FEBID 3D-Nanoprinting at Low Substrate Temperatures: Pushing the Speed While Keeping the Quality

Jakob Hinum-Wagner[1], Robert Winkler[1], David Kuhness[1] and Harald Plank[1,2,3]

1. Christian Doppler Laboratory DEFINE, Graz University of Technology, 8010 Graz, Austria
2. Graz Centre for Electron Microscopy, 8010 Graz, Austria
3. Institute of Electron Microscopy and Nanoanalysis, Graz University of Technology, 8010 Graz, Austria

Introduction

Focused electron beam induced deposition (**FEBID**) is a method for functional nano-fabrication that enables mask-less, additive manufacturing of free-standing 3D nanostructures.

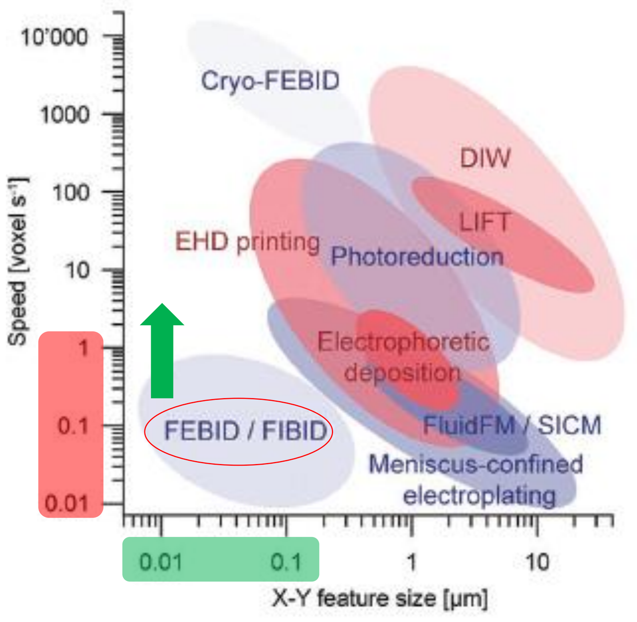

Figure 1: Comparison of 3D-nanoprinting techniques [1]

Although this direct-write technique offers unique advantages (Fig. 1), deposition speed is rather *slow*. In general, the number of available precursor molecules at the growth front limits the growth rate. In particular for the fabrication of single-wire 3D structures, the quasi-stationary electron beam locally heats up the growth region.

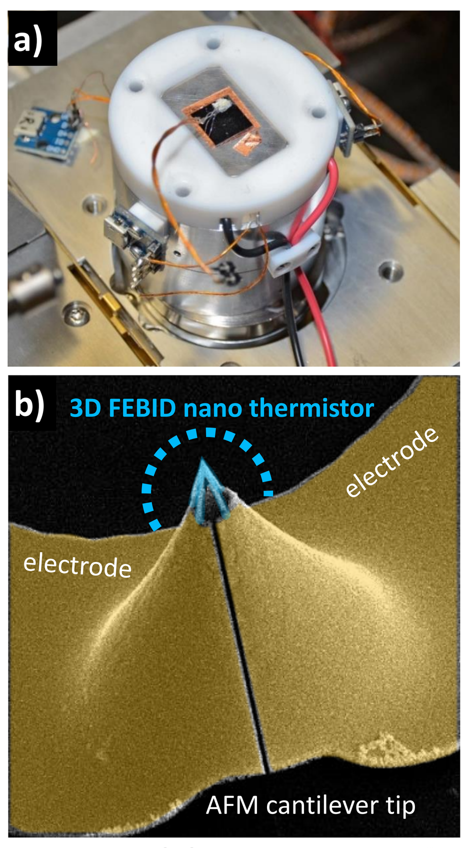

Figure 2: (a) Peltier stage for 3D-FEBID experiments.[3] **(b) A FEBID 3D nano-thermistor probe on an electrical accessible self-sensing AFM cantilever as an example of an industrial relevant application.** [4]

This temperature rise results in a reduced residence times of the precursor and therefore to lower growth rates[2] and consequently to stability problems for larger 3D structures. Based on those insights, we here turn around the situation and lower the substrate temperature with a home-build Peltier cooling stage (Fig. 2a) to study the implications on growth stability and fabrication precision in *3D*-FEBID in a temperature range of +5 °C (slightly higher temperature than precursor condensation) to +30 °C (slightly higher temperature than standard substrate conditions).

