 4b). Similar low-temperature behavior was observed in other Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}-IC films (see Supporting Information Figure S11). The logarithmic dependence on temperature is consistent with weak localization, a phenomen-
on caused by electron backscattering and often observed in 2D metals.\textsuperscript{35} To provide further insight into the transport properties, MR measurements were performed in the low temperature ($\rho(T)/\rho(0) < 0$) and high temperature ($\rho(T)/\rho(0) > 0$) regimes. The appearance of negative MR in the low temperature regime (Figure 4c) is again consistent with weak localization, verifying that these materials are indeed 2D.$^{35-37}$

\section*{CONCLUSIONS}

In conclusion, epitaxial Ti\textsubscript{x}C\textsubscript{y} films can be readily produced with the room temperature etching of epitaxial Ti\textsubscript{x}AlC\textsubscript{y} thin films in HF or NH\textsubscript{4}HF solutions. The latter etchant yields films intercalated with NH\textsubscript{3} and NH\textsubscript{4}\textsuperscript{+} species, that have $c$ lattice parameters ($\sim 25$ Å) that are 25% larger than films etched with HF. The Ti\textsubscript{x}C\textsubscript{y}T\textsubscript{z}IIC films have higher transparencies and resistivities than their Ti\textsubscript{x}C\textsubscript{y}T\textsubscript{z} counterparts. Ti\textsubscript{x}C\textsubscript{y}T\textsubscript{z} and Ti\textsubscript{x}C\textsubscript{y}T\textsubscript{z}IIC films of ~15-nm nominal thickness were found to be 68 and 85% transparent, respectively. Both films also exhibited metallic conductivity down to 100 K; below 100 K, the resistivities increase with decreasing temperatures and exhibit negative MRs at the lowest temperatures, both attributes consistent with, and evidence for, their 2D metallic nature.

The MXene films produced herein are promising materials for transparent conductive electrodes, sensors and other applications. By better control of the deposition process, such that nonbasal growth is eliminated or minimized, the potential exists for enhancing their conductivities. A parallel approach is to modify, or eliminate, the surface terminations such as F, O, or OH.

Synthesis of single-layer Ti\textsubscript{x}C\textsubscript{y} films is the next frontier. Other MXenies (Ti-based and others containing other transition metals such as Nb, V, Ta, etc. or nitrogen in addition to carbon) may also show attractive optical and electrical properties and should be produced and studied in their thin-film state. It is vital to note here that the production of epitaxial uniform multilayer MXene films is a necessary and crucial first step to applying this novel and unique family of materials in the field of electronics, optoelectronics and photonics. Given the vast richness of MXene chemistries, together with the multiple different intercalants (from cations to polymers to organic molecules), it is obvious that we are standing at the edge of a truly vast terra incognita.

\section*{ASSOCIATED CONTENT}

\section*{Supporting Information}

XRR, thickness determination, XPS analysis of Ti\textsubscript{x}AlC\textsubscript{y}, Ti\textsubscript{x}C\textsubscript{y}T\textsubscript{z}, and Ti\textsubscript{x}C\textsubscript{y}T\textsubscript{z}IIC thin films, XRD analysis of byproducts from etching Ti\textsubscript{x}AlC\textsubscript{y} with NH\textsubscript{4}HF\textsubscript{2}, intercalation and deintercalation of Ti\textsubscript{x}C\textsubscript{y}T\textsubscript{z} thin films, optimization of the etching process, EDX mapping of Ti\textsubscript{x}C\textsubscript{y}T\textsubscript{z} thin films, and electrical transport and transmittance properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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\section*{Author Contributions}

