

## Supplementary Information

### Catalytic Nickel-Silicide as an Alternative to Noble Metals in Metal-assisted Chemical Etching of Silicon

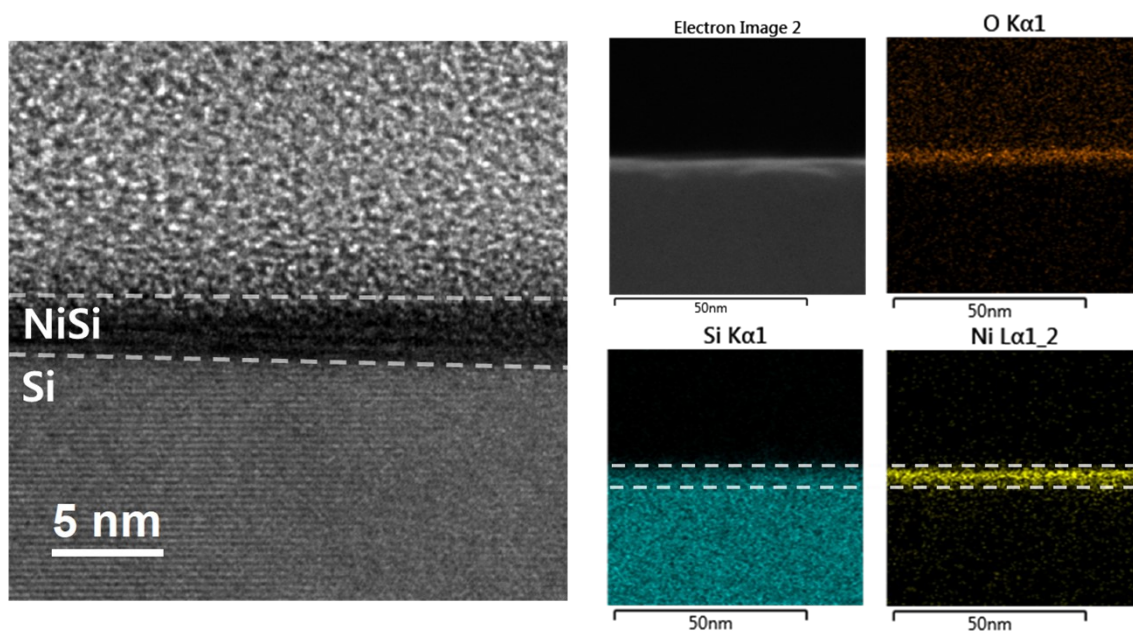
