Unraveling the composition of each atomic layer in the MXene/MAX phase structure – identification of oxycarbides, oxynitrides, and oxycarbonitrides subfamilies of MXenes

Electronic Supplementary Information

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1 Secondary ion mass spectrometry measurements with atomic depth resolution

The exact details of the secondary ion mass spectrometry (SIMS) experiments are presented elsewhere.[1] Some of the modifications of the measurement procedure are particularly relevant to the current article and thus will be briefly introduced.

In classical SIMS the parameters for secondary ion extraction are optimized globally and this step is performed on a single test sample, usually silicon. However, for ultra-low impact energy (100 eV) Cs^+ primary ion beam at a high incident angle (75°) the extraction parameters should be optimized individually for each signal using a sample that contains this specific element.

Moreover, the CAMECA IMS SC Ultra instrument used in these experiments can only measure one type of ion at any given time, and thus if more signals are needed they are measured sequentially. A single acquisition of all signals is called a cycle and typically, each signal is integrated for several seconds. For measurements with atomic depth resolution, such an approach is not feasible as the acquisition of a specific signal may not synchronize with the sputtering of a layer where this element is present. Thus, the concept of a super-cycle has been introduced - the integration time of each signal has been reduced to 0.4 s, and several such short cycles have been integrated together to keep the desired total integration time. In this way, the signals are interchanged fast enough to ensure that the composition of each layer can be determined.

2 Recalibration of the measurement parameters

The original procedure for SIMS profiling of the MAX/MXene samples with atomic depth resolution was not quantitative.[1] Some signals were not integrated for a sufficiently long time and as a consequence, they were truncated before they could reach their maximum intensity. Figure S1 compares a depth profile of a pure carbide material with oxycarbide MXene which was estimated to contain about 30% of oxygen. Despite this difference, the intensity of carbon peaks remains the same for both samples. If only carbon signal is registered (Figure S2) a very clear difference can be observed and the intensity of carbon peaks for oxycarbide MXene are about 25-27% less intense than for pure carbide.

This observation has led to the conclusion that the multiple-signal mode requires additional tuning to provide realistic results. To achieve it, the beam intensity has been reduced from 6 to 4 nA and the integration time has been set to 6 s for all signals. As was discussed in the Methods section in the original publication about MAX/MXene profiling[1], the extraction parameters were optimized individually using silicon carbide, sapphire, and titania samples for carbon, oxygen, and titanium signals, respectively. Here, the extraction parameters have been optimized on the actual MAX/MXene sample that has been later measured. It has significantly increased the intensity of measured signals and countered the problem that a decreased intensity of the beam may have caused.

With these modifications, the multiple-signal mode is finally able to register all signals as in the single-signal mode, i.e. without signal truncation. As can be seen in Figure S3 carbon peaks for pure

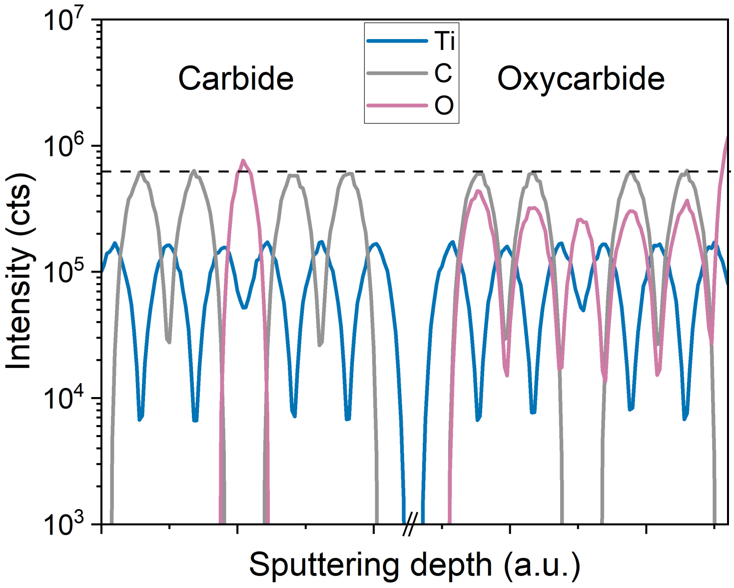

Figure S1: A comparison of depth profiles of pure carbide (left part) and oxycarbide (right part) $Ti_3C_2T_x$ samples obtained with the old procedure in the multiple-signal mode. Despite the detection of a substantial amount of oxygen in the X layers for the oxycarbide sample, the intensity of carbon peaks is similar for both samples which suggest that they have been truncated.