J.H. planned and performed the thin film depositions; performed and developed the etching process; performed XRD of the films before and after etching; and measured the room temperature resistivities. M.R.L. performed the intercalation and deintercalation experiments; carried out the XRD scans and analysis of the intercalated, and deintercalated samples; performed the SEM; and made the figures for the manuscript. K.M.C. measured and analyzed the optical transmittance properties. C.R.S. and S.J.M. performed and analyzed the temperature dependent resistivity and MR measurements. J.L. performed and analyzed the TEM micrographs with contributions from J.H., L.H., and P.E. XPS experiments were performed by L.-Å.N. Additionally, J. H. analyzed the results with contributions from K.M.C. and L.-Å.N. The manuscript draft was written by J.H. and P.E. All authors were involved in the discussions and commented on and revised successive drafts of the manuscript. M.W.B., L.H., and Y.G. conceived and initiated the research. M.W.B, L.H., Y.G., and P.E. supervised the work.

\section*{Notes}

The authors declare no competing financial interest.

\section*{ACKNOWLEDGMENTS}

Hossein Fashandi is acknowledged for his help and useful discussions about growth of Ti\textsubscript{x}AlC\textsubscript{y} thin films. The authors acknowledge funding from the Swedish Research Council (VR) Grant Nos. 621-2012-4430 and 621-2011-4420, the VR Linnaeus Strong Research Environment LiLi-NFM. M.W.B., J.H., and P.E. also acknowledge the Swedish Foundation for Strategic Research (SSF) through the Synergy Grant FUN-CASE (M.W.B., J.H., and P.E.) and the Ingvarg Carlsson Award 3 (P.E.). The Knut and Alice Wallenberg Foundation supported the Ultra-Electron Microscopy Laboratory at Linköping University operated by the Thin Film Physics Division. S.J.M. and C.R.S. were supported by the U.S. Office of Naval Research (ONR N00014-11-1-0109); the acquisition of the Physical Properties Measurement System was supported by the U.S. Army Research Office under grant number W911NF-11-1-0283. M.L. and Y.G. were supported by the US Department of Energy, Energy Storage Systems Research Program through Sandia National Laboratory.

\section*{REFERENCES}

Supporting Information

Transparent Conductive Two-Dimensional Titanium Carbide Epitaxial Thin Films

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I. X-ray reflectometry and thickness determination

Films’ thickness has been determined from XRR for \( \text{Ti}_3\text{AlC}_2 \) films, before and after etching, deposited for 5 and 10 min, examples of the XRR data and their fittings shown in Figures S1, and S2. For \( \text{Ti}_3\text{AlC}_2 \), film deposited for 30 mins, thicknesses before and after etching were obtained by direct measurement in TEM (Figures 2a-c, and Figure S9c). Figure S1 shows the measured X-Ray reflectometry for \( \text{Ti}_3\text{AlC}_2 \) (black curve), and best-fitted simulation from TiC incubation layer/\( \text{Ti}_3\text{AlC}_2 \) (red curve): for a film deposited for 5 min (Figure S1a) giving a thickness of 15.2 ± 0.5 nm and a film deposited for 10 min (Figure S1b) giving a thickness of 27.7 ± 0.8 nm. Figure S1c shows the relationship between the thickness of \( \text{Ti}_3\text{AlC}_2 \), \( \text{Ti}_3\text{C}_2\text{T}_x \) and \( \text{Ti}_3\text{C}_2\text{T}_x\text{-IC} \) and deposition time of \( \text{Ti}_3\text{AlC}_2 \). Films deposited for 20 min: their thickness before and after etching was obtained from interpolation (Figure S3c).

II. XPS analysis of \( \text{Ti}_3\text{AlC}_2 \), \( \text{Ti}_3\text{C}_2\text{T}_x \), and \( \text{Ti}_3\text{C}_2\text{T}_x\text{-IC} \)

Analysis of the high-resolution XPS spectra was performed through peak fitting using symmetric Gaussian-Lorentzian curves resting on a Shirley background.

