

## Electronic Supplementary Information

# **Formation of GaP Nanocones and Micro-mesas by Metal-assisted Chemical Etching**

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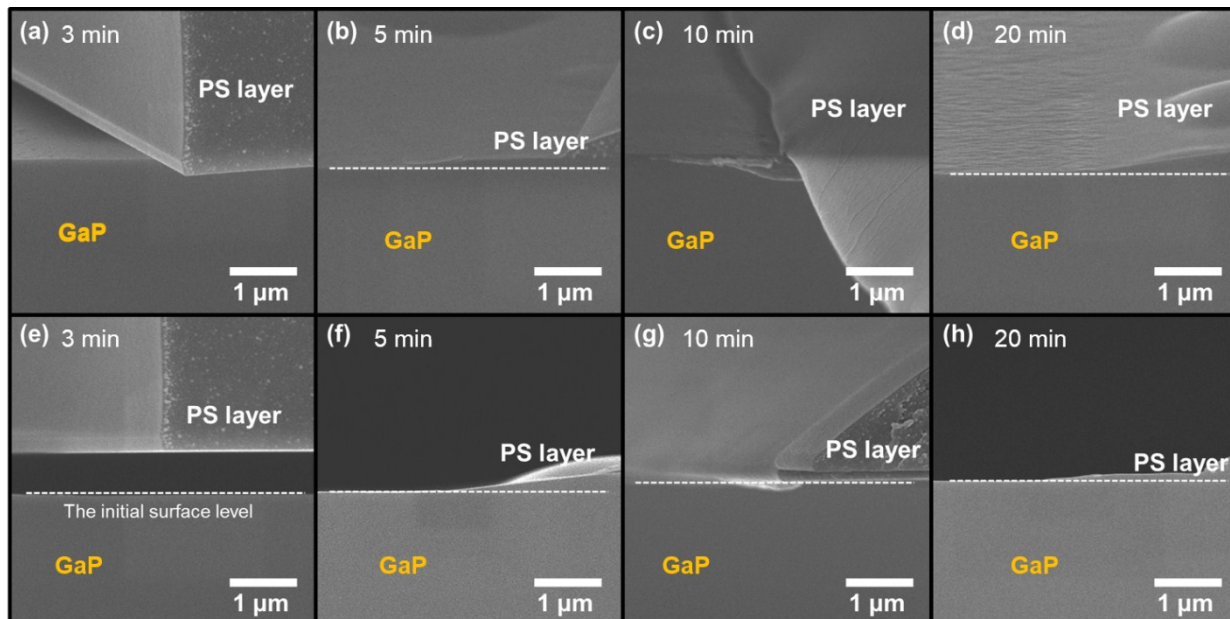
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## S1. Experimental methods

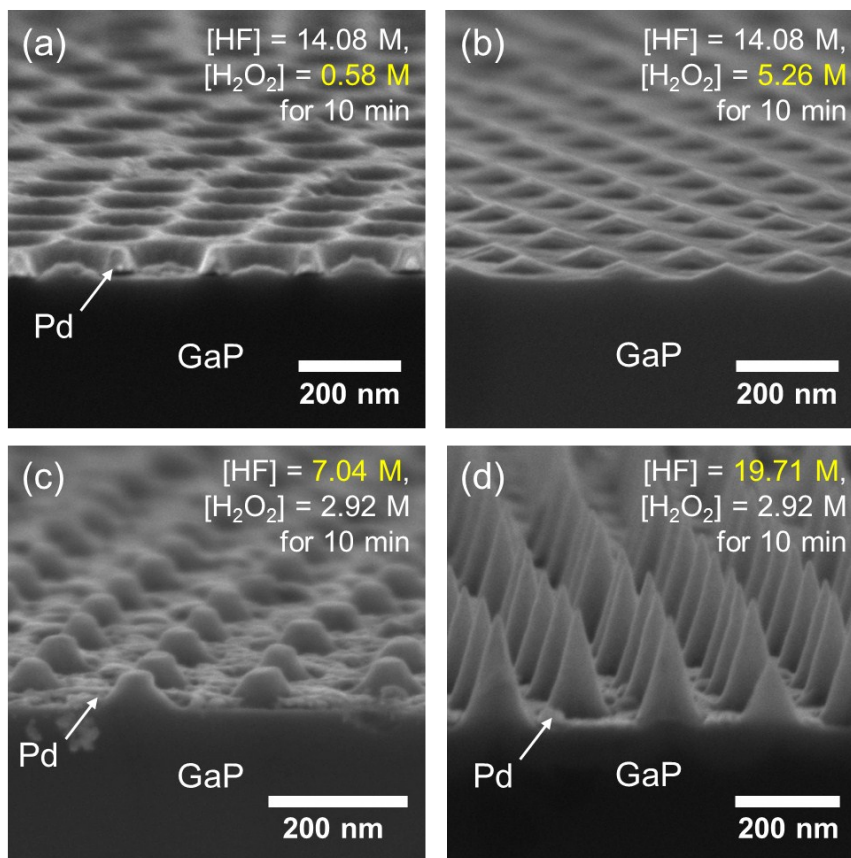
N-type (100) Gallium Phosphide (GaP) wafers (sulfur-doped, doping concentration of  $2 - 8 \times 10^{17} \text{ cm}^{-3}$ ) were used in this work. GaP wafers were cut into pieces of  $\sim 1.0 \text{ cm} \times 1.0 \text{ cm}$  and were dipped into dilute HCl (HCl : H<sub>2</sub>O = 5 : 1 volume ratio) for 15 seconds to remove a native oxide layer, followed by deionized (DI) water rinse.<sup>1</sup> In order to fabricate the ordered GaP nanocones arrays, nanosphere lithography (NSL) was used to form a patterned metal catalyst for MaCE. Polystyrene (PS) colloidal nanoparticles (ca. 200 nm diameter particles suspended in water as a 10% w/w, Thermo Scientific) were used for NSL. The NSL process is described elsewhere.<sup>2</sup> After formation of a hexagonally close-packed PS monolayer on a GaP substrate, the diameter of the PS particles was reduced to about 140 nm using oxygen plasma treatment. Then, 30 nm-thick Pd nanomeshes were formed by sputtering and a lift-off process using toluene for 5 minutes in sonication bath. Finally, GaP substrates with Pd nanomeshes were immersed in a solution of 14.08 M of HF (48.0-51.0 wt%, ACS reagent, J.T. Baker) and 2.92 M of H<sub>2</sub>O<sub>2</sub> (35 wt%, extra pure (EP) grade, Junsei) at room temperature.