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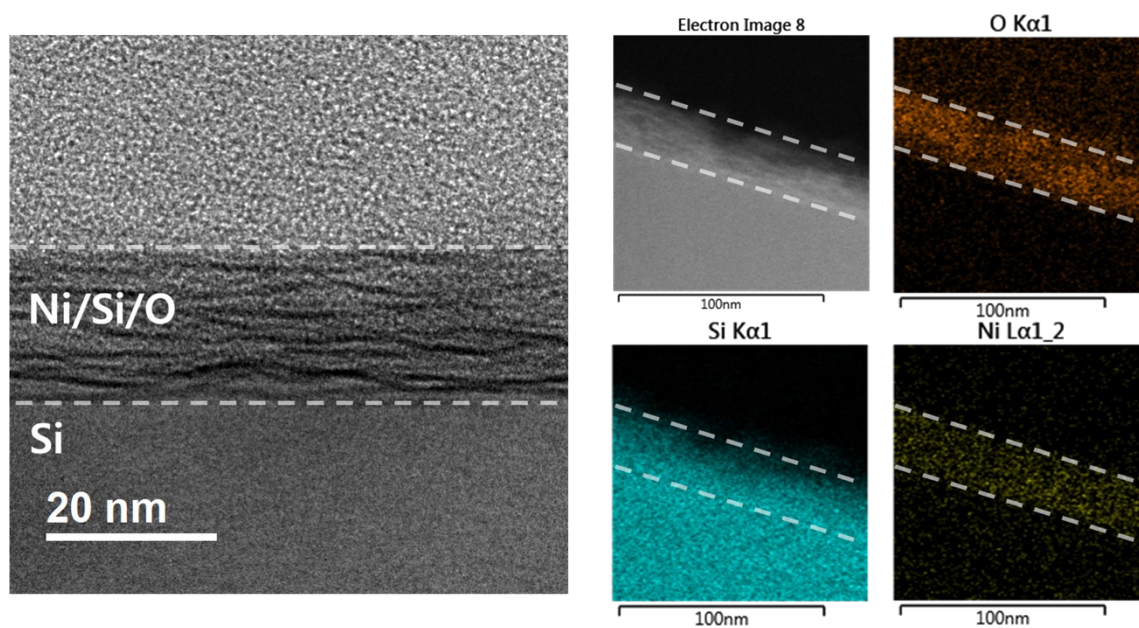
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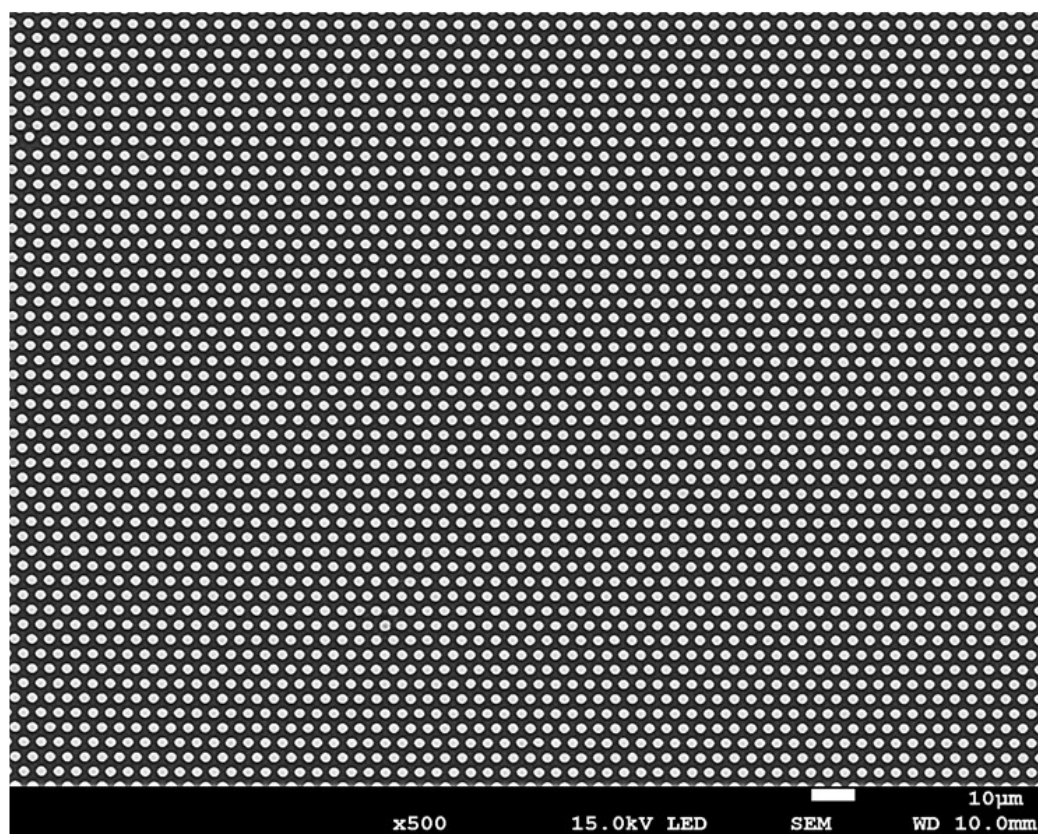