Fig. S2 presents the Ti 2p, C 1s, and Al 2p regions for the \( \text{Ti}_3\text{AlC}_2 \) thin film together with the obtained Shirley background and Gaussian-Lorentzian curves for each region. In the Ti 2p region (Figure S2a), which contains both the 2p\(_{1/2}\) and the 2p\(_{3/2}\) spin-orbit split components, the XPS spectrum could be best fit with four pairs of Gaussian-Lorentzian curves, where each pair is the 2p\(_{1/2}\) and the 2p\(_{3/2}\) component that we assign to Ti-Al, Ti-C, Ti(II) oxide, and Ti(III) oxide, respectively.\(^{1,4}\)

The C 1s region (Figure S2b) could be fit with four Gaussian-Lorentzian curves. The low binding energy feature is a sharp asymmetric peak that is assigned to the Ti-C bond.\(^{1,2}\) The asymmetry is due to extrinsic energy losses caused by delocalized states. This asymmetry, in turn, required the Ti-C XPS peak to be fit with two symmetric Gaussian-Lorentzian curves. In addition to the Ti-C peak there are two peaks assigned to surface hydrocarbon (-CH\(_2\) & -CH\(_3\)) and carboxylate (-COO)\(^3\) contamination common for samples exposed to laboratory air.\(^6\)
In the Al 2p region (Figure S2c) the low binding energy feature contains the 2p_{1/2} and the 2p_{3/2} spin-orbit split components assigned to Ti-Al. The high binding energy feature is assigned to an aluminum oxide components, fitted with a symmetric Gaussian-Lorentzian curve, due to surface oxidation which is common for MAX phase materials. The results obtained from the peak fitting of the Ti₃AlC₂ thin film are summarized in Table S1.

**Figure S2.** Deconvolution of high resolution XPS spectra for elements in Ti₃AlC₂ films. (a) Ti 2p, (b) C 1s and (c) Al 2p XPS high resolution spectra for Ti₃AlC₂ thin films.
Table S1. Ti$_3$AlC$_2$ XPS peak fitting results. Parameters obtained from the peak fitting of the Ti$_3$AlC$_2$ thin film XPS spectra using symmetric Gaussian-Lorentzian curves.

<table>
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<th>BE [eV]$^a$</th>
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<th>Fraction</th>
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<th>Reference</th>
</tr>
</thead>
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<td>Ti 2p$_{3/2}$</td>
<td>453.9 (459.9)</td>
<td>0.5 (2.0)</td>
<td>0.20</td>
<td>Ti-Al</td>
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<td>(2p$_{1/2}$)</td>
<td>454.3 (460.3)</td>
<td>0.5 (1.3)</td>
<td>0.37</td>
<td>Ti-C</td>
<td>1,2</td>
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<td>1.9 (3.0)</td>
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<td>Ti(II) oxide</td>
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<td>-CH$_2$ &amp; -CH$_3$</td>
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<tr>
<td>Al 2p$_{3/2}$</td>
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<td>(2p$_{1/2}$)</td>
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<td>Al$_2$O$_3$</td>
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$^a$Values in parenthesis corresponds to the 2p$_{1/2}$ component.

Figures S3a-d and Figures S3e-h represent the Ti 2p, C 1s, O 1s, and F 1s regions for the Ti$_3$C$_2$T$_x$ thin film and the Ti$_3$C$_2$T$_x$-IC thin film, respectively. For both MXene thin films, the XPS spectrum of the Ti 2p region (Figures S3a, and S3e) could be best fitted with five pairs of Gaussian-Lorentzian curves, where each pair is the 2p$_{1/2}$ and the 2p$_{3/2}$ component that we assign to Ti-C, Ti(II) oxide, Ti(III) oxide, Ti(IV) oxide, and Ti-F, respectively. The C 1s region for both MXene thin films (Figures S3b, and S3f) shows features assigned to Ti-C,$^1,2$ hydrocarbons (-CH$_2$ & CH$_3$), and carboxylates (-COO). In this case intense contributions from graphite (C-C) and alcohol (C-O) formation are also present.$^5$ The O 1s region for both MXene thin films (Figures S3c, and S3g) could be fit by two components assigned to titanium oxide: one component for stoichiometric TiO$_2$ and one component for sub-stoichiometric TiO$_x$.$^9$ The O 1s region also suggests Ti-OH formation and H$_2$O uptake.$^9$
Figure S3. Deconvolution of high resolution XPS spectra for elements in Ti$_3$C$_2$T$_x$ and Ti$_3$C$_2$T$_x$-IC. (a) Ti 2p, (b) C 1s, (c) O 1s and, (d) F 1s regions for Ti$_3$C$_2$T$_x$-C; and, (e) Ti 2p; f, (f) 1s, (g) O 1s and, (h) F1s regions for Ti$_3$C$_2$T$_x$-IC thin films.