For the fabrication of GaP micro-mesa arrays, n-type GaP substrates with Pd micro-patches patterned by conventional photolithography and lift-off process were used. A 45 nm-thick Pd metal layer was used in this case. To fabricate GaP micro-mesas MaCE was conducted with the same etching conditions as described above.

Characterization of GaP nanocones and micro-mesa structures was carried out using a field emission scanning electron microscopy (FE-SEM, Nova 230 and Magellan400, FEI Co.) and Double Cs corrected transmission electron microscopy (TEM, Titan cubed G2 60-300, FEI Co.). In addition, we used UV-Vis spectroscopy (Cary 300, Agilent Tech.) with an integrated sphere to measure the optical reflectance of the etched GaP nanocones and planar GaP in the range of visible wavelength, respectively.



**Fig. S1** 15°-tilted (a-d) and cross-sectional (e-h) scanning electron microscope (SEM) images of n-type (100) GaP without Pd catalyst, etched in a HF:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O (2:1:1 volume ratio) solution at room temperature for various etching times. Chemical dissolution of GaP is negligible even after etching for 20 minutes in the solution when Pd catalyst is absent. The half-covered polystyrene (PS) layer is used to indicate chemical dissolution.

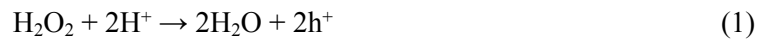


**Fig. S2** 8-tilted SEM images of GaP nanostructure arrays etched for 10 minutes in the different mixed solutions with (a) low and (b) high H<sub>2</sub>O<sub>2</sub> concentrations at a fixed HF concentration, and (c) low and (d) high HF concentrations at a fixed H<sub>2</sub>O<sub>2</sub> concentration at room temperature. Note that the exact concentrations are marked on the each figure.

## S2. Possible galvanic reactions for dissolution and re-deposition of Pd during MaCE

In our experiments, as etching time increased, it is clearly observed that Pd nanomesh thickness is gradually thinned and the aspect ratio of GaP nanocones gets lower. Based on this observation, we believe that Pd could be dissolved and re-deposited on the exposed surface of the etched GaP by the galvanic replacement reaction. Such a re-deposited Pd on GaP substrate can induce additional lateral etching, leading to shortened pyramid-shaped nanostructures with decreased aspect ratios. The possible dissolution and re-deposition of Pd reactions, in terms of cathodic and anodic reactions as following:

Cathodic reactions 1 (at the surface of metal as well as bare GaP):



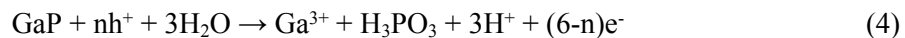
Anodic reactions 1 (dissolution of the metal, Pd)