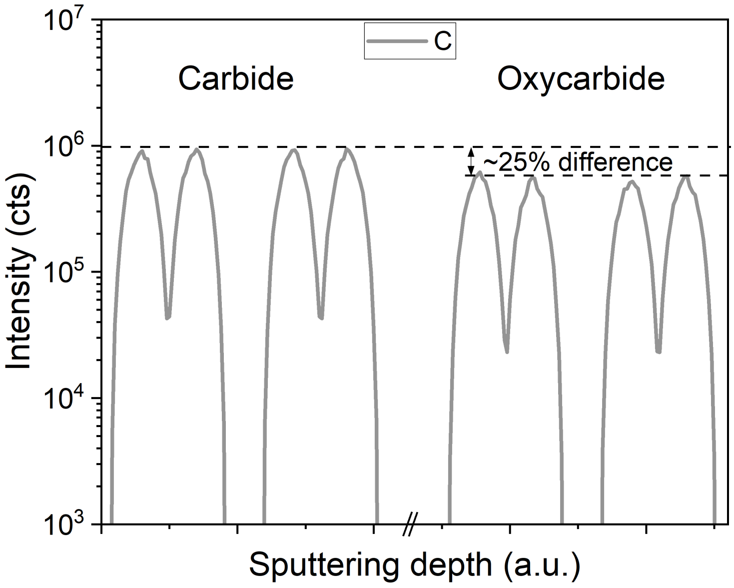

Figure S2: A comparison of depth profiles of a pure carbide (left part) and oxycarbide (right part) $Ti_3C_2T_x$ samples obtained with the old procedure in the single-signal mode. Carbon peaks are about 25-25% more intense for the pure carbide material.

carbide and oxycarbide materials are substantially different and very similar to the situation registered in the single signal mode (cf. Figure S2)

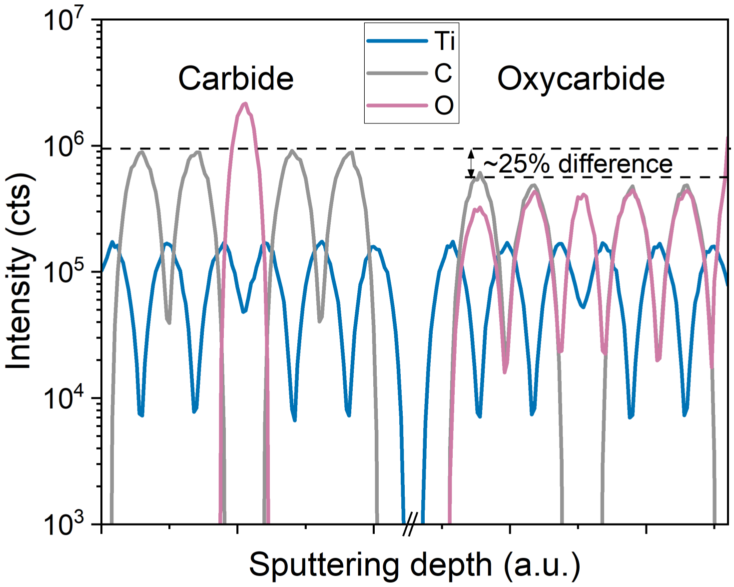

Figure S3: A comparison of depth profiles of a pure carbide (left part) and oxycarbide (right part) $Ti_3C_2T_x$ samples obtained with the new procedure in the multiple-signal mode. Carbon peaks are about 25-25% more intense for the pure carbide material.

3 Deconvolution and calibration procedure

Despite the Gaussian-like shape, it is not possible to model the experimental data with a single function. Figure S4 shows such an attempt for Gaussian and Lorentz functions. Both of them overestimate the signal intensity between peaks, which may result in overestimating the concentration of a particular element.