Temperature Dependence of Multipod Growth and Wire Dimensions

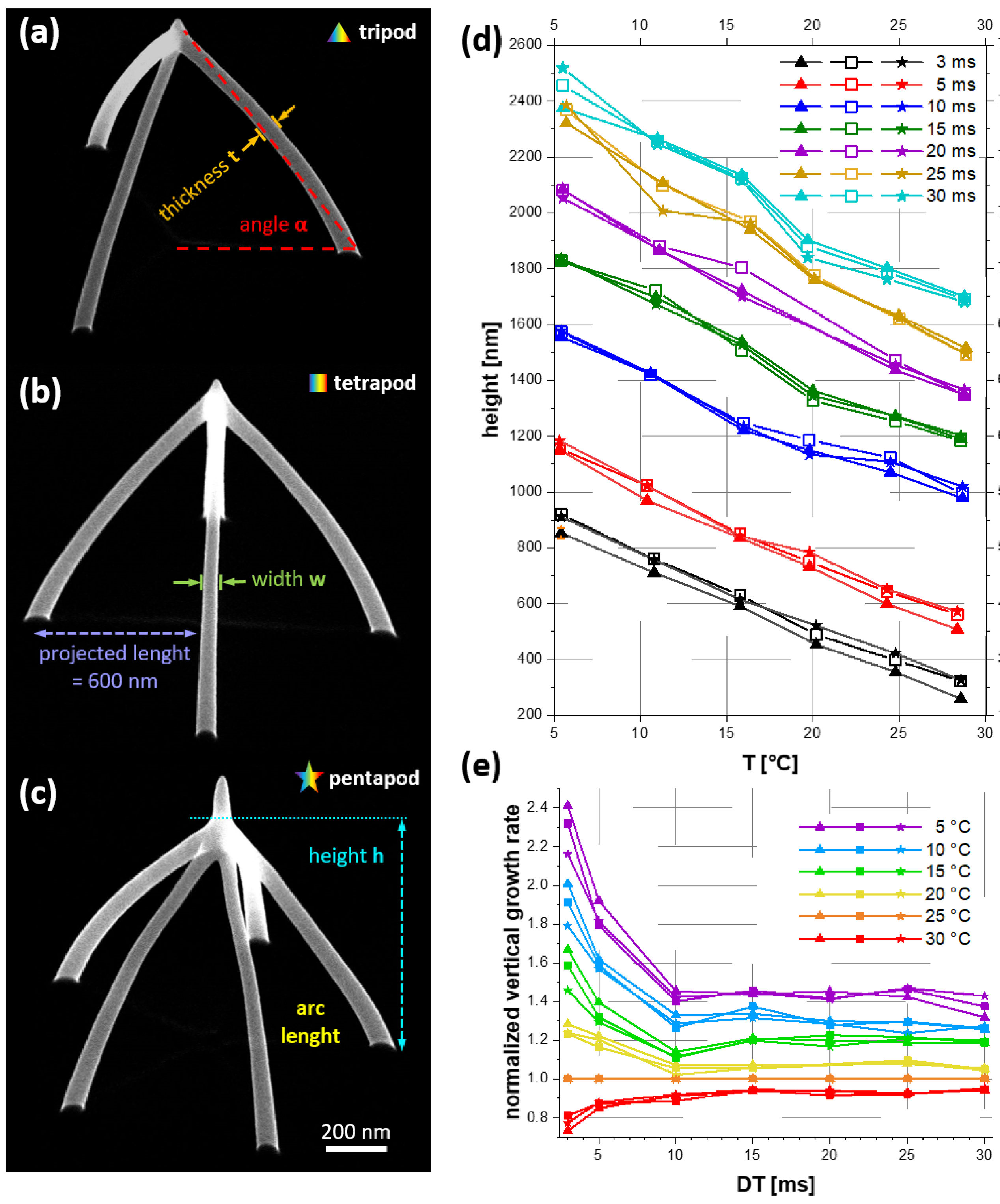

Figure 3: (a-c) PtC multipods (5 keV, 28 pA) on cooled Si-SiO$_x$ substrate. (d) Structure heights as a function of the substrate temperature and (e) vertical growth rates.[3]

