

Supplementary Information

Additive Manufacturing of Zn with Submicron Resolution and Conversion into Semiconducting ZnO

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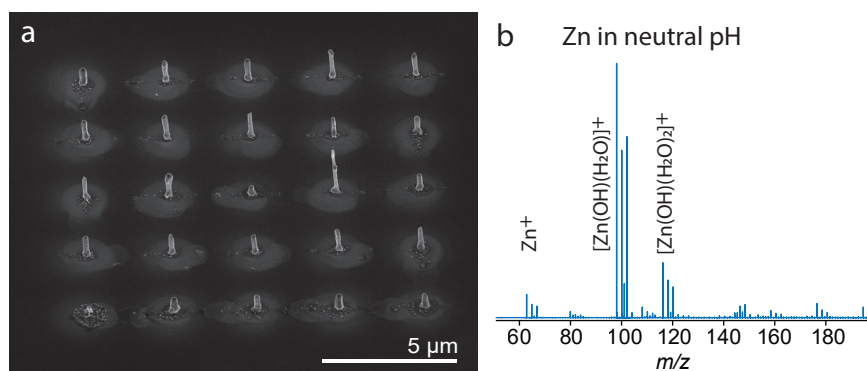


Figure 1 Deposition of Zn in aqueous solvents (a) Array of Zn pillars deposited from a HCl solution with pH 5. The pillars have a different height, despite having the same deposition time. (b) Mass spectra of a Zn anode immersed in pure water. Zn compounds can clearly be identified by their isotopic ratio.