**Figure S1.** TEM image and EDS mapping images of NiSi catalyst after MACE for 5 s.

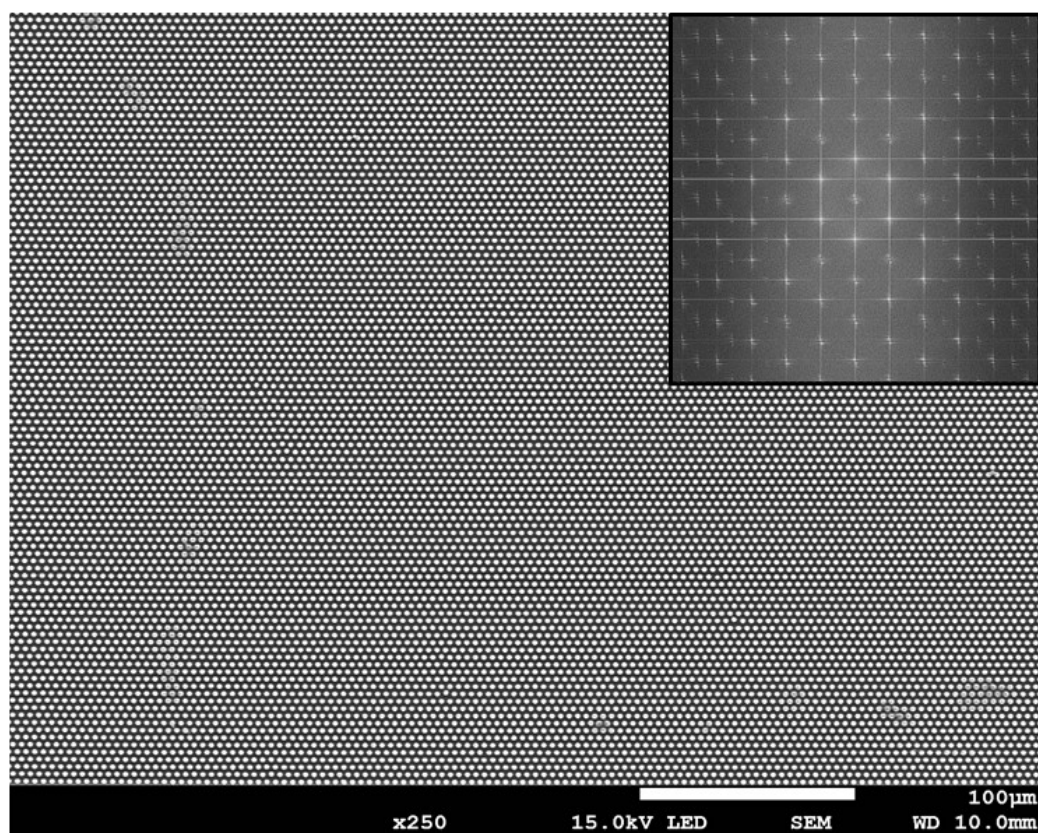


**Figure S2.** TEM image and EDS mapping images of NiSi catalyst after MACE for 30 min at room temperature.

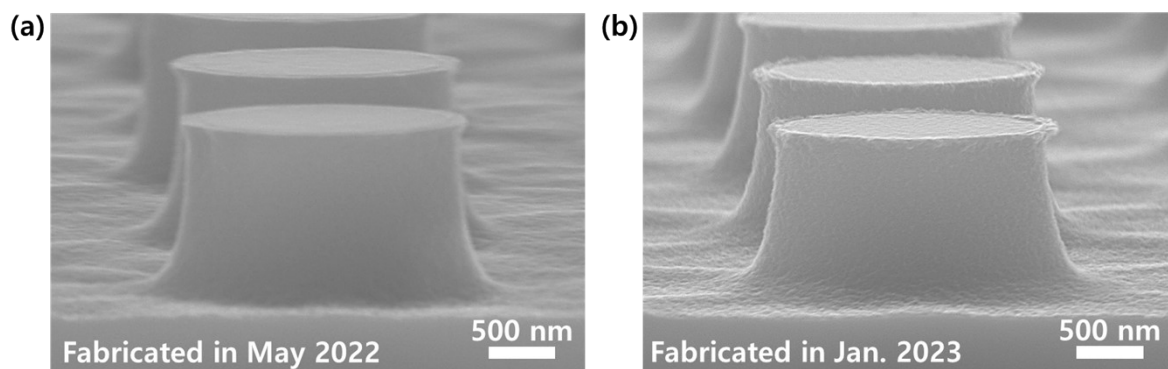
(a)