The F 1s region for both MXene thin films (Figs. S3d and S3h) shows a dominating contribution from fluorinated titanium,$^8$ Ti-F, but also a small component assigned to aluminum fluoride,$^9$ Al-F, which is corroborated by the appearance of a weak feature at
73.6 eV in the Al 2p spectra shown in Figure 2b. The results obtained from the peak fitting of the Ti$_3$C$_2$T$_x$ thin film and the Ti$_3$C$_2$T$_x$-IC thin film are summarized in Tables S2 and S3.

**Table S2.** Ti$_3$C$_2$T$_x$ XPS peak fitting result. Parameters obtained from the peak fitting of the Ti$_3$C$_2$T$_x$ thin film XPS spectra using symmetric Gaussian-Lorentzian curves.

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<td>0.37</td>
<td>Ti-C</td>
<td>1, 2, 7</td>
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<td>455.6 (460.9)</td>
<td>1.3 (2.0)</td>
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</table>

$^a$Values in parenthesis corresponds to the 2p$_{1/2}$ component.
Table S3. Ti$_3$C$_2$T$_x$-IC XPS peak fitting result. Parameters obtained from the peak fitting of the Ti$_3$C$_2$T$_x$-IC thin film XPS spectra using symmetric Gaussian-Lorentzian curves.

<table>
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$^a$Values in parenthesis corresponds to the 2p$_{1/2}$ component.

$^b$The peak for the aluminum fluoride component shifts to a higher binding energy compared to that for Ti$_3$C$_2$T$_x$, while its FWHM maximum increases, which may be due to the formation of (NH$_4$)$_3$AlF$_6$ rather than AlF$_3$ as indicated by XRD in Figure S6.
The high-resolution XPS spectra of the Ti 2p and C 1s regions for the Ti\textsubscript{3}AlC\textsubscript{2}, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}-IC thin films show that the removal of Al causes a shift of the Ti-C contribution in the Ti 2p and C 1s XPS spectra toward higher binding energies, indicative of a loss of charge, and a concomitant charge redistribution within the material. Note that this decrease of charge is not due to the removal of Al atoms, because the latter needs to leave behind the charge they gained when forming Ti\textsubscript{3}AlC\textsubscript{2}. The charge redistribution is instead a consequence of the higher electronegativities of the OH, O and F surface functional groups, as mentioned in the main text.

In addition there is a slight shift to higher binding energies for the Ti 2p spectrum of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}-IC thin film compared to the corresponding spectrum of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}. Since the matching C 1s spectra do not show any changes in the binding energies, the observed binding energy shift could be due to the intercalated nitrogen species (Figure 2e) interacting with the surface of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}-IC thin film.