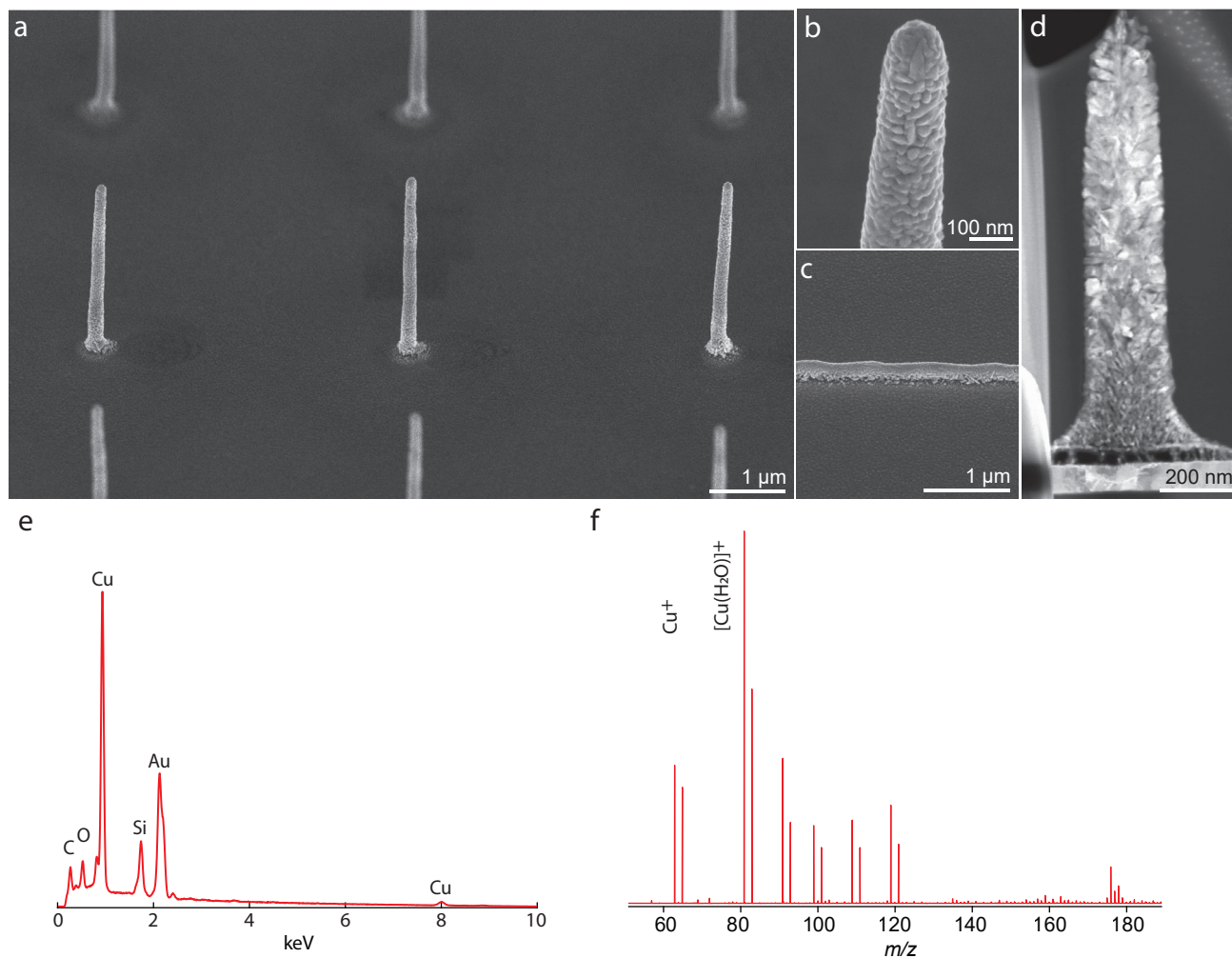


Figure 2 Printed Cu structures. (a) Array of Cu pillars indicates a homogeneous printing in aqueous solutions of pH 3 (HCl). (b) A close-up shows a rough surface. The surface appears similar to Cu printed in acetonitrile at high voltages. However, Cu printed in acetonitrile at lower voltages of 90 V is smoother on the surface. (c) The homogeneous printing allows the deposition of Cu lines. (d) A TEM micrograph (dark field) shows a microstructure with grainsize increasing over the length of the pillar. This coarsening of the grain size is less pronounced in acetonitrile, where a more homogenous grain size distribution is observed. Interestingly, a horizontal pore is identified at the interface of the pillar with the Au substrate. This pore could have formed because of hydrogen formation as a parasitic side reaction during the initial deposition phase¹. (e) An EDX analysis shows that Cu has been deposited. The low amounts of oxygen and carbon might arise from contamination deposited during SEM imaging and the presence of a native oxide layer. There are no obvious differences in the chemical composition compared to Cu deposited in acetonitrile, as similar amounts of oxygen and carbon are present, and no chloride is detected. (f) Mass spectra of a copper electrode in aqueous solutions of pH 3 (HCl). Various Cu adducts are identified. However, none contain any chlorine as the distinctive isotope pattern of chlorine is not observed.

