Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Elementary processes governing V_2AlC chemical etching in HF

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KEYWORDS : MAX phase; MXene; V_2AlC pillars; Hydrofluoric Acid Etching; Single Crystal

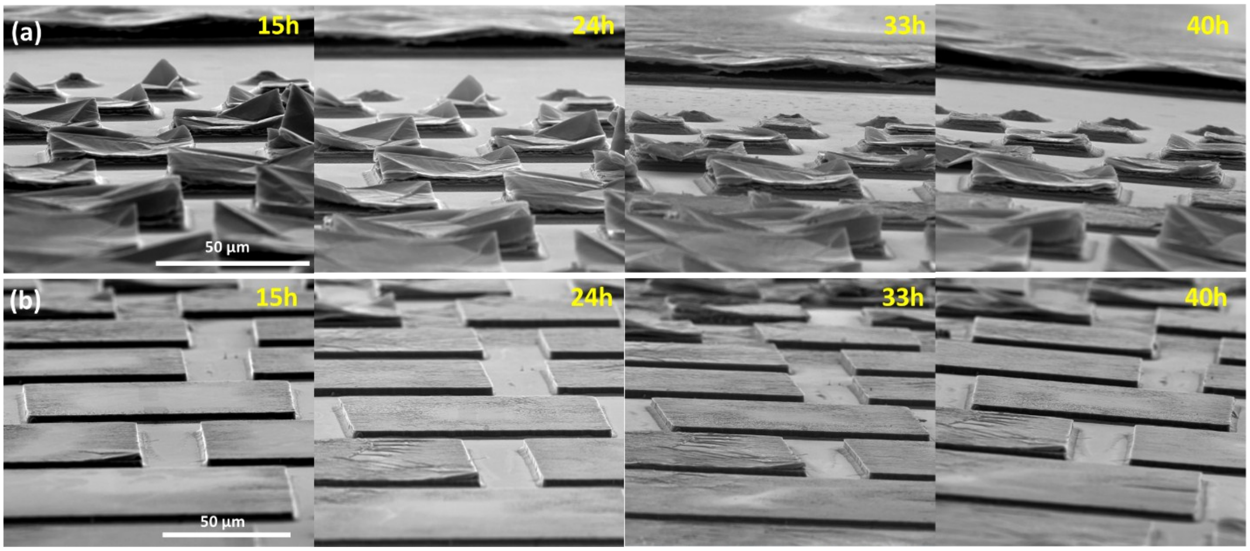

Fig. S1 82° tilted SEM images of (a) stressed and, (b) stress-free pillars as a function of HF etching time.