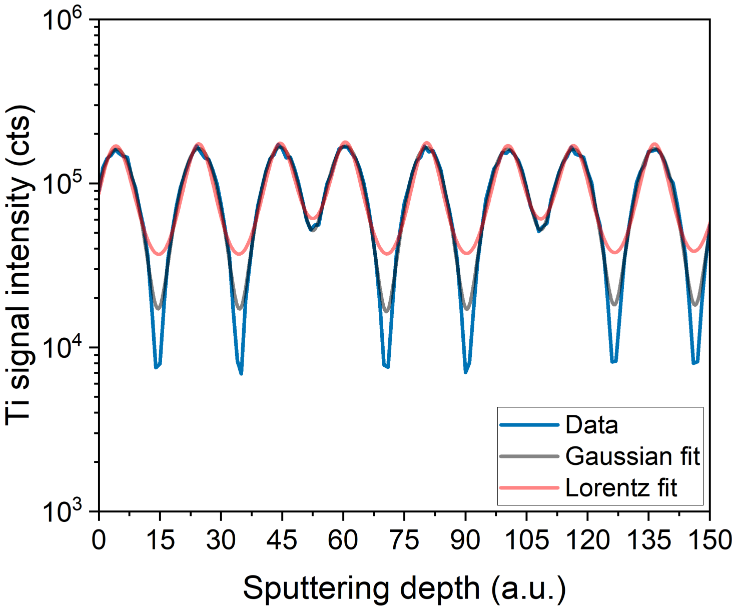

Figure S4: Gaussian and Lorentz functions fitting to the titanium signal. Both functions overestimate the intensity of the signal between the peaks which can result in the overestimation of the concentration of this element.

Data analysis reveals that the span of a layer is 10, 6, 10, and 3 data points for the M, A, X, and T_x layers respectively. Thus each peak can be represented as a set of 10/6/10/3 Gaussian functions. Their parameters are fitted to reproduce the experimental data. Figure S5 shows such a fitting procedure for a single carbon peak registered for a Ti_2CT_x MXene sample.

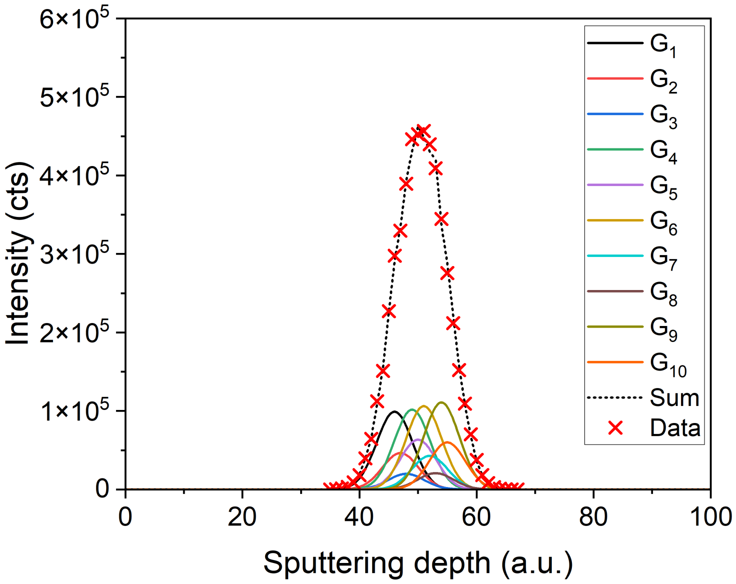

Figure S5: Parameters of ten Gaussian functions (G_1-G_{10}) are fitted so that the sum of these functions (dotted black line) reproduces the experimental data (red symbols).

The width of each Gaussian function for all registered signals, layers, and elements is the same. It is not surprising as the blurring of the signal is directly related to the SIMS mixing effect. Thus, in the idealized case (no mixing effect) no blurring should be observed and thus the width of each Gaussian should equal 0. The plots are transformed into step-functions, as shown in Figure S6.

