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Sub-resolution Nanostructuring of 2D Materials by Anisotropic Etching

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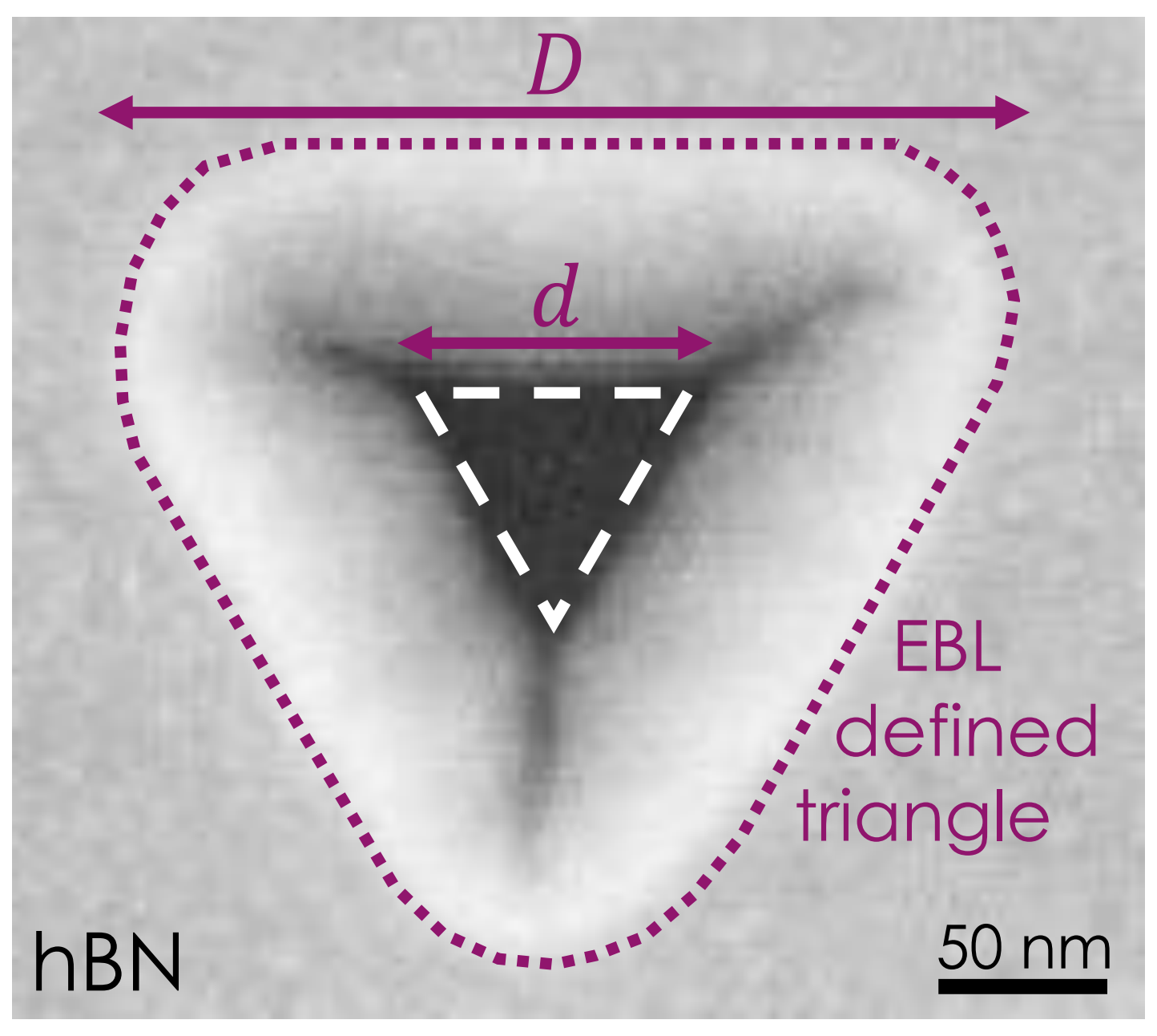
Introduction

Nanostructuring of two-dimensional (2D) materials is challenging due to the demand for low edge disorder and low contamination. We explore new routes towards extreme nanostructuring by employing anisotropic etch mechanisms in different 2D materials [1].