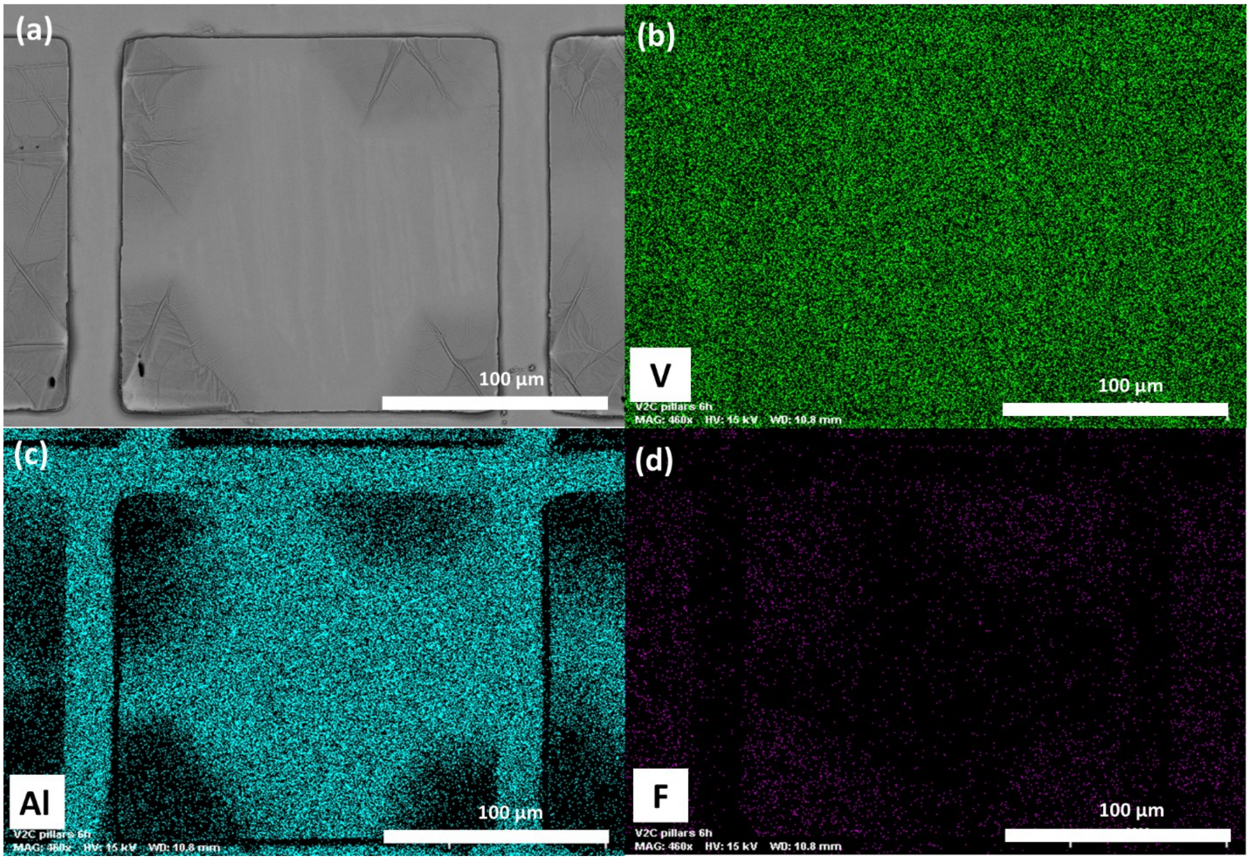

Fig. S2 Micrographs and elemental maps of 160×160 µm^2 pillar after 6 h etching in 49% HF; (a) SEM image, (b) V, (c) Al and (d) F elemental EDS maps.

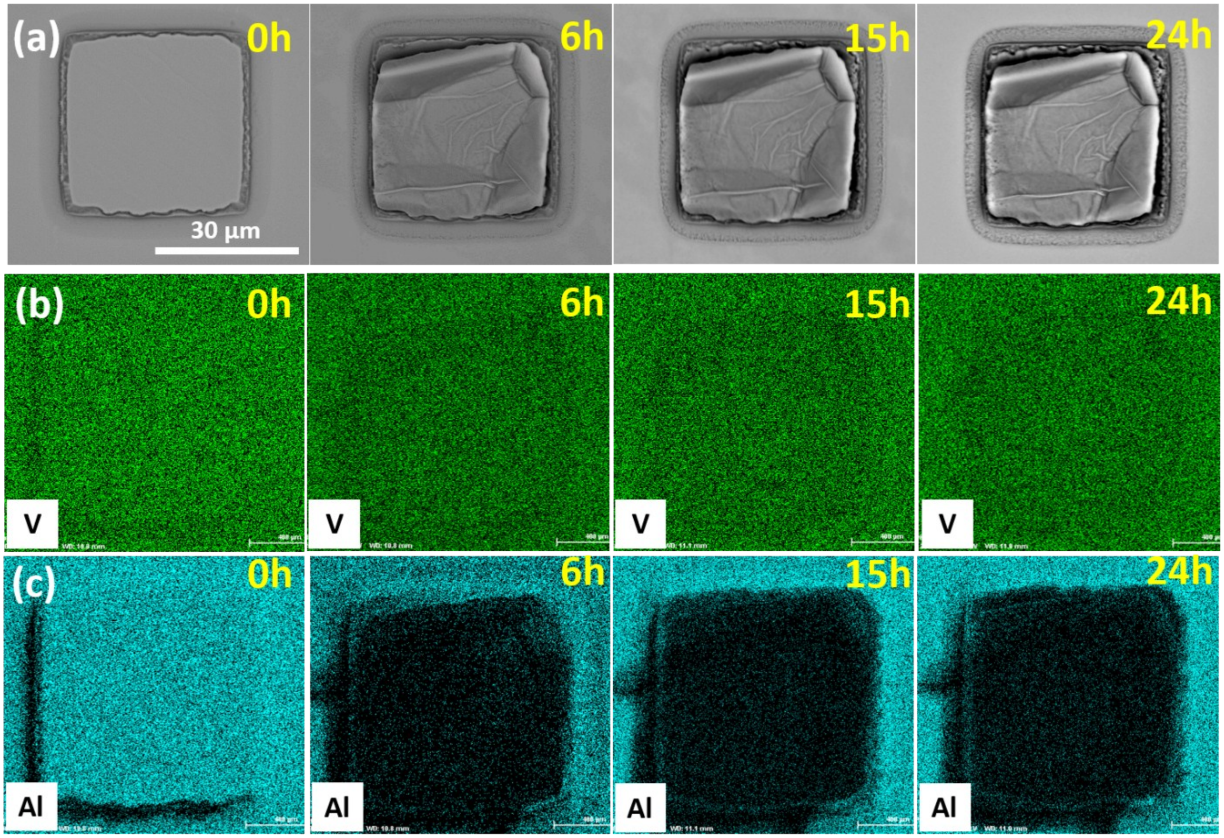

Fig. S3 Micrographs and elemental maps of 40×40 μm^2 pillars as a function of etching time in 49% HF. (a) SEM images, (b) V, and (c) Al elemental EDS maps.