The SEM based growth analysis of tri-, tetra- and pentapods (Fig. 3a-c), fabricated from MeCpPt$^{(IV)}$Me$_3$ at substrate temperatures T of 5, 10, 15, 20, 25 and 30 °C revealed

- Multipods get *taller* at lower substrate temperatures (Fig. 3d)
- No/minor influence of *number of legs* on multipod heights (Fig. 3d)
- *Growth boost* for *low* single pulse *dwell times* (Fig. 3e)

At the same time, the shape fidelity was maintained over the entire temperature range.

Measuring the widths and thicknesses of the wires as a function of the projected length showed slightly larger wires at reduced substrate temperatures. This is valid for both, wires fabricated under constant DTs of 15 ms (Fig. 4a; Fig. 4b), as well as for constant heights (Fig. 4c; Fig 4d).

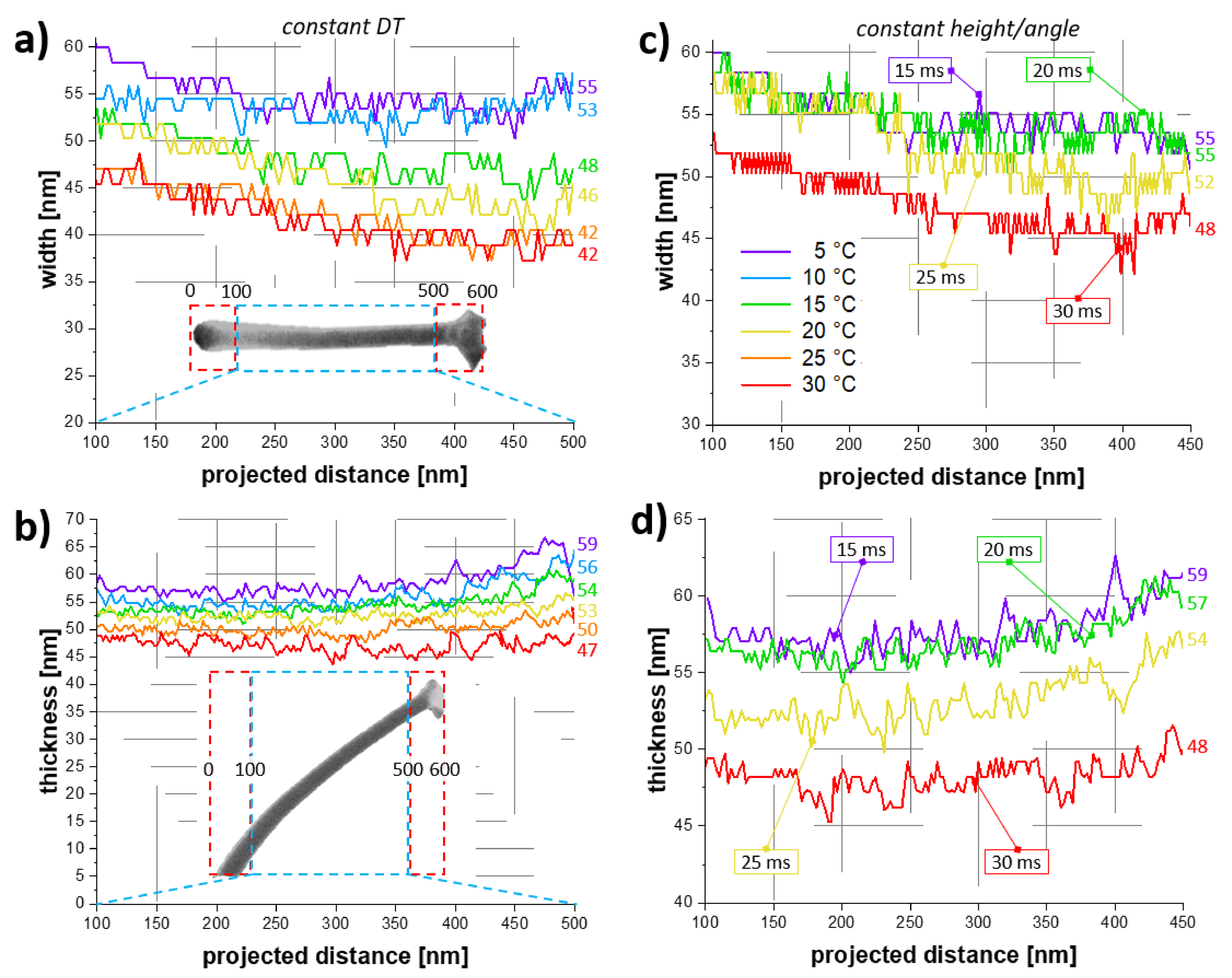

Figure 4: Width and thickness variations along the wires of a tripod. (a,b) compares multipod wires fabricated at 15 ms DT, (c,d) for comparable tall tripods.[3]