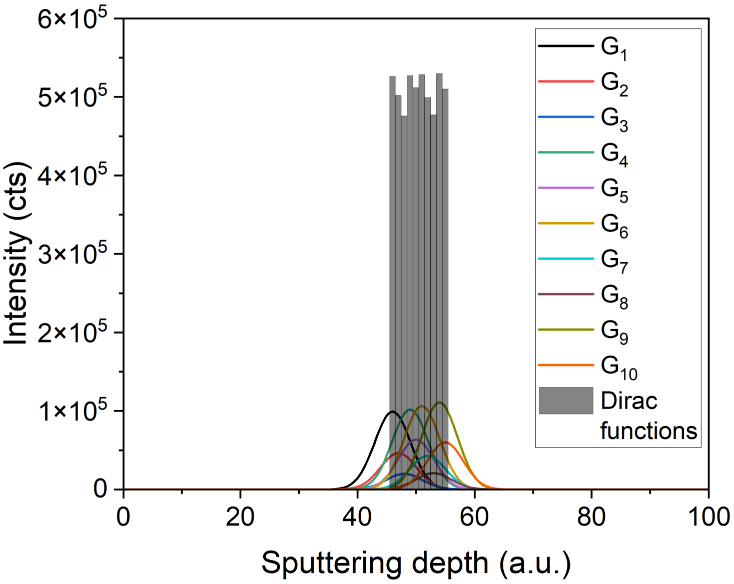

Figure S6: In the idealistic situation (no mixing effect during the SIMS experiment) the width of each Gaussian function equals 0 and thus the functions are transformed into step-functions.

The procedure works for any MAX and MXene samples. It is particularly important for the latter as the two neighboring termination layers seem to be blurred (cf. Figure S7, region around 45-60 data points). In the original procedure[1] termination layers were registered in a completely different mode, i.e. they were measured separately and no information about the composition of M and X layers was obtained.

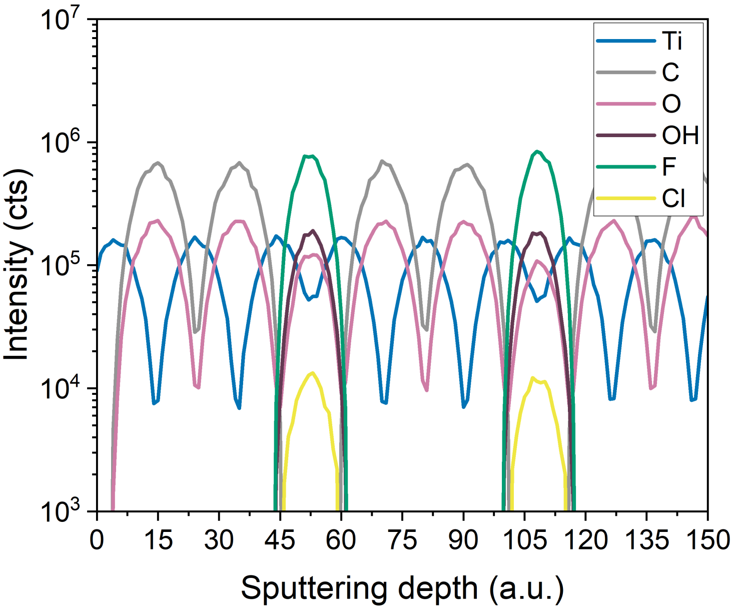

Figure S7: As registered depth profile of a $Ti_3C_2T_x$ MXene sample.

However, the newly proposed deconvolution procedure rectify this problem. As shown in Figure S8 two neighboring termination layers are fully distinguishable (for example F concentration is about 59 and 51% for two neighboring layers as shown in the region around 50-55 data points). It is important to emphasize that with the new procedure the composition of M and X layers can be simultaneously registered.