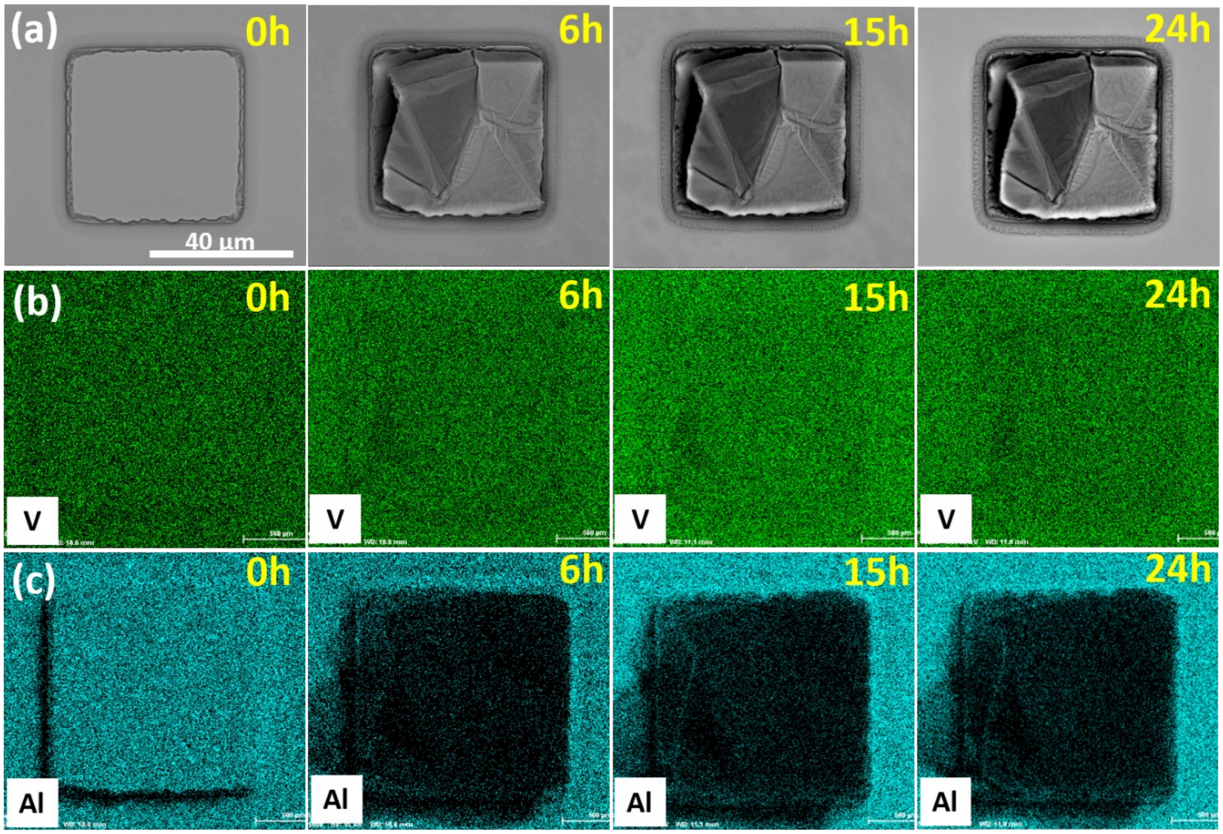

Fig. S4 Micrographs and elemental maps of 50×50 µm^2 pillars as a function of etching time in 49% HF. (a) SEM images, (b) V, and (c) Al elemental EDS maps.