Grain Size Analysis - TEM

Transmission Electron Microscopy (TEM) was used to determine the grain size as a function of the substrate temperature as relevant parameter for the material properties. Bright field images (Fig. 4a-d) and Feret-diameter analysis (Fig. 4e) suggest similar grain sizes down to 10 °C (~3 nm) and a slight increase at substrate temperatures of 5 °C (a).

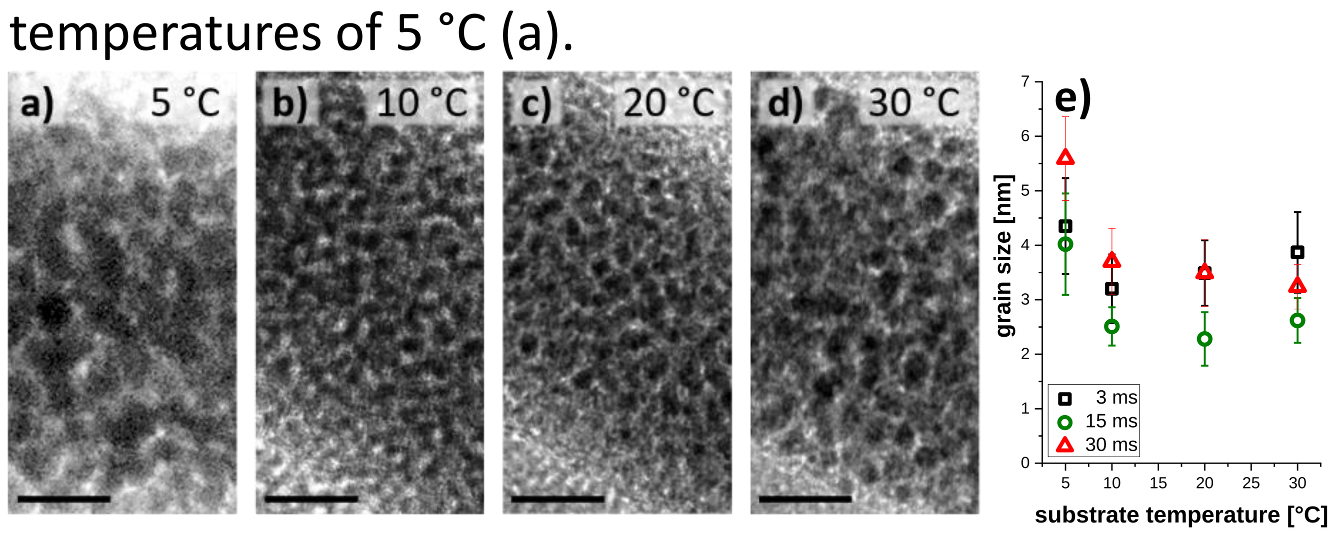

Figure 4: TEM microstructure analysis. TEM images of PtC$_x$ tetrapod branches fabricated at (a) 5 °C, (b) 10 °C, (c) 20 °C and (d) 30 °C. Scale bars are 10 nm. (e) Mean grain sizes (Feret diameter) for wires fabricated at different substrate temperatures.[3]

Influence of the Support Geometry

Deposition of a pillar on top of the multipods showed that the number of legs has a strong influence on the vertical growth rates (Fig. 5). This is explained by the varying number of paths for surface diffusion and thermal conduction of heat towards the cooled substrate.