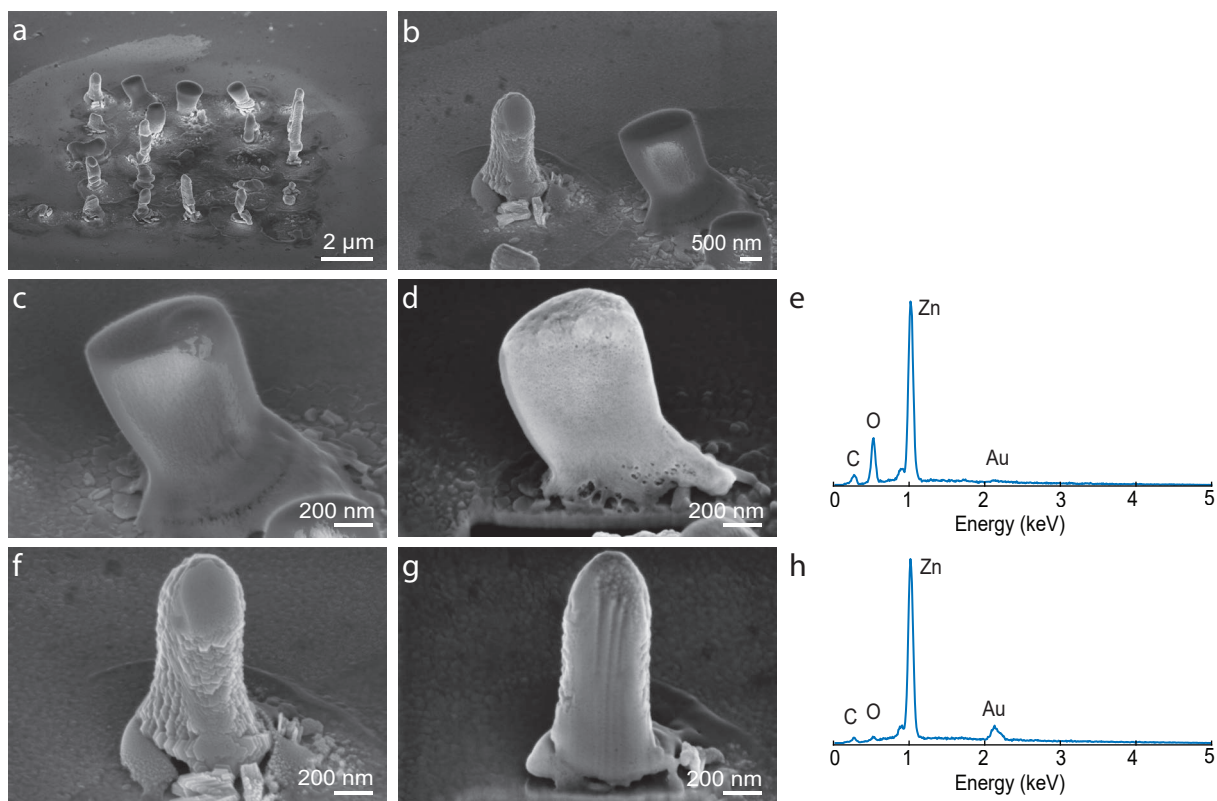


Figure 3 Zn deposited from diluted nitric acid (pH 3) (a) Overview image of an array of Zn pillars. (b) A close-up reveals two distinct morphologies of deposits (c and f). (c) a smooth pillar without a platelet-like surface morphology. Charging is obvious in the SEM ("glowing" corona-like feature at the top). (d) A cross-section of this pillar reveals porosity at the interface to the substrate. (e) EDX analysis shows a higher oxygen content compared to Zn printed with diluted HCl. (f) A Zn pillar printed with the same parameter and solvent shows a surface morphology similar to the pillars printed in diluted HCl. The reason for this variation is not known. (g) The cross-section reveals also a pore at the interface to the substrate. (h) EDX analysis shows a low oxygen and carbon content.