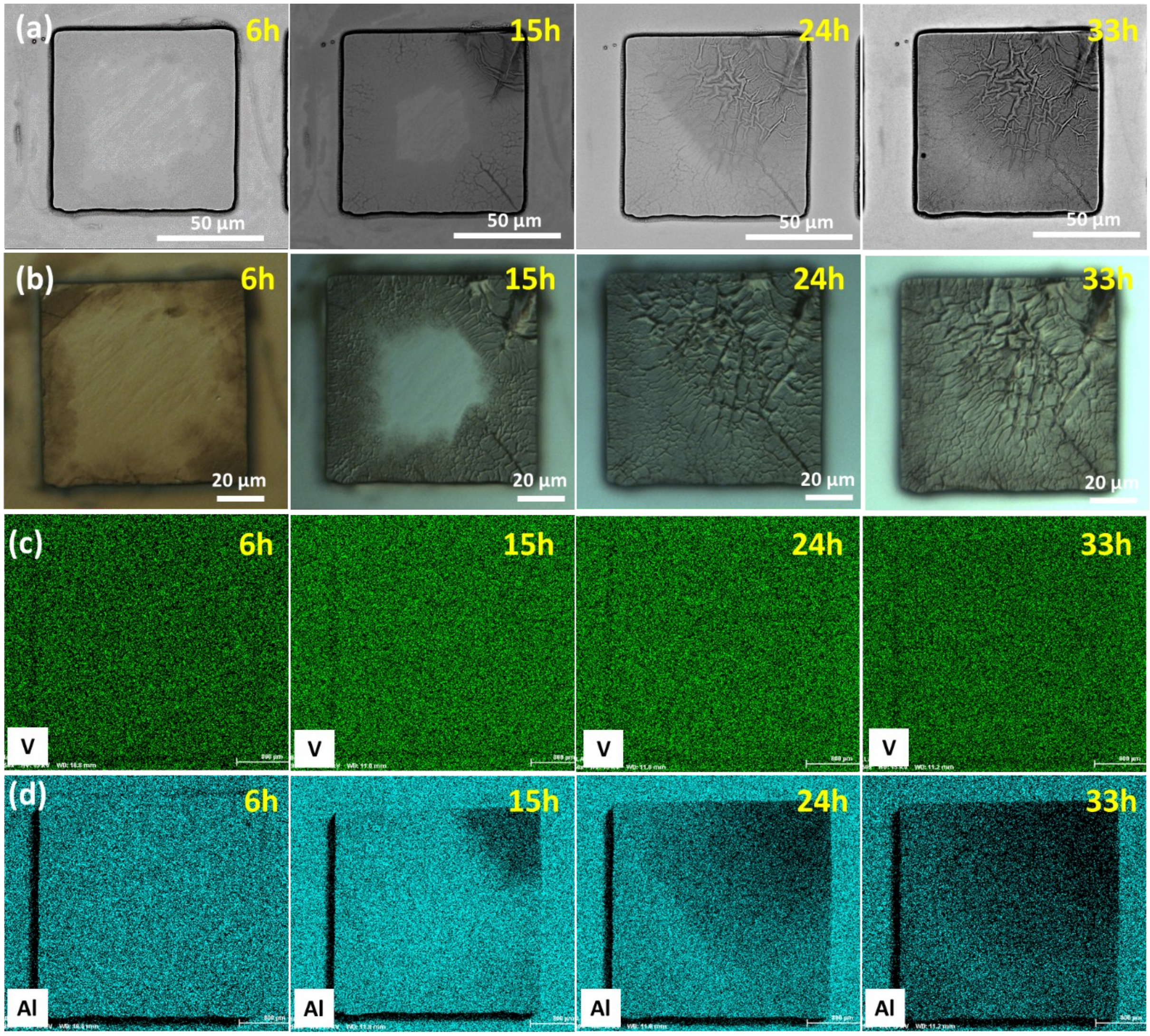

Fig. S5 Micrographs and elemental maps of 90×90 µm^2 pillars as a function of etching time in 49% HF. (a) SEM images, (b) OM images (c) V, and (d) Al elemental EDS maps.