The peak fitting of the XPS high-resolution spectra suggests the chemical compositions to be Ti\textsubscript{3}C\textsubscript{2.2}O\textsubscript{2}F\textsubscript{0.6} and Ti\textsubscript{3}C\textsubscript{2.3}O\textsubscript{1.2}F\textsubscript{0.7}N\textsubscript{0.2} for Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} and Ti\textsubscript{3}C\textsubscript{2}-IC, respectively. Fitted peaks that correspond to surface oxidation and contamination, i.e. TiO\textsubscript{2}, H\textsubscript{2}O, hydrocarbons, alcohols, carboxylates, and aluminum fluoride, are not included in these elemental quantifications. The obtained quantification data indicates that the etching of Ti\textsubscript{3}AlC\textsubscript{2}, using HF or NH\textsubscript{4}HF\textsubscript{2}, provides near-stoichiometric Ti\textsubscript{3}C\textsubscript{2} 2D-structures, surface terminated with a mixture of fluoride- and hydroxyl groups. Additionally, etching in NH\textsubscript{4}HF\textsubscript{2} results in the intercalation of the nitrogen species, NH\textsubscript{4}\textsuperscript{+} and NH\textsubscript{3}.\textsuperscript{11,12}

### III. XRD Analysis of the Byproducts from Etching Ti\textsubscript{3}AlC\textsubscript{2} with NH\textsubscript{4}HF\textsubscript{2}

One half of a gram of Ti\textsubscript{3}AlC\textsubscript{2} powder (the method of preparation is described elsewhere\textsuperscript{13}) were soaked in 5ml of 1M NH\textsubscript{4}HF\textsubscript{2} solution at room temperature. The mixture was left untouched until the solvent evaporated. XRD diffraction of the dry powders (Figure S4) indicates the existence of two byproduct compounds (NH\textsubscript{4})\textsubscript{3}AlF\textsubscript{6} (PDF# 22-1036) and AlF\textsubscript{3}3H\textsubscript{2}O (PDF# 46-1459) comparing the intensity of the maximum peaks for both gives a ratio of about 7:1 respectively. It follows that the major byproduct from etching Ti\textsubscript{3}AlC\textsubscript{2} with NH\textsubscript{4}HF\textsubscript{2} is (NH\textsubscript{4})\textsubscript{3}AlF\textsubscript{6}. 
Figure S4: X-Ray diffraction pattern of Ti$_3$C$_2$T$_x$ intercalated MXene (Ti$_3$C$_2$T$_x$-IC) after etching Ti$_3$AlC$_2$ powder with 1M NH$_4$HF$_2$, and allowing the mixture to sit until the solvent dried. In contrast to our previous work, here the resulting salt was not washed away with water. The XRD pattern also includes peaks associated with un-reacted Ti$_3$AlC$_2$ and TiC present as an impurity in the as-received powders.

IV. Intercalation and de-intercalation of Ti$_3$C$_2$T$_x$

In order to verify the assumption that intercalation is the pertinent mechanism, Ti$_3$C$_2$ powder (the method of preparation is described elsewhere$^{13}$) were immersed in 1 M of NH$_4$F or in 5 M NH$_4$OH for 24 h at room temperature while stirring. XRD patterns before and after treatment, shown in Fig. S5a, confirm that the increase in $c$, from 19.8 Å to 25 Å, in both solutions is similar to that observed when NH$_4$HF$_2$ was used as etchant. It is thus reasonable to assume that, intercalant compound should be the common species between NH$_4$HF$_2$, NH$_4$F and NH$_4$OH, viz. NH$_4^+$.

To investigate the reversibility of the intercalation process, a 43 nm nominal thickness Ti$_3$C$_2$T$_x$-IC film was heated in a vacuum at 250 °C for 90 min. The XRD patterns for the film before and after de-intercalation are compared in Figure S5b. After the vacuum treatment, the (0002) peak shifts to an angle that corresponds to a $c$ lattice parameter of 21 Å. It is thus possible to de-intercalate ammonia from Ti$_3$C$_2$T$_x$-IC. This value is also quite similar to, the lattice parameter obtained from SAED pattern shown in Figure 3e, suggesting that the TEM sample was partially de-intercalated during the sample preparation.
Figure S5. (a) X-Ray diffraction pattern of initial MXene (Ti$_3$C$_2$Tx) powder (black curve), and after 24 h treatment at room temperature with 1 M NH$_4$F (red curve) and 5 M NH$_4$OH (blue curve). (b) Ti$_3$C$_2$Tx-IC film of 43 nm nominal thickness before and after heating in vacuum at 250 °C for 2 h.