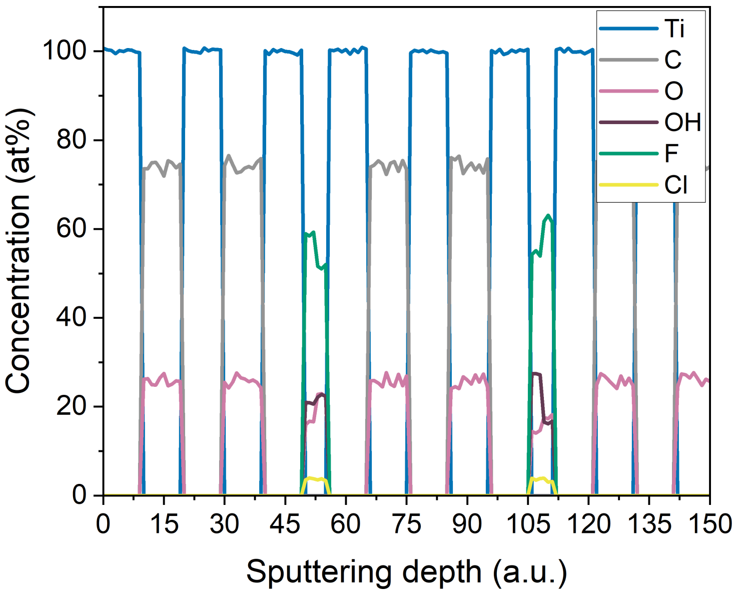

Figure S8: Fully calibrated profile of a $Ti_3C_2T_x$ MXene sample.

It should be, however, noted that clear visualization of such a complicated data set with six different signals is always challenging. Particularly, for the interface between two neighboring termination layers it may seem that the inner point has a different value than both layers. However, this is an imperfection of a line chart with just a few data points. An alternative is to present the data as a stacked column chart (cf. Figure S9). Here, a very distinct difference between two neighboring termination layers can be noted but it is more difficult to exactly determine the absolute value of each signal. Thus it is essential to always consult the numerical data and treat plots for visualization purposes only.

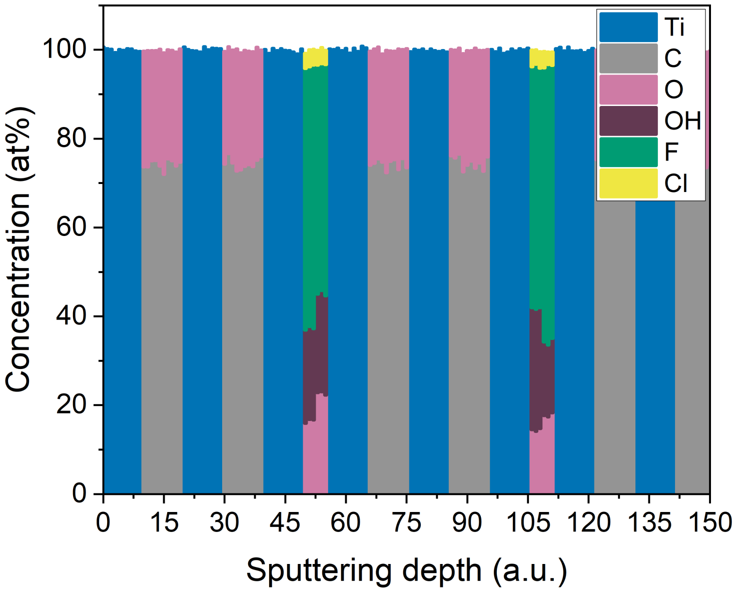

Figure S9: Fully calibrated profile of a $Ti_3C_2T_x$ MXene sample presented as a stacked column chart.

4 Additional measurements

The application of the calibration procedure can also reveal imperfection of the overetched $Ti_3C_2T_x$ MXene sample. As shown in Figure S10 the concentration of Ti in the outer layers is 5-10% lower than for a standard sample. The inner M layer is not affected.