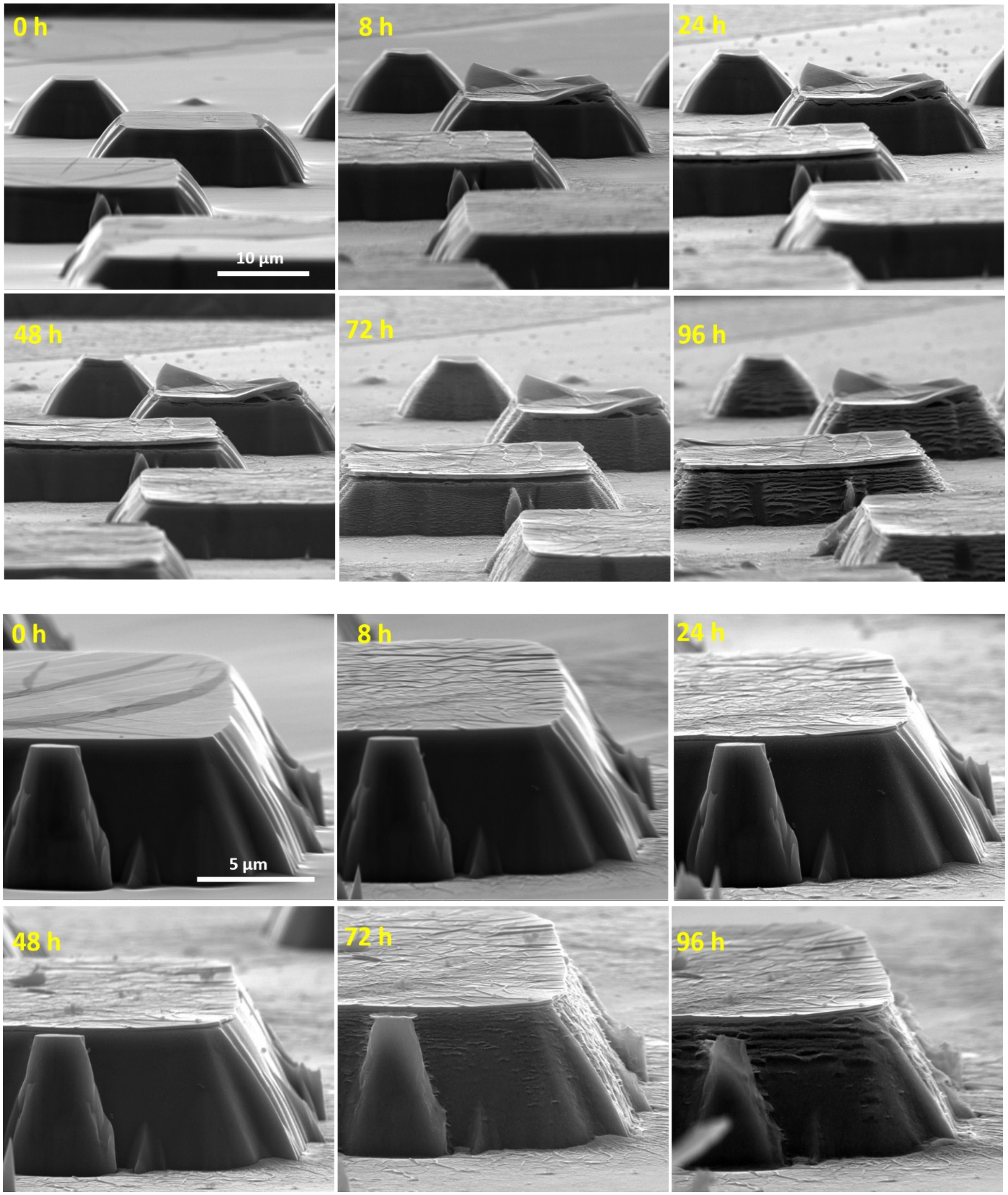

Fig. S6 82° tilted SEM images of un-stressed V_2AlC pillars as a function of HF etching time.