1 Downsizing and Sharpening of Structures

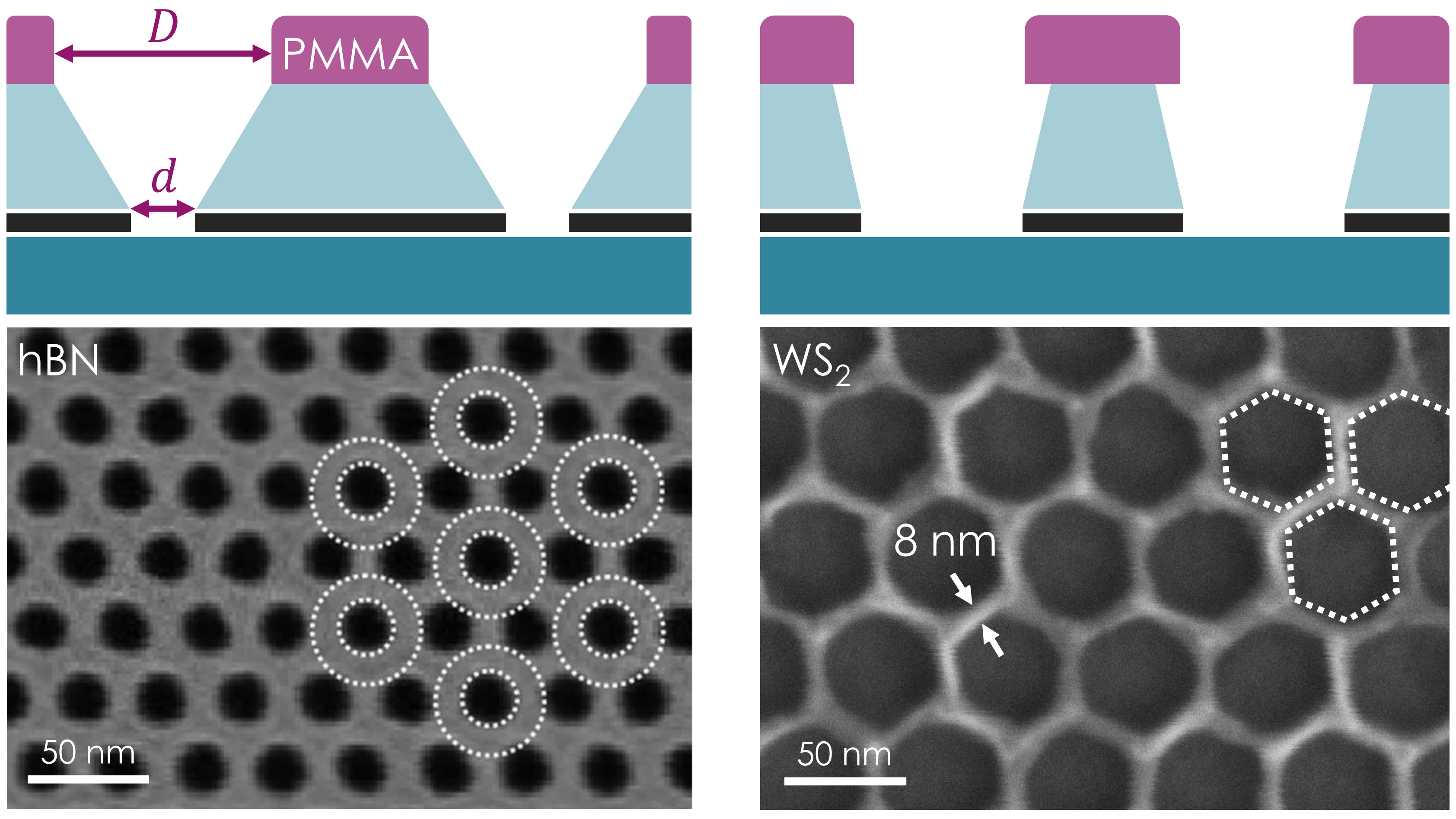


Fluorine-based reactive ion etching (RIE) of hBN tends to show robust etching angles (45°-70°) across a variety of chemistries (CF_3, CHF_4, SF_6) and conditions. This helps to create 1D edge contacts to encapsulated 2D materials, but can also be utilized for downsizing of features below the resolution of electron beam lithography (EBL) systems. Initially, an EBL-defined triangle on top of an hBN flake will have rounded corners. Upon etching, this evolves into an ultra-sharp triangle at the bottom of the flake due to the perfect in-plane isotropy and uniform etch angle for pure SF_6 etch in hBN [1,2].