V. Optimization of the etching process

The resistivities of all films increased with increase in etching times. Table S4 lists the resistivities of Ti$_3$C$_2$Tx films produced by HF etching for samples, of the same nominal thicknesses, etched for different times. For example, the resistivities of Ti$_3$AlC$_2$ films, 60 nm nominal thick, etched for 160 mins and 360 mins were 1.8 µΩm and 3.4 µΩm, respectively.

The etching time required to fully transform the Ti$_3$AlC$_2$ films to MXenes was determined by repeatedly measuring the XRD diffraction patterns, of a given film, after successive etching steps until the XRD peaks belonging to Ti$_3$AlC$_2$ disappeared (Figure S6). This procedure was adopted in order to compare the properties of all etched films at the point all the Al layers were etched out. Said otherwise, the etching times varied from film to film. The dependence is not linear, however. For example, the etching times for Ti$_3$AlC$_2$ films of nominal thicknesses 15 and 28 nm were 10 and 15 mins, respectively. Similarly, at 150 min and 160 min, the time needed to fully etch 15 nm and 28 nm thick Ti$_3$AlC$_2$ films in NH$_4$HF$_2$, were quite comparable (See Table 1).

A perusal of the results shown in Tables 1 and S4 suggest that the final resistivities one obtains is a complicated function of film thickness, etching times and the nature of the etchant. On the one hand, thin films are more resistive than their thicker counterparts. It is this variability - reflected in Table 1 - that is most probably responsible for some of the
anomalies observed. For example, the etching times for Ti$_3$C$_2$Tx films of nominal thicknesses of 15, 28 and 43 nm were 10, 15 and 60 min, respectively.

**Table S4**: Resistivity of Ti$_3$AlC$_2$ films after etching in 50% HF for various times. The thicknesses listed in the first column are thicknesses before etching

<table>
<thead>
<tr>
<th>Thickness [nm]</th>
<th>Etching time [minutes]</th>
<th>Resistivity [µΩm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9.5</td>
<td>39 ± 1.21</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1820 ± 150</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>22 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>42 ± 3.3</td>
</tr>
<tr>
<td>60</td>
<td>160</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>3.4 ± 0.1</td>
</tr>
</tbody>
</table>
**Figure S6.** X-Ray diffraction patterns of 43-nm thick Ti$_3$AlC$_2$ films as a function of etching time in 50 % HF at room temperature.

**VI. EDX mapping of Ti$_3$C$_2$T$_x$**

Figure S7 presents an EDX map showing the distribution of C, Ti, F, and O atoms over the corresponding high-resolution STEM image of Ti$_3$C$_2$T$_x$ produced by HF etching. The fluorine signal is concentrated primarily in the spaces between the Ti-C layers, which suggests that F atoms are attached to the surfaces of the Ti-C layers.
VI. Morphologies of Ti₃AlC₂ and Ti₃C₂Tx films

Figure S8a shows the morphology of a typical Ti₃AlC₂ surface, where the hexagonal striations reflect to the symmetry of the basal planes together with some three-sided grains that are protruding out of plane due to their tilted orientations. Such nonbasal grains are preferentially etched, leading to premature over-etching and thus higher resistivities. Figure S8b shows the surface of Ti₃AlC₂ film after etching (Ti₃C₂Tx). Pinholes have appeared near the tilted grains in the Ti₃C₂Tx, presumably a result of the preferential etching of the tilted grains with respect to the grains parallel to the substrate surface.

Figures S9a,b show TEM images of the tilted grains of Ti₃AlC₂ and Ti₃C₂Tx, respectively. In Figure S9a, Ti₃AlC₂ grain has grown over Ti₂AlC. The nonbasal grain nucleated on the substrate and overgrew the basal grains, since growth along basal planes is faster than normal to it. For the Ti₃C₂Tx grain (Figure S9b), defects appear in the interface between both the tilted and horizontal grains.