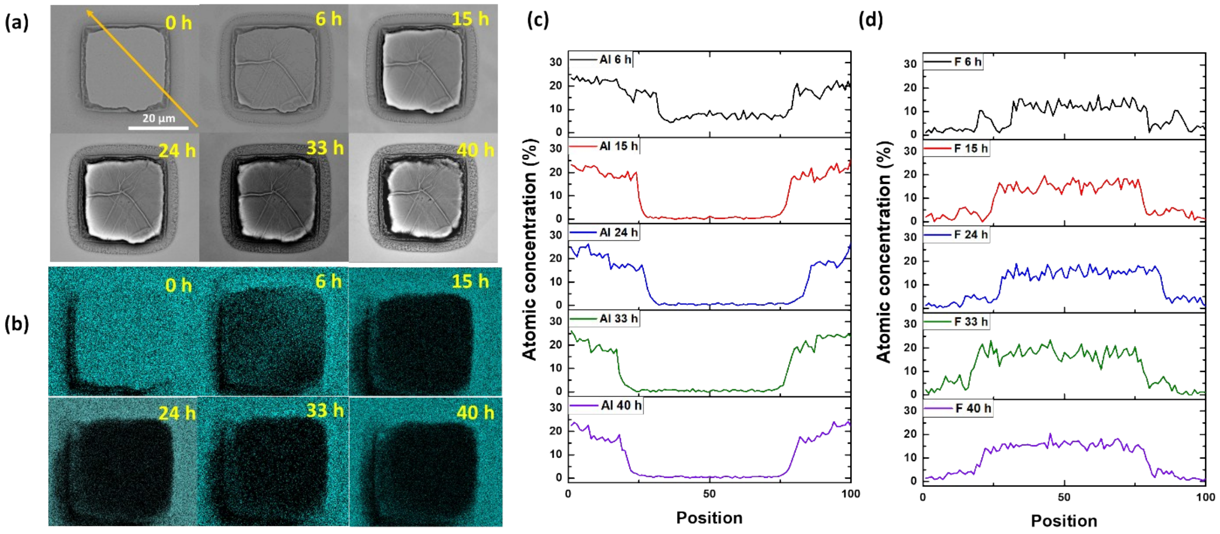

Fig. S7 (a) SEM images of 30×30 μm^2 size defect-free V_2AlC pillar depending on HF etching time. (b) Al and (c) F concentrations measured with EDS line profiles as a function of etching time (arrow in (a) indicate line profile sweeping direction).

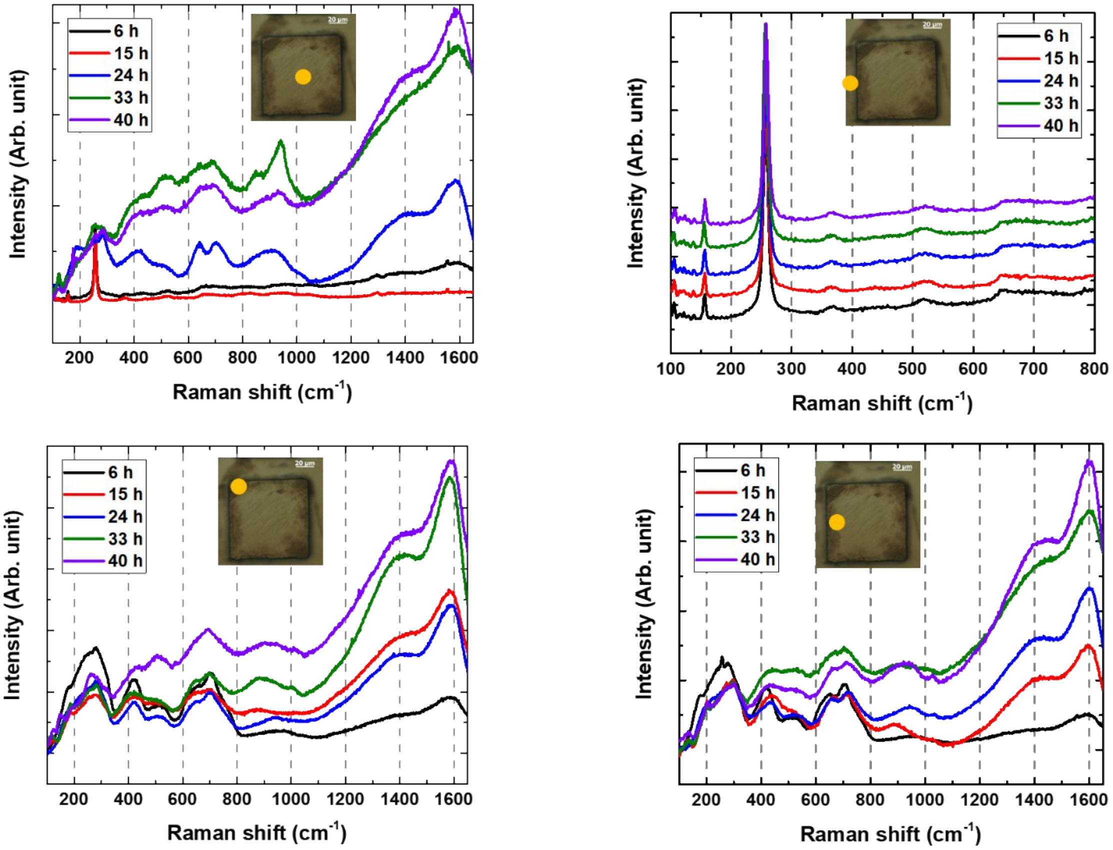

Fig. S8 Effect of etching time on Raman spectra of a 90 µm size V_2AlC pillar at various positions on pillar top surface (yellow dot corresponds to measured positions).