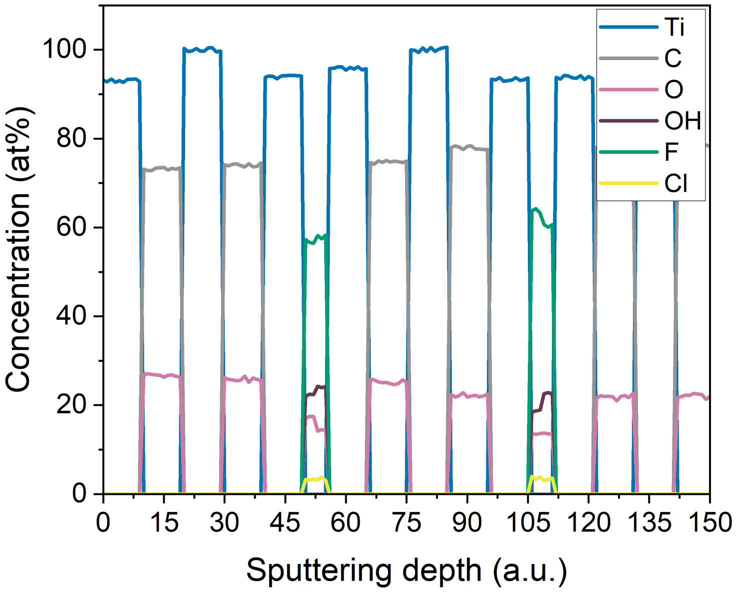

Figure S10: A composition of an overetched $Ti_3C_2T_x$ MXene sample.

Some of the tested MAX phase samples have unusually high oxygen concentration in the A layer, as shown in Figure S11.

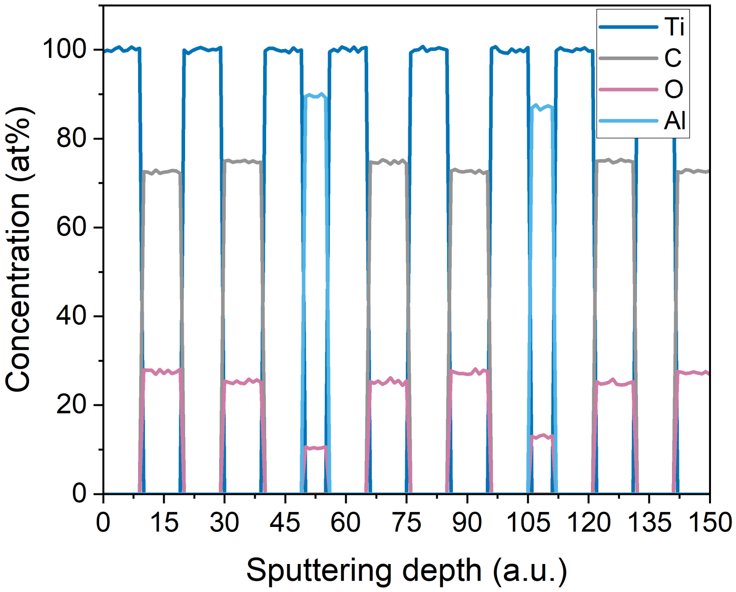

Figure S11: Ti_3AlC_2 MAX phase sample with high oxygen concentration in the A layer.

As shown in Figure S12, for an under-etched Ti_2AlC sample the procedure enables quantification of the termination layers as well as residual aluminum in the A layer (10-15%).

The analysis of Ti_2NT_x and Ti_2CNT_x MXene samples (Figures S13 and S14, respectively) reveals substantial amount of oxygen in the X layers. Thus, these materials are oxynitrides and oxycarbonitrides and not nitrides and carbonitrides as was assumed.

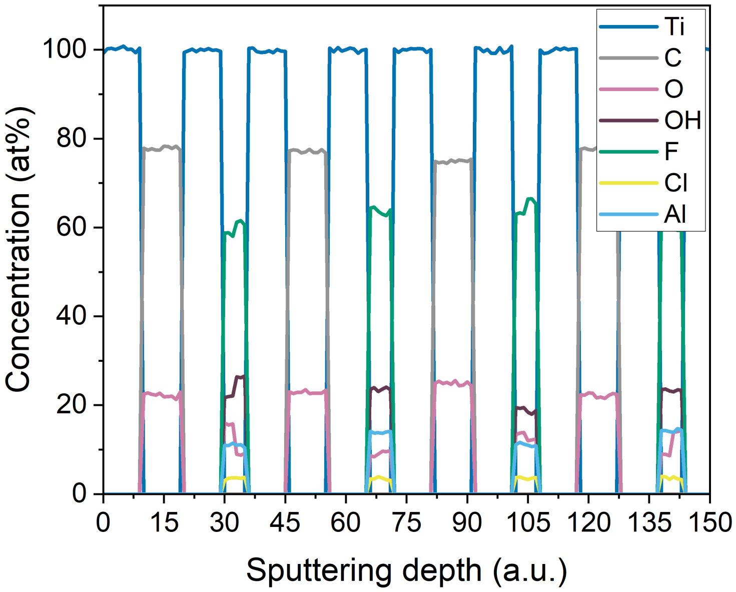

Figure S12: Depth profile of an under-etched Ti_2AlC sample.