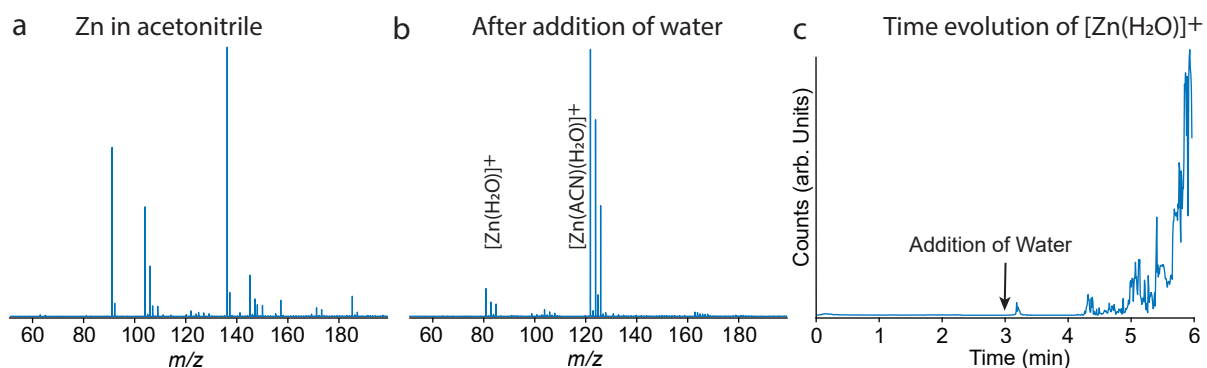


Figure 4 Mass spectra of Zn in acetonitrile (a) Mass spectra of ejected ions in pure acetonitrile. No species exhibiting the isotope pattern of Zn can be identified. (b) Mass spectra of the same experiment, after water was added to the acetonitrile with a syringe. Species containing Zn can be identified. (c) Time evolution of the $[\text{Zn}(\text{H}_2\text{O})]^+$ species show that this species only appears after water has been added. The delay between addition of the water and a stable signal is most likely due to diffusion.