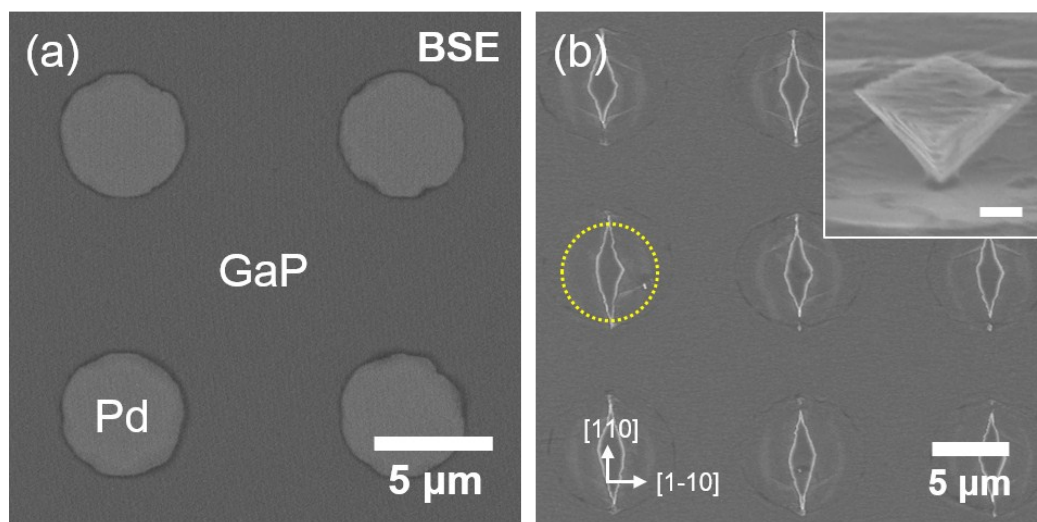


Cathodic reactions 2 (re-deposition on Pd as well as the bare surface of GaP)



Anodic reactions 2 (at the bare GaP as well as the GaP underneath Pd catalyst)





**Fig. S3** (a) Plan-view backscattered electron (BSE) image of Pd micro-dot arrays on a GaP substrate before etch and (b) SEM image of micro-structured GaP arrays after etching in a HF and H<sub>2</sub>O<sub>2</sub> solution for 20 minutes at room temperature. The concentrations of H<sub>2</sub>O<sub>2</sub> and HF are 5.26 M and 14.08 M, respectively. Inset in (b) shows a 15°-tilted SEM image of single micro-structured GaP. Scale bar in the inset is 200 nm. Yellow dotted circle in (b) indicates the initial size of Pd micro-dot before etching.

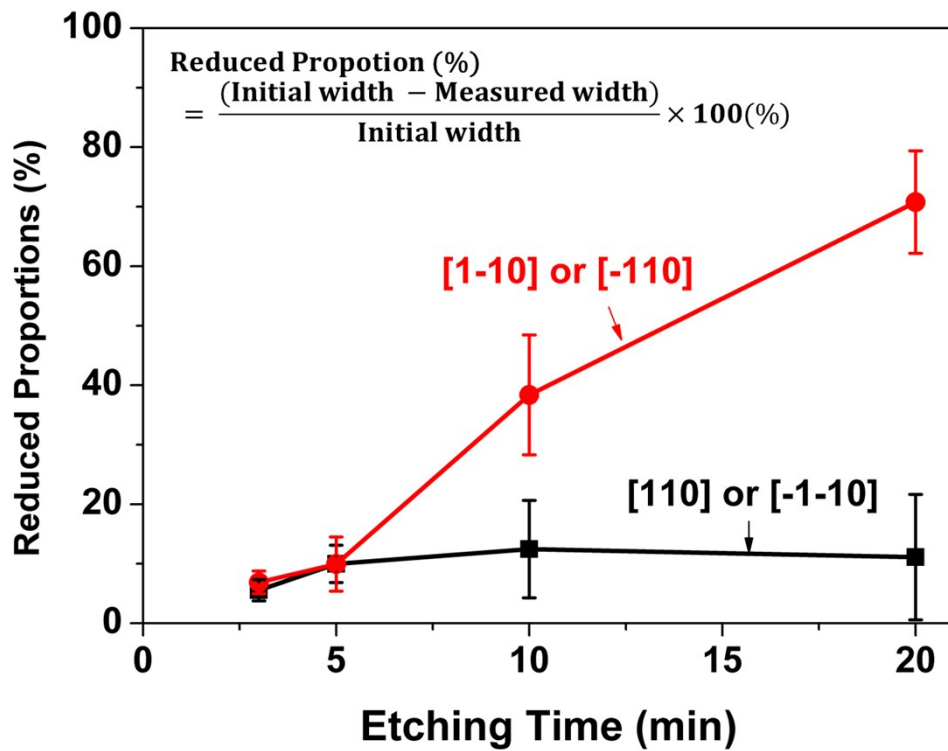


Fig. S4 Anisotropic etch undercut of GaP micro-mesas by the inverse metal-assisted chemical etching (MaCE). Fast lateral etch along [1-10] (or [-110]) crystallographic direction is clearly observed as etching time increases.

## References

1. D. E. Aspnes, *Appl. Phys. Lett.*, 1981, **39**, 316.
2. J. R. Oh, J. H. Moon, S. Yoon, C. R. Park and Y. R. Do, *J. Mater. Chem.*, 2011, **21**, 14167-14172.