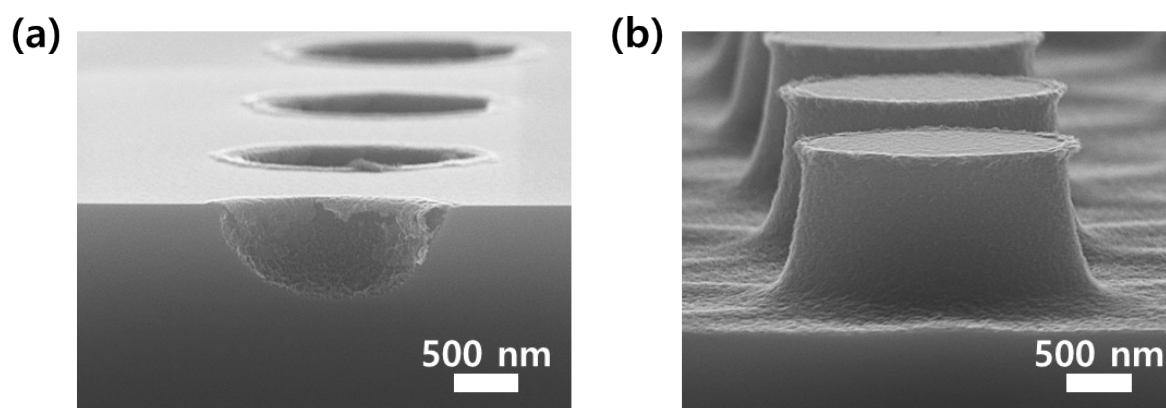
(b)



**Figure S3.** Series of low magnification top-view SEM images of Si pillar arrays. Inset in (b) is the corresponding FFT pattern of (b).

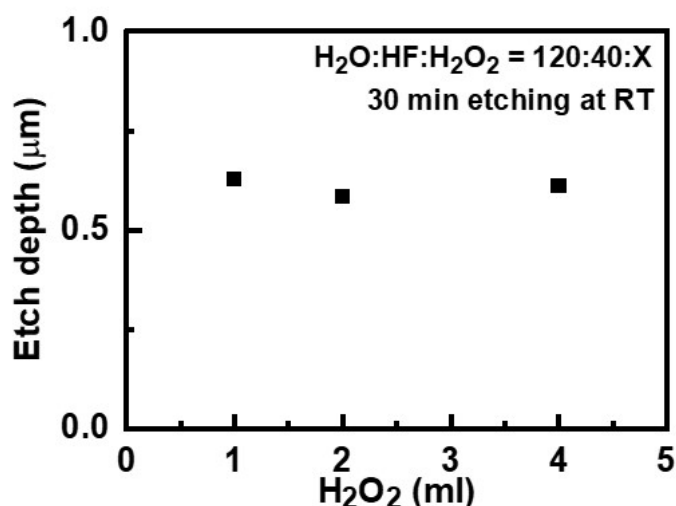


**Figure S4.** SEM images of Si pillars fabricated in (a) May 2022, and (b) January 2023 under an identical process.



**Figure S5.** Cross-sectional view SEM images of a (a) Si hole and (b) Si pillar fabricated by MACE with NiSi catalyst for 30 min at 50°C.

Figure S5 compares the etch profiles of the Si hole array and pillar array. The etch depth of the hole array is shallower than that of the pillar array. Under the same process conditions, the etch depth decreases from 1.27  $\mu\text{m}$  to 0.76  $\mu\text{m}$ . Also, etch profile is close to isotropic etching. In MACE with noble metals an (i) electric field<sup>1</sup> or (ii) magnetic field<sup>2</sup> have been utilized to enhance the etching directionality. These two external forces could improve the directionality of NiSi-assisted chemical etching, leading to the fabrication of well-defined hole arrays.



**Figure S6.** Graph showing the etch depths of the Si pillar arrays as a function of  $\text{H}_2\text{O}_2$  concentration.

In MACE, higher oxidant concentration leads to a faster hole generation rate, and the etch rate increases. However, the etch rate of MACE with NiSi catalyst remains at a rather consistent rate, despite changes in the oxidant concentration. The explanation we suggest upon such results is that the nickel silicide does not exhibit catalytic properties as good as that of noble metals, and hence, due to the corrosion of nickel silicide by the etchant, the etch rate remained constant even though the oxidant concentration increased. A significant boost in etch rate can be expected only after the enhancement in the catalytic properties of the NiSi catalyst.

## References

- 1 L. Li, X. Zhao, C.-P. Wong, ACS Appl. Mater. Interfaces 2014, 6, 16782-16791
- 2 D. W. Chun, T. K. Kim, D. Choi, E. Caldwell, Y. J. Kim, J. C. Paik, S. Jin, R. Chen, Nanotechnology, 2016, 27, 455302