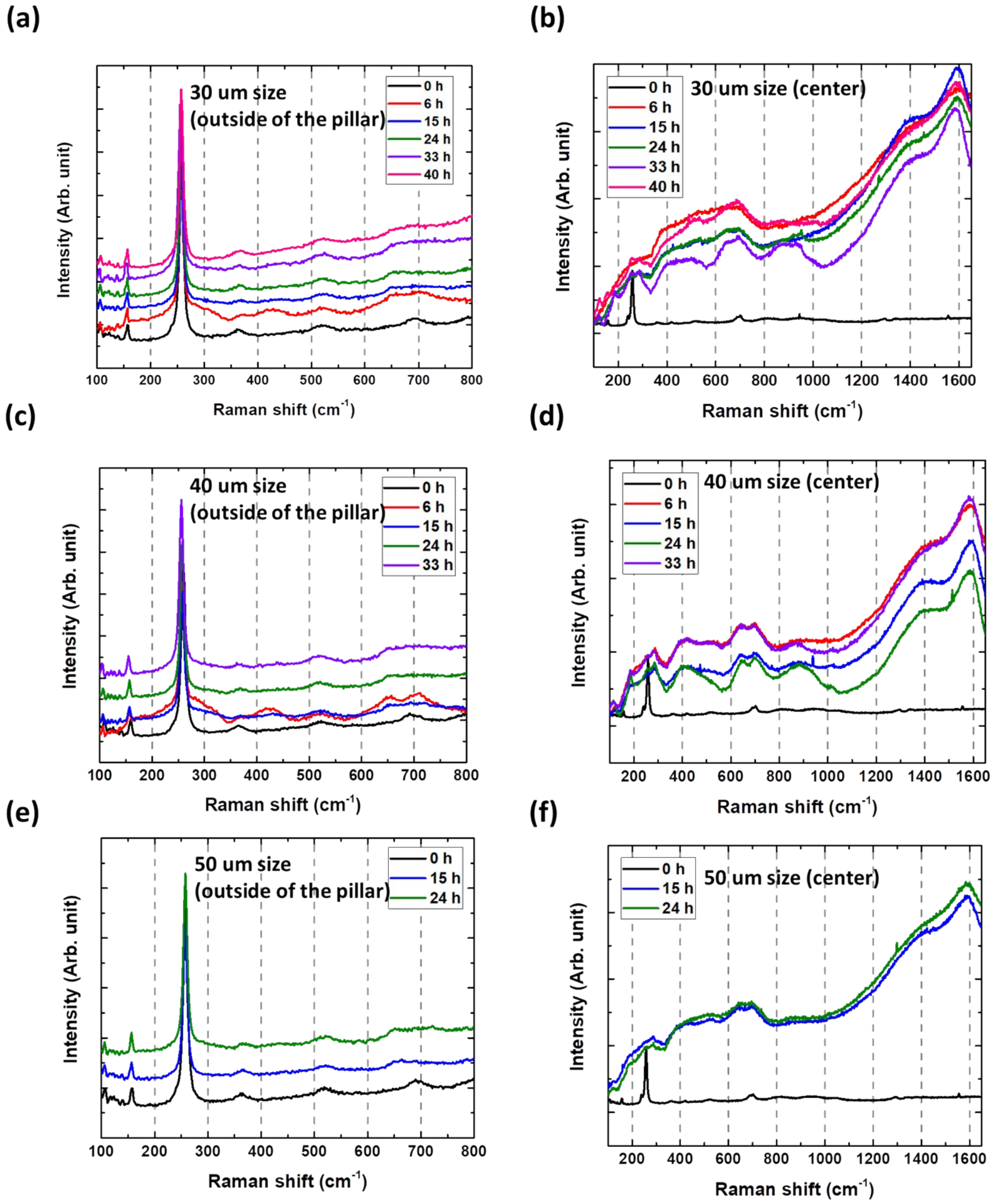

Fig. S9 Effect of HF etching time on Raman spectra measured at out of the pillar (a, c, e) and the center of the pillar surface (b, d, f) for V_2AlC pillars of 30 µm size (a, b) 40 µm size (c, d) and 50 µm size (e, f). The same pillars are measured with SEM and EDS which are shown in Fig S3, S4 and S7 respectively, and are therefore defective ones. Partial delamination of those pillars during the etching may thus induce erratic fluctuations in the Raman spectrum intensity.