3 Dense nanostructures

The finite etch angle in **hBN** complicates the fabrication of high-density nanopatterns, which requires very thin hBN top-layers to be used, as we showed in Ref [2].

In contrast to hBN, **TMDs** tend to exhibit in-plane anisotropy, and more vertical etch angles. This allows exceptionally small structures to be defined, which can be used as etch masks for the underlying, active layer.



Dense nanostructures in hBN lead to arrays of circular holes, whereas dense arrays in WS_2 result in arrays of hexagons, which in turn define (down to) 8 nm wide nanoribbons or triangles, depending on how we design the initial EBL patterns and align it with the crystal.

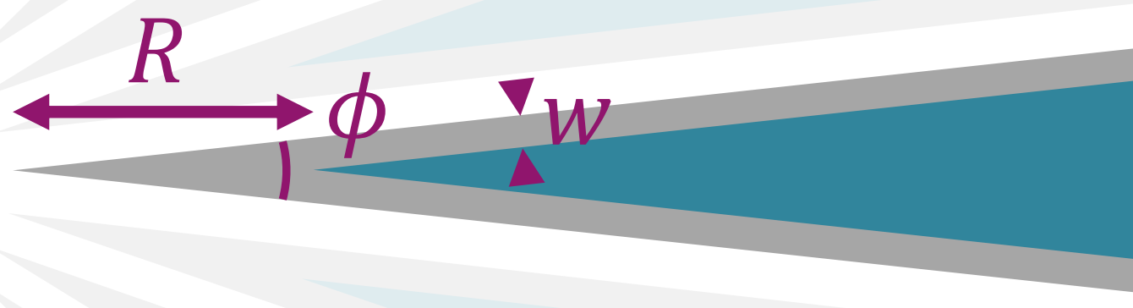
Process Parameters

EBL is performed with a 100 keV JEOL JBX-9500 and 2200k PMMA from MicroChem resist. Etching is performed in a SPTS Pro ICP system, typically with: SF_6 gas flow of 40 sccm, pressure of 10 mTorr, forward power of 30 W at 13.56 MHz, and an etch time of 30 s.

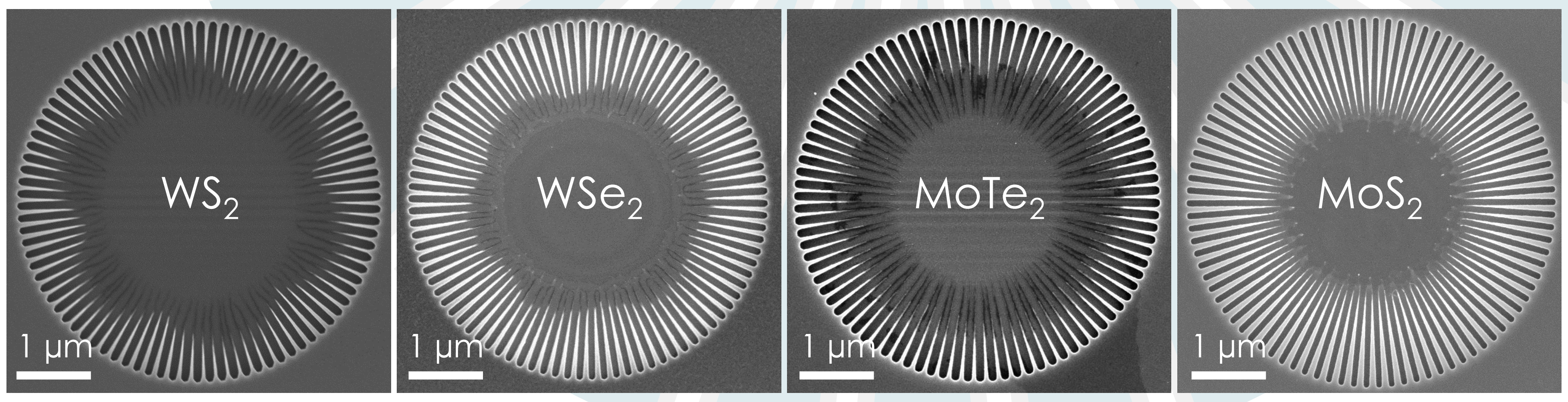
2 Anisotropic Etch Rates

The crystallographic, angular-dependent etch rate, $r(\theta)$, is visualised and measured from the "wagon wheel" structures (below) using:

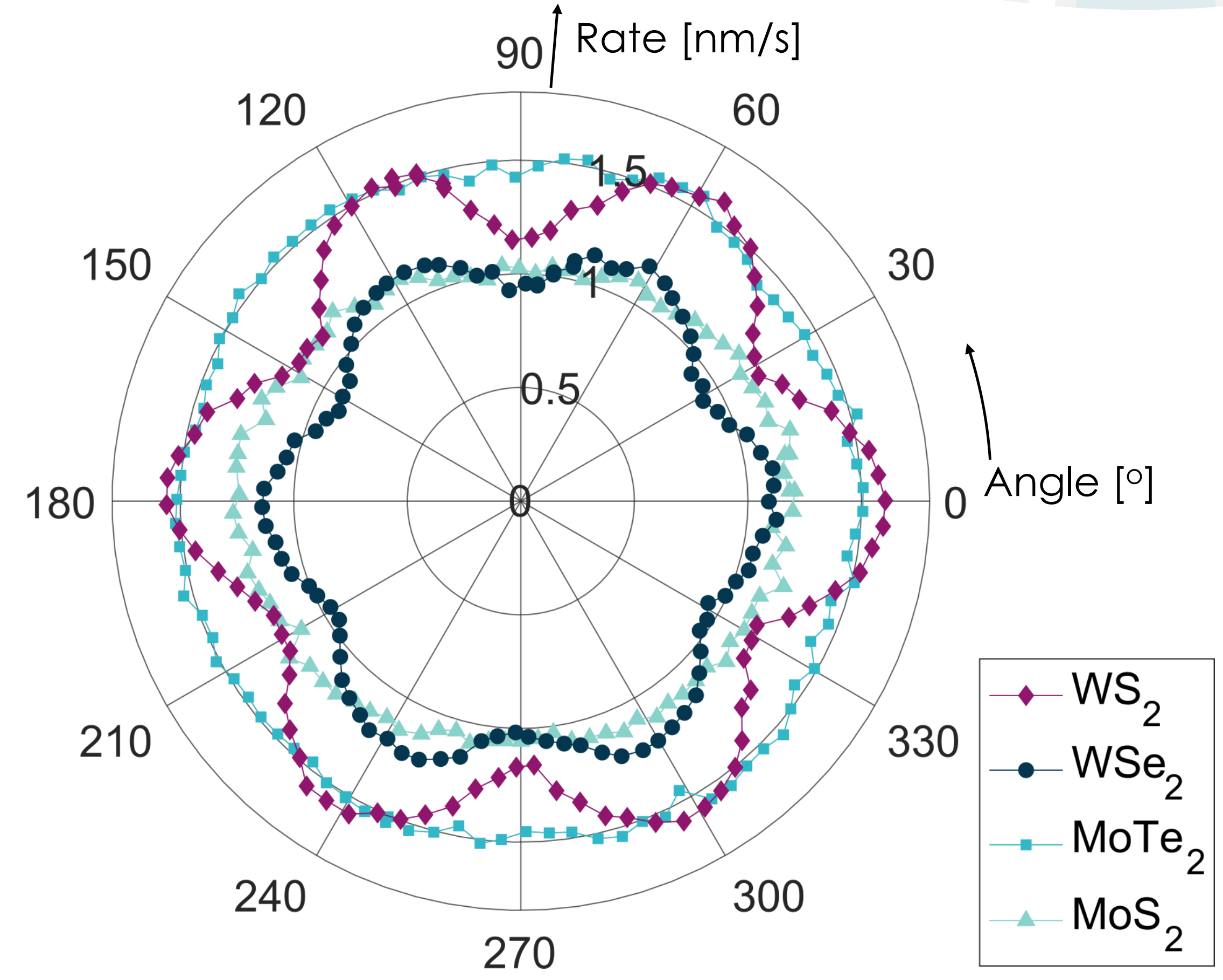
$$r(\theta - 90^o) = \frac{w(\theta - 90^o)}{\Delta t} = \frac{R(\theta)\sin(\phi/2)}{\Delta t}$$