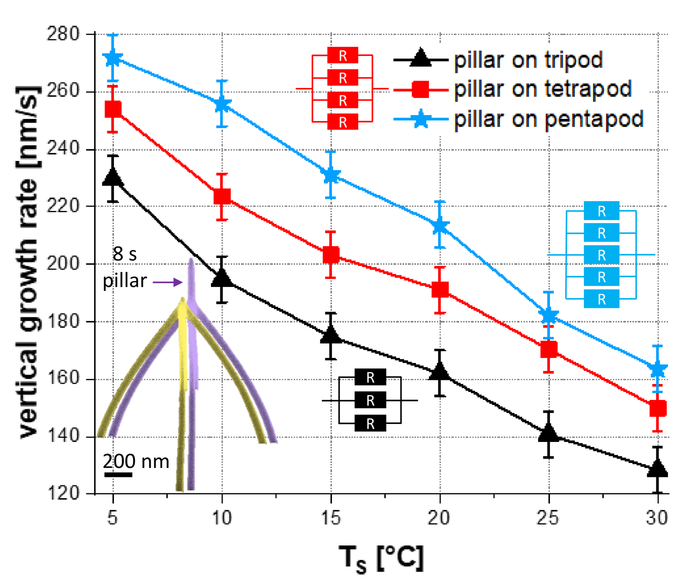

Figure 5: Pillar growth rates after the merging zone, demonstrating that for proper 3D-FEBID design the support geometry has to be considered.[3]

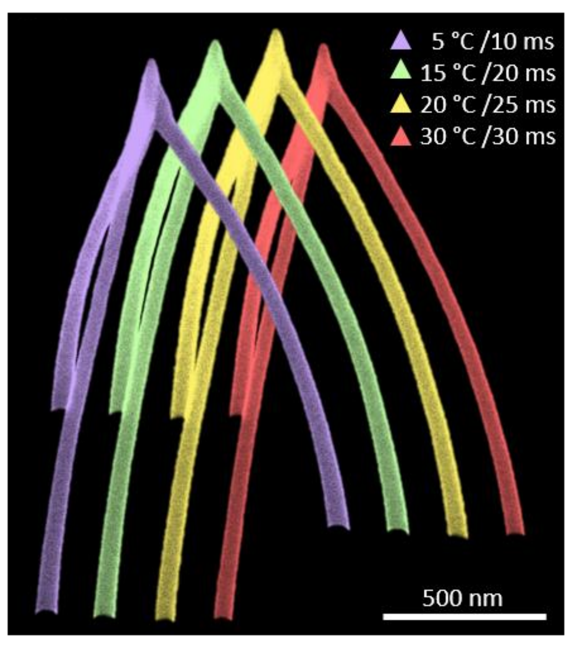

Figure 6: Comparison of tripods with same heights fabricated at different substrate temperatures shows no shape degradation.[3]

Conclusion

The study revealed a *boost in growth rates* by cooling the substrate in 3D-printing via FEBID up to a factor 5.6, with *no or only minor variations in the structural integrity / shape fidelity* (Fig. 6) and the *microstructure* (essential for final functionalities). This situation is beneficial in terms of upscaling and applications, as no serious drawbacks were found in our study.

References

[1] Hirt et al., *Adv. Mater.* Vol. 29, 17 (2017)
[2] Mutunga et al., *ACS Nano* 13 (2019)
[3] Hinum-Wagner et al., *Nanomaterials* 11 (2021)
[4] Sattelkow et al., *ACS AMI* 11 (2019)

Acknowledgements

Christian Doppler Forschungsgesellschaft

Special thanks go to the FELMI-ZFE team, in particular to the work group of Prof. Plank. Furthermore, the support from Jason Fowlkes is highly appreciated.

Contact

robert.winkler@felmi-zfe.at
harald.plank@felmi-zfe.at

www.felmi-zfe.at

(FEBID QR-Code, 3D-AFM height image) 3 µm