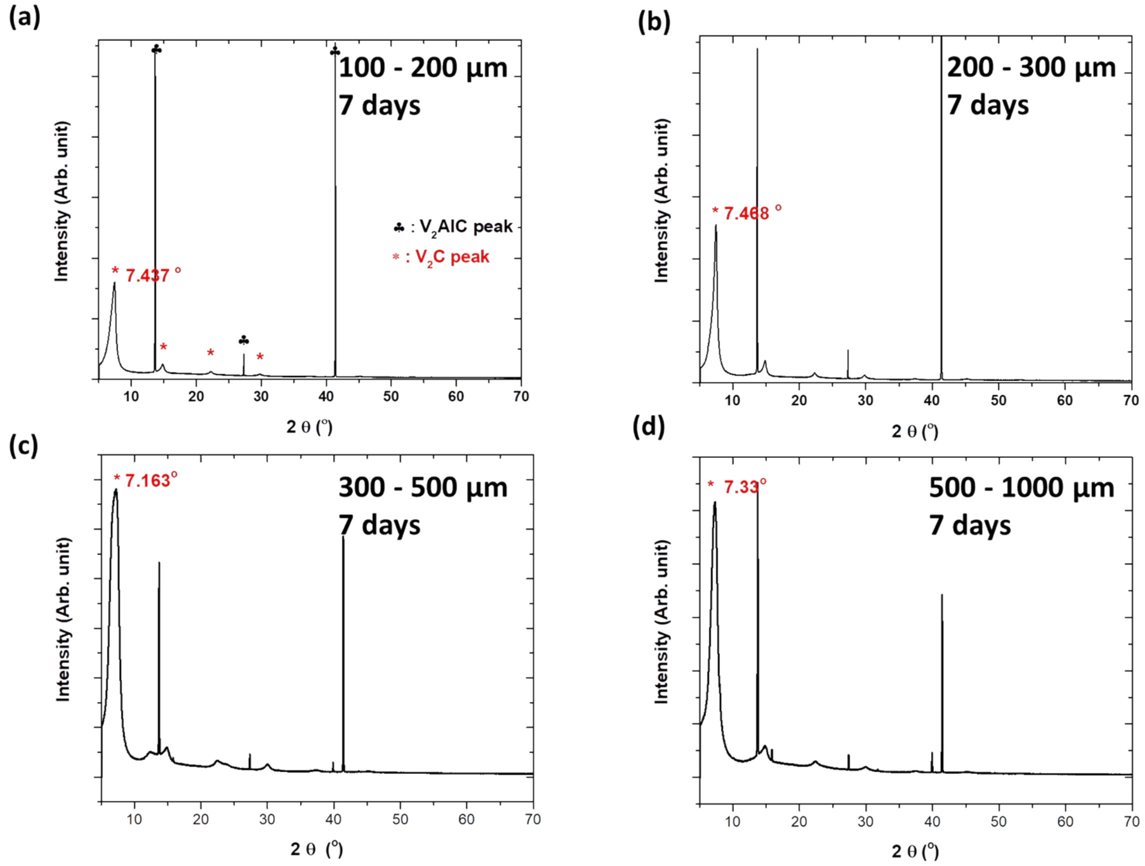

Fig. S10 XRD patterns of single crystalline V_2AlC powders after etching in 49% HF at room temperature for 7 days, sieved with a) 100 µm, b) 200 µm, c) 300 µm and d) 500 µm size meshes.

A number of points should be considered for interpreting the XRD data:

1/ A sieve with a 100µm grid selects crystal sizes from 100 to 200µm if the sieve above is the one with a 200µm grid, etc.

2/ In crystals selected by sieve shaking, a lateral crystal size is very frequently smaller than another, and if the larger dimension prohibits the crystals to fall through the sieve, its smaller dimension makes crystal conversion easier (in other words, a narrow and long crystal is etched as easily as a much smaller crystal with all dimensions like the width of the former, bigger crystal).

3/ A large part of the fully converted MXenes is lost during the successive centrifugation steps, and the trend is to keep the non-converted crystals with a larger mass, at the bottom of the container. This obviously modifies the statistics (it tends to increase the amount of non-fully converted samples).

4/ At the end of the process, the liquid is filtered and the segregated part is mostly eliminated. This obviously modify the statistics and eliminates the bigger crystals, assumed to be possibly not fully converted.

5/ The selected samples are dried and tend to self-organize, putting more weight on some XRD peaks than others. The way they are oriented has no reason to be exactly the same for non-converted crystals and MXenes; this also modifies the statistics.

Points 2-5 modify the statistics of the finally measured MXenes, and as shown by the XRD results, all spectra are not much different, even if they show a gross agreement with the results obtained from non-defective pillars: there is some kind of saturation in the conversion process with typical sizes around 100µm. Points 2-5 could very well contribute to select just a partial crystal distribution (the one which survives and stays colloidal after all centrifugation steps). This may well eliminate the bigger crystals, but also the smaller, fully converted ones, and thus tends to make the results of the different sizes more homogeneous, as long as the average sizes stay reasonably close to one another.