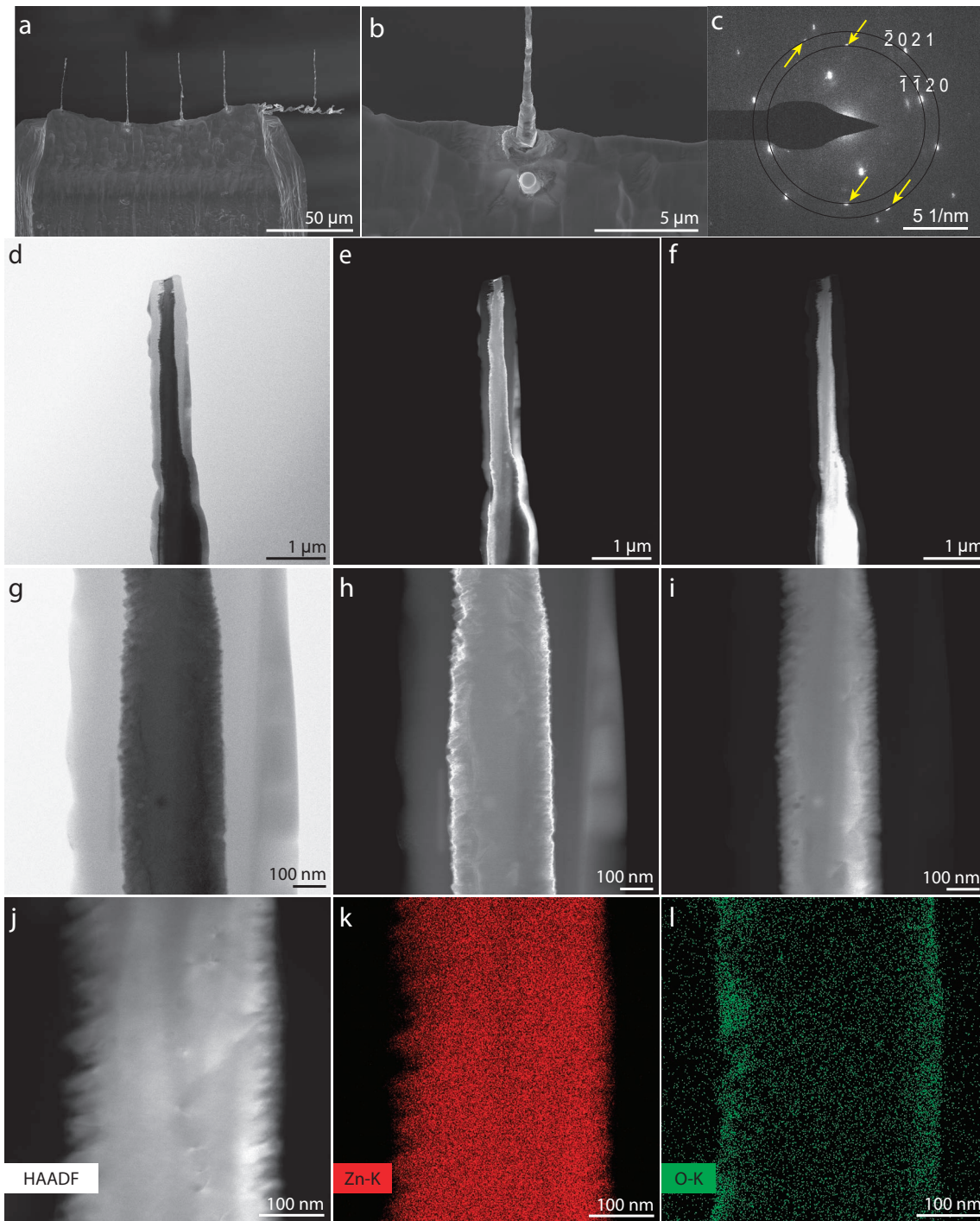


Figure 5 TEM analysis of as-printed Zn. (a) Zn pillars were directly deposited onto a Mo omniprobe half-grid. This omits the need for a lift-out procedure and shortens sample preparation as only thinning and polishing is required. (b) Close-up image of the pillar shown in c-k. (c-h) Bright field, dark field and high angle annular dark field (HAADF) images of a polished pillar. The pillar exhibits a dense microstructure without major pores. (i-j) Elemental maps of Zn and O, respectively, with the corresponding HAADF image. A higher concentration of oxygen is visible at the surface of the pillar, indicating an oxide shell has been formed after deposition.

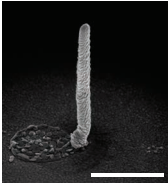











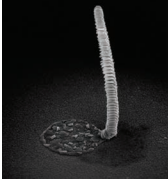

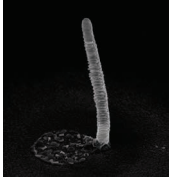





As Printed			After Oxidation			
SEM Image	Contour	Volume (10^{-20} m^3)	SEM Image	Contour	Volume (10^{-20} m^3)	Rel. Change
		4.95			6.31	1.2167
		3.72			5.26	1.2187
		5.21			5.69	1.0148
		3.73			4.34	1.0689
		10.67			11.41	1.0303

Figure 6 Volume comparison of as-printed and post-oxidation pillars The SEM images for each pillar before and after oxidation were taken with the same settings. The contour of the pillars was obtained using ImageJ. Subsequently, the number of pixels within each contour along horizontal sections were counted using matlab. The number of pixels of each horizontal segment were multiplied with the size of a pixel (usually $1.35\text{E}10^{-9} \text{ m}$ for the used magnification and resolution) and divided by 2 to calculate the radius of the pillar at each segment. The volume was then calculated by assuming a cylindrical shape of the pillar.