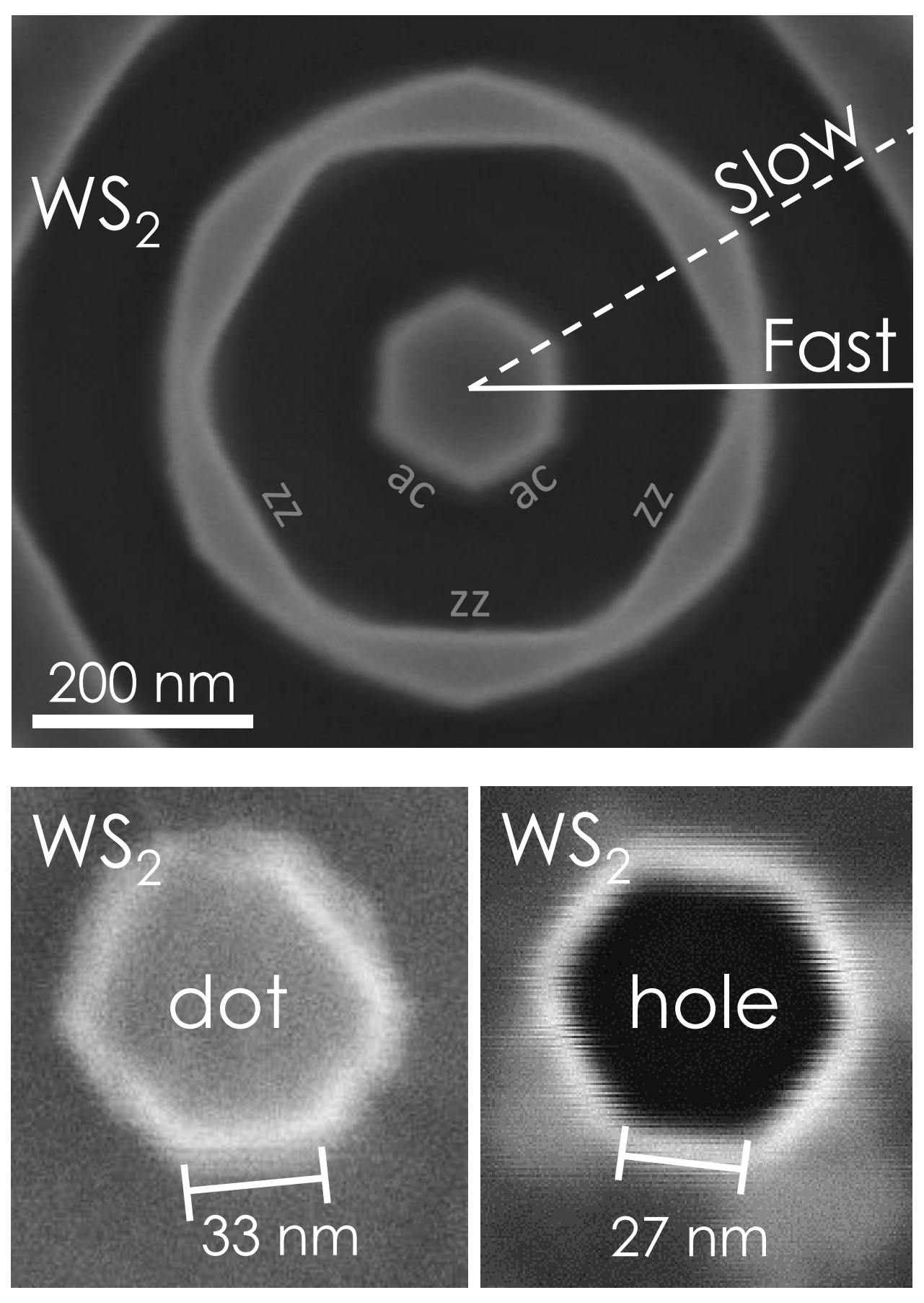
where Δt is the etch time, ϕ is the angle of the tip of the wedge, R and w are the length and width reduction of the wedge, respectively, and θ is the angle of the wedge in the wagon wheel, with respect to horizontal.