Low magnification cross-sectional TEM images of two Ti₃C₂Tx films are shown in Figure S9c. The two samples are facing each other so that the surface of Ti₃C₂Tx is
inwards. The globules appearing between the two films are carbon particles coming from the glue being used to hold the samples together on the TEM grid. The Ti$_3$C$_2$T$_x$ films shown are uniform with some tilted grains (Figure S9a).

**Figure S8.** SEM image of Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$ of 60 nm nominal thickness.

**Figure S9.** Cross-sectional TEM images of defective regions in Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$: (a) TEM image of two cross-sections of Ti$_3$C$_2$T$_x$ of 60 nm nominal thickness placed face to face. Lighter regions in the center of micrograph is the glue used during sample mounting. (b) TEM image of 60 nm thick Ti$_3$AlC$_2$ film grown on a sapphire substrate with TiC incubation layer showing a region not covered with TiC that ultimately resulted in a tilted grain of Ti$_3$AlC$_2$. (c) TEM image for Ti$_3$C$_2$T$_x$ of 60 nm nominal thickness.
VIII. Comparison of different transparent conductive materials

Figure S10. Transmittance vs. sheet resistance for different transparent conductors: ITO on polyethylene terephthalate (PET), Kapton® and glass,14 black dot, square, and rhombus respectively, graphene,15 orange triangle, carbon nanotube (CNT);16 gold triangles, Ag nanowires;17 green triangles, Ti$_3$C$_2$Tx of 15 nm nominal thickness; blue dot and Ti$_3$C$_2$Tx of 15 nm nominal thickness; red dot.
IX. Electrical transport measurements and analysis

To understand what causes the low-temperature insulating behavior, there are numerous possible models to consider. We consider the following four models: i) thermally activated, in which case $\rho \sim \exp(E_A/kT)$; ii) 3D variable range hopping for which $\rho \sim \exp(T_0/T)^{1/4}$, iii) 2D variable range hopping for which $\rho \sim \exp(T_0/T)^{1/3}$, and, iv) a weak localization model for which $\rho \sim \ln(T)^{18-21}$.

The low-temperature ($< 75$ K) resistivity data for Ti$_3$C$_2$T$_x$ films of 28 nm nominal thickness were fitted to all of the aforementioned models. Results of these fits are shown in Figures S10 and S11. The poor fit for the first three models to the experimental obtained (Figure S11) suggest that they can be discarded. In contradistinction, the fit for the weak-localization model is nearly perfect for all samples (insets in Figure S10). The low-temperature behavior of the resistivity is thus consistent with the weak localization model, a phenomenon typically observed in 2D metallic films.$^{19-21}$

The negative magnetoresistance observed in the same temperature range is also consistent with the weak localization model.$^{22}$ This evidences a truly 2D behavior of the electronic transport properties of Ti$_3$C$_2$T$_x$, in that the charge carriers are confined and weakly localized within individual Ti$_3$C$_2$T$_x$ layers.

![Figure S11](image1.png)

**Figure S11.** Temperature dependencies of electrical resistivities of a: (a) 60 nm thick Ti$_3$C$_2$T$_x$ film, (b) 28 nm thick Ti$_3$C$_2$T$_x$-IC film. Insets in both figures show the fits of resistivities, in the 2 to 74 K temperature range, to the weak localization model, viz. $\rho \sim \ln(T)$.

![Figure S12](image2.png)

**Figure S12.** Fitting of resistivity of 28 nm nominal thickness Ti$_3$C$_2$T$_x$ films on temperature in the 2 to 74 K temperature range assuming: (a) a thermally activated process; (b) a 3D variable range hopping model; (c) a 2D variable range hopping model.$^{18}$
REFERENCES