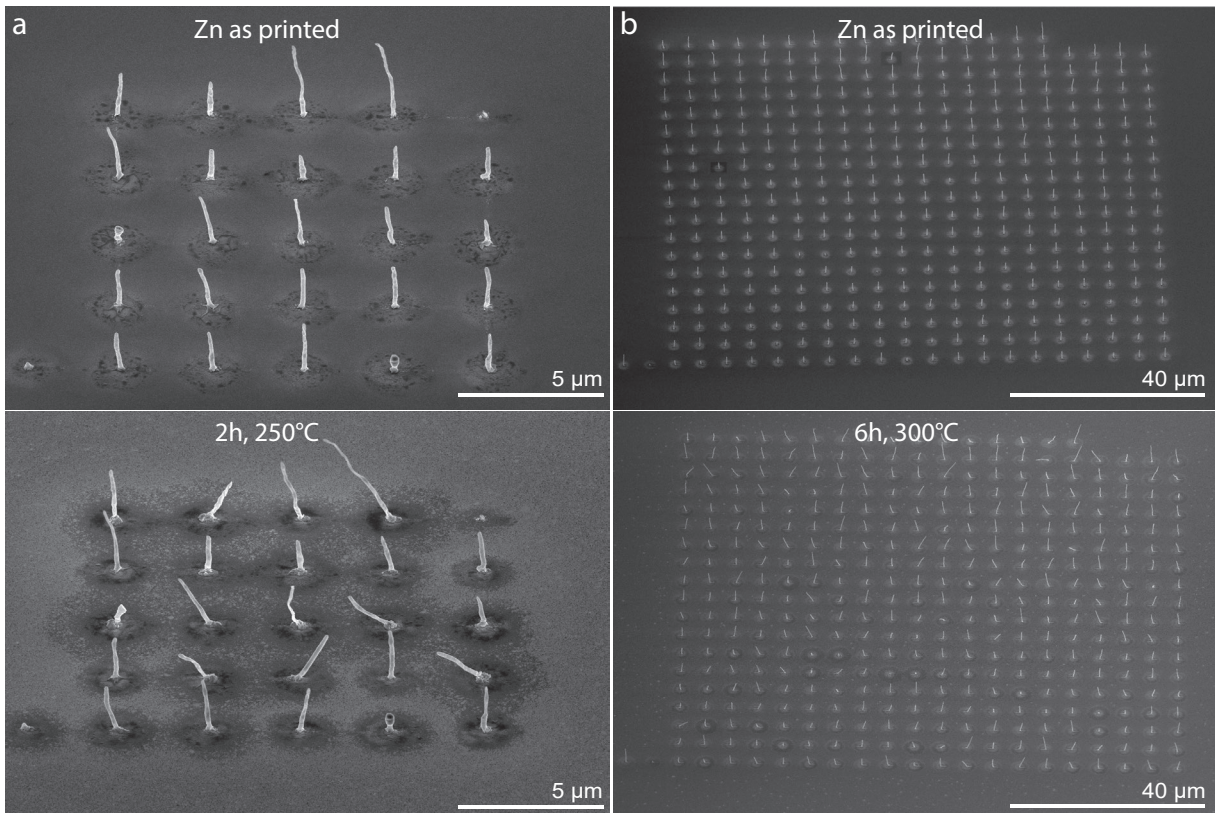


Figure 7 Influence of different oxidation temperatures on the tilting of Zn pillars. (a) A pillar array annealed at 250 °C (b) A pillar array annealed at 300 °C. Both arrays exhibit tilted pillars after the annealing, therefore implying that a reduction in the oxidation temperature does not prevent the tilting. The array oxidized at 250 °C presents in fact more tilting. However the Zn pillars in the as-printed state in (a) have different height despite similar deposition times, which might imply that the Zn in this experiment was more contaminated with carbon than in the arrays used for higher temperatures.

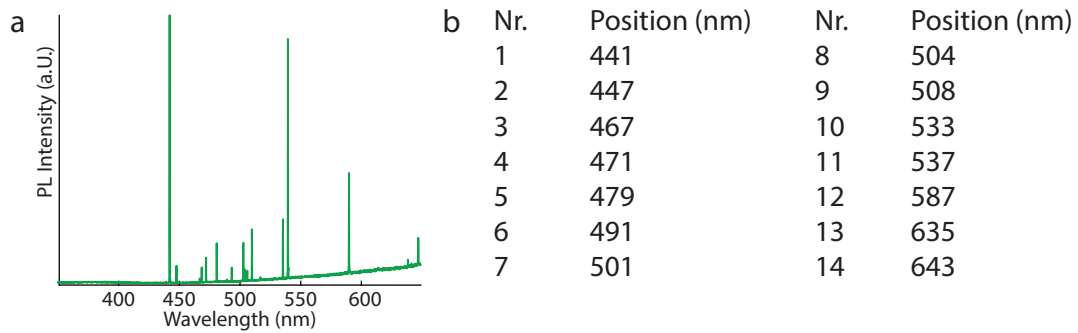


Figure 8 Background for Photoluminescence analysis (a) PL spectra taken on a blank substrate. (b) List of peaks considered to originate from the He-Cd laser. These peaks have been removed from the spectra shown in the results.

Notes and references

- [1] R. Y. Wang, D. W. Kirk and G. X. Zhang, *Journal of The Electrochemical Society*, 2006, **153**, C357–C364.