In-plane etch rate as a function of angle

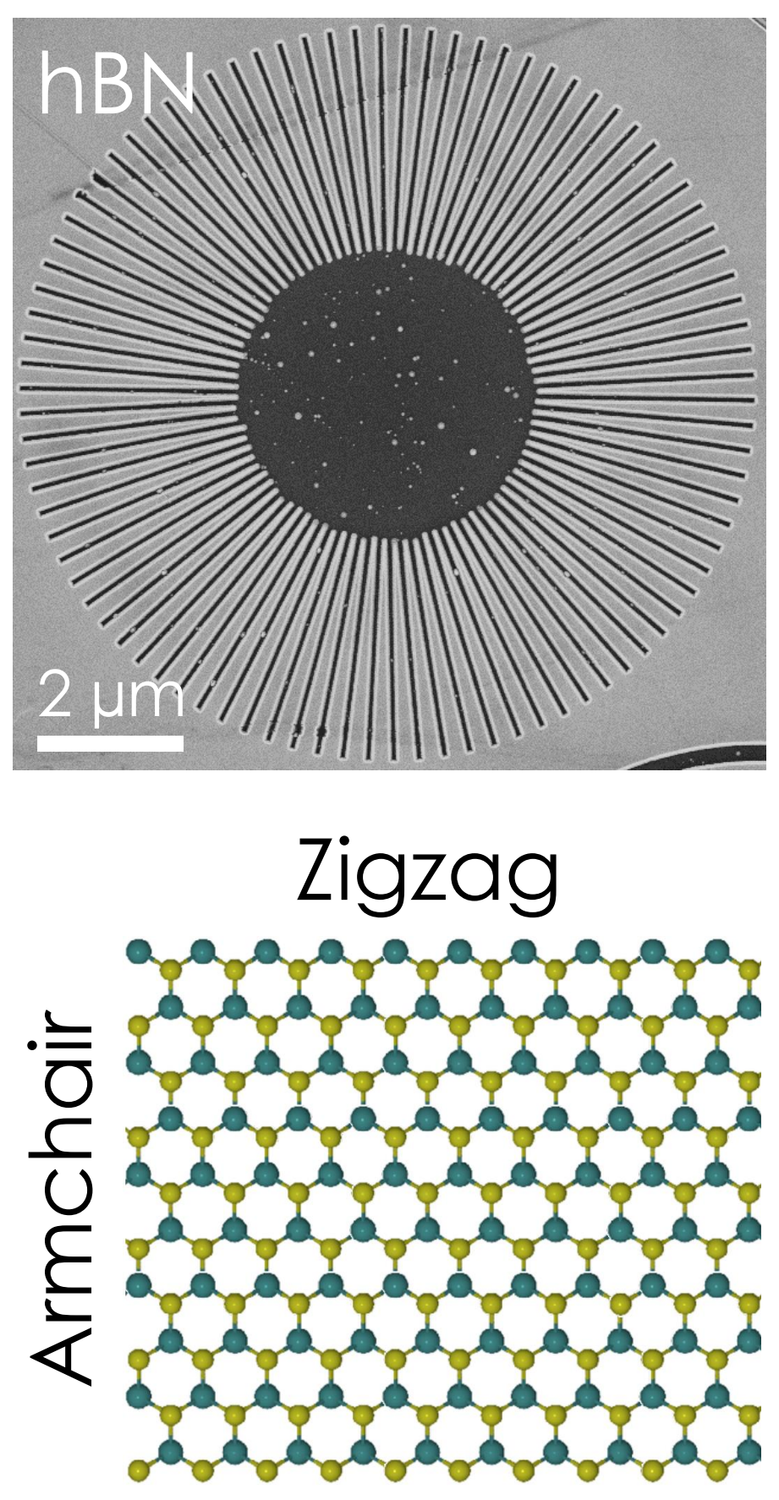


"Bull's eye" structure



Material	WS_2	WSe_2	MoS_2	$MoTe_2$	hBN	Gr	PMMA
Etch rate [nm/min]	230	250	230	170	570	0	80

4 Crystallographic shaping



The fluorine-based dry-etch leads to strong in-plane anisotropic etching for some TMDs, in particular WS_2 and WSe_2. In contrast, the etch angle and in-plane rate of hBN do not show strong dependence on the crystallographic orientation [2]. The TMD-specific etch anisotropy transforms nanoscale holes into hexagons, presumably with zigzag etches [3], and conversely hexagonal islands with armchair edges. Zigzag edges are more stable and etch slower than armchair edges [4,5]: In the bull's eye structure above, the protruding ring has a six-fold symmetry of thick and thin regions corresponding to slow and fast etching directions.

Outlook

In this pilot study, we show that well-controlled downsizing and nanoshaping of structures in 2D materials below the lithographic limit of EBL, can be achieved by exploiting the intricate interplay between material-specific crystallographic etch rates, vertical etch angles and pattern layout. The nanostructured material can be used as active layer or etch mask subsequent pattern transfer, with exceptional possibilities for sophisticated architectures when applied to vdW heterostructures.

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