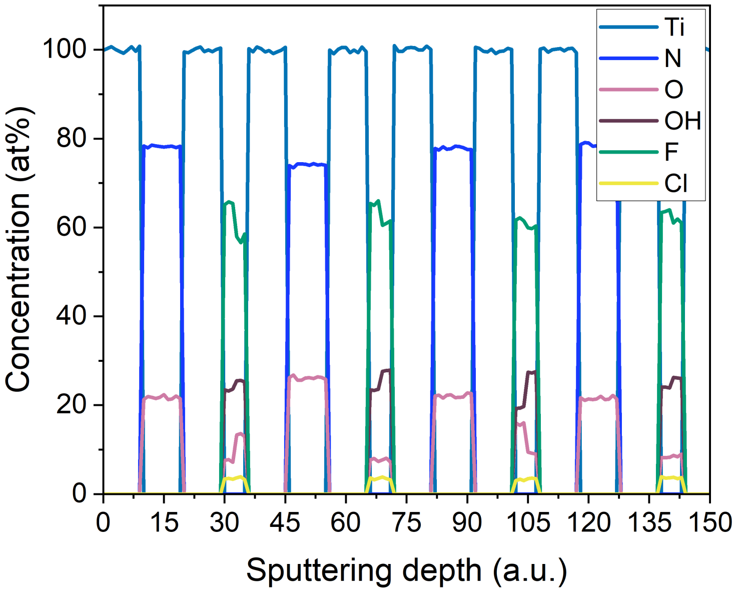

Figure S13: Depth profile of a Ti_2NT_x MXene sample.

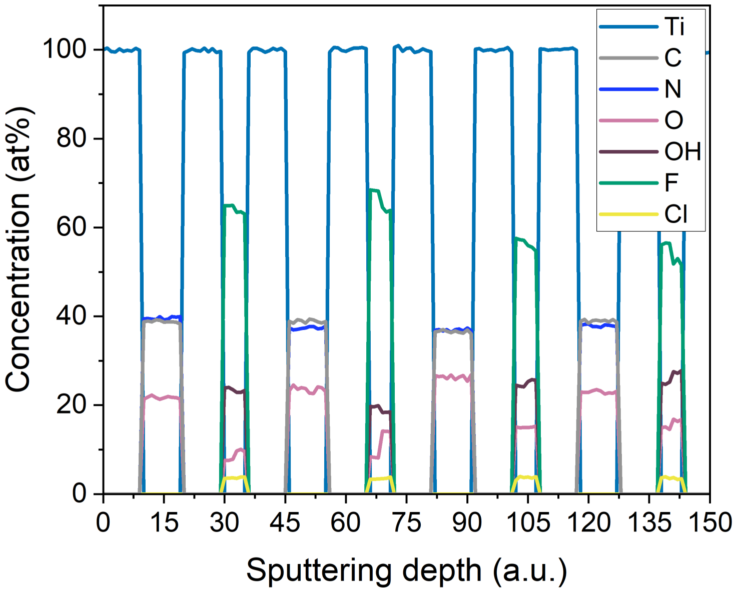

Figure S14: Depth profile of a Ti_2CNT_x MXene sample.

References

[1] Paweł P. Michałowski, Mark Anayee, Tyler S. Mathis, Sylwia Kozdra, Adrianna Wójcik, Kanit Hantanasirisakul, Iwona Jóźwik, Anna Piatkowska, Małgorzata Możdżonek, Agnieszka Malinowska, Ryszard Diduszko, Edyta Wierzbicka, and Yury Gogotsi. Oxycarbide MXenes and MAX phases identification using monoatomic layer-by-layer analysis with ultralow-energy secondary-ion mass spectrometry. *Nature Nanotechnology*, 17(11):1192–